A SCHEME OF QUALITATIVE ORGANIC ANALYSIS

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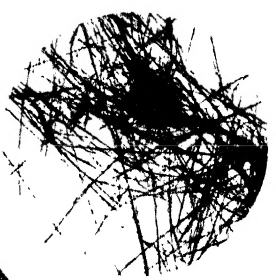

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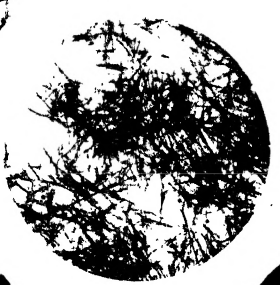

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A SCHEME OF QUALITATIVE ORGANIC ANALYSIS

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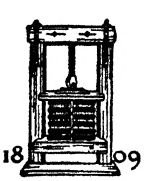

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PREFACE

Qualitative Organic Analysis has long been a part of courses in Organic Chemistry, and has advanced far from the days when the recognition of characteristic odours of original substances and the application of isolated tests were relied on to obtain results. Its development is in part due to the fact that many of the commoner organic reactions can be illustrated and practised on a small scale, and not only does this supplement in valuable fashion the theoretical side of Organic Chemistry, but it affords training in manipulation of small amounts of material, which is an essential preliminary to research and micro-analytical work.

We would emphasize that while the application of Qualitative Organic Analysis has as its object the identification of an unknown substance, it should never be regarded as an isolated branch of Organic Chemistry, and particularly while knowledge and skill are being acquired should it be made an integral part of the study of this subject.

The scheme set out in this book is an amplification of notes which have been in use in our classes for some ten years and have been well tested in practice.

No claim for originality is made with regard to the subject-matter, for most of the methods described have been published elsewhere, but we hope that the method of presentation may have some appeal, our aim being to develop a systematic scheme of examination whereby classes of organic compounds are eliminated one by one. It is not possible (nor perhaps desirable) to apply this procedure to the same degree as in Inorganic Qualitative Analysis, and accurate observation and sound deduction must play a vital part if errors are to be avoided.

The scheme has not been designed with any particular examination syllabus in view, but it has been in use by students preparing for Ordinary and Higher National Certificates in Chemistry, the Associateship and Fellowship of the Royal Institute of Chemistry, and London B.Sc. degrees. It is with these last two classes in mind as well as in the hope that the book may be of value to other than

examination candidates that we have made the scope of compounds dealt with, and derivatives prepared, rather wider than is usual in a student's textbook. We consider that the more advanced students who have acquired facility in preparing the simpler derivatives should attempt the more difficult ones, even where these involve the use of comparatively expensive reagents.

Because of the desirability of correlating practical work and theory, we have formulated the majority of reactions involved. We hope also to guard against the tendency for a scheme such as this to become a mere collection of " recipes ". Students should understand what they are doing, as well as know how to do it.

Our material being drawn from such a wide variety of sources, makes it impracticable to offer full individual mention, but a general acknowledgment is hereby made to all those workers whose results we have utilized. We must, however, record our particular indebtedness to Mr. O. Ormerod, B.Sc., A.R.I.C., who laid the foundations on which the scheme is built; to Associate-Professor S. Z. Hassid of the University of California, who so generously provided the photographs of the osazones reproduced in the frontispiece; to Mr. G. W. Brownlee, Ph.C., A.R.I.C., for assistance with the section on alkaloids, and to the body of students who have, sometimes unwittingly, obtained experimental data for us.

Finally, in our Tables we have tried to clear up some of the discrepancies in melting-points and boiling-points encountered in the literature. The recent monograph " Organic Reagents for Organic Analysis " of Messrs. Hopkin and Williams has here proved of great value. We fear that this task has not been fully accomplished, and shall welcome any corrections of remaining errors together with criticisms of the general work.

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July, 1947

CONTENTS

CHAPTER I

Introductory

The problem of the identification of an organic compound may present itself in two alternative forms:—

A. When no information is available as to the purity of the substance.

B. When it is known that the substance is of a fairly high degree of purity.

It is obvious that in case A, preliminary purification by fractional crystallization or fractional distillation to yield material of definite melting-point or boiling-point is essential before beginning the examination of the substance.

It is assumed that students using this book are familiar with the processes referred to and therefore no detailed instructions on these points are given. Furthermore, the scheme of analysis developed is intended primarily to deal with case B, i.e. the identification of single compounds by students as a part of their training in practical Organic Chemistry, and thus the substances used are usually free from all but traces of impurities.

The basis of the scheme is as follows:—

I. Determination of the elements present which enables the compound to be placed in one of nine main groups.

II. A preliminary examination yielding certain general information.

III. The application within the group of classification tests for functional groups which, considered in conjunction with the results of I and II, determine the type of compound.

IV. The preparation of crystalline derivatives and determination of their melting-points, or the determination of physical constants of the original substance leading to final identification of the compound.

It is a debatable point as to whether early observations, particularly with regard to physical state, colour and odour, should be used as a means to curtail the systematic procedure recommended,

especially since recognition of odour varies greatly with the individual. Much time may be wasted, and even incorrect conclusions arrived at, by omitting parts of the examination, and it is much better to regard odour, &c., as a rough indication of the nature of a compound and see if this is borne out by the remainder of the evidence.

The importance of the preliminary examination lies in the fact that since classification tests are carried out in a definite order, it will show (in many cases) whether more than one functional group is present and indicate the necessity for further classification tests after a single positive result has been obtained. For example, ethyl salicylate will give a positive result in the test for phenols, but since (*a*) it does not dissolve in cold dilute sodium hydroxide but forms a white solid, (*b*) it yields alcohol on boiling with sodium hydroxide, the compound is *obviously* not a simple phenol.

The preliminary examination may also indicate the absence of certain groups and confirmation of this will be obtained in the classification tests. Thus, a substance insoluble in sodium hydroxide cannot be a simple acid or a phenol, while a nitrogen-containing compound which is insoluble in water and in dilute mineral acid is unlikely to contain the nitrogen in the form of the amino ($-NH_2$) group.

It should always be remembered that the results of the classification tests *must* agree with the deductions drawn from the preliminary examination, i.e. the two are essentially complementary. Any discrepancy calls for repetition of the tests involved.

Derivatives

The derivative selected for preparation should preferably be one which can be prepared relatively quickly from easily accessible reagents and which has a melting-point within the range 50°–250° C. If the melting-point is much lower than the minimum suggested the compound frequently separates as an oil, and its conversion to a crystalline solid is often slow and difficult, particularly if ice or a refrigerator is not available. Drying is also much slower from the nature of the method imposed. If the melting-point is much above 250° C. not only is an electrical method of heating almost essential, but, owing to the length of the emergent stem of the thermometer, the deviation of observed melting-point from the corrected melting-point (usually given in the literature) will be considerable, amount-

ing to about 7° C at 250° C., and this may lead to incorrect deductions.

The melting-point of the derivative should also show a divergence of some 10° C. at least, from that of the corresponding derivative of another closely related compound of the same class. For example, the *p*-nitrobenzyl ester of benzoic acid melts at 89° C. and that of *o*-toluic acid at 91° C., and this derivative will obviously not serve to distinguish between these two acids. On the other hand, the amides with melting-points 128° C. and 140° C. respectively would give useful information.

As a general rule two crystalline derivatives or one derivative coupled with a numerical constant, e.g. the equivalent weight of an acid, will suffice for complete identification. Occasionally a third derivative may be necessary.

It should be an invariable rule that, in the absence of specific instruction to the contrary, no determination of melting-point should be carried out on the derivative until it has been recrystallized at least once. In some cases several recrystallizations are necessary and this appears to be the case with certain semicarbazones where three recrystallizations may raise the melting-point 10° to 20° C. above that of the initially prepared material. In general, appropriate solvents are indicated in the method given for the preparation of a particular derivative.

When recrystallizing a substance, dissolve it in the *least possible quantity* of the solvent, using heat if permissible, and boiling in a tube or small flask under a reflux condenser in the case of inflammable solvents. If the solution is not quite clear, filter while hot through a warmed Buchner funnel, and if crystallization starts in the Buchner flask transfer crystals and mother-liquor to a tube and warm till clear. With low melting derivatives it is best to allow the solution to cool slowly or an oil may separate, but with high melting compounds cooling in water or ice may be employed. If no crystallization takes place after cooling to as low a temperature as possible, scratch the inside of the tube gently with a glass rod. This will often induce the formation of crystal nuclei along the scratch lines and, once started, separation of crystals usually proceeds readily.

Occasionally, if crystallization is slow due to the high solubility of the substance in a particular solvent, the solubility may be lowered by the addition of a solvent in which the compound is sparingly soluble. Such addition should be made to the cold solu-

tion until a turbidity (due to precipitation) occurs. The liquid should then be heated till clear and allowed to cool slowly when crystallization usually sets in. Alcohol/water, alcohol/petrol-ether and benzene/petrol-ether are examples of such mixed solvents.

In recrystallization *never* allow all the solvent to evaporate. Some mother-liquor must be left to hold the impurities in solution otherwise no purification is effected.

Having obtained the crystalline product, filter with the aid of a Buchner funnel of suitable size, using suction. Always use a filter paper of the correct size, i.e. one which just covers the perforated base of the funnel, and see that it fits snugly by moistening with the solvent used in the crystallization process and applying slight suction before commencing filtration. The all-too-common practice of cramming an over-size paper into the funnel, leaving flutes round the edges, is not only slovenly but adversely affects rapid and successful filtration. If the crystals are very fine, moderate suction will give a faster filtration rate than vigorous suction, which tends to draw the crystals into the pores of the paper and clog it. Use some of the filtrate to transfer the last traces of crystals to the funnel, wash the crystals with a *little* of the pure solvent to remove adhering mother-liquor (use discretion with regard to the amount or the product may redissolve) and finally apply strong suction as an aid to drying.

Final drying is very important, the tendency being to take a melting-point before the substance is really dry, and this gives a low figure. The method of drying will obviously be determined by the melting-point of the derivative. Partial drying may be effected by pressing the substance firmly on to a pad of smooth-surfaced filter paper with a spatula, breaking up any large crystals and working until a fine powder is obtained. If the melting-point is suspected to be below 100° C., leave in a warm dry place covered with a clock glass, or place in a desiccator (a vacuum desiccator is best) to complete the drying. If the melting-point is only a little above 100° C. the above procedure should be followed, as damp samples placed in a drying oven at 100° C. will often melt. If the melting-point is of the order of 150° C. or more, rapid drying may be carried out in the drying oven.

Determination of the melting-point

Though not perfectly satisfactory from the point of view of the accuracy of the result, the capillary tube method for determining melting-points is the most convenient for use in the identification of organic compounds.

Prepare the capillary tube by heating evenly thin-walled glass tubing of about 1·0 cm. bore in a batswing burner, and when sufficiently softened, drawing out to give a capillary tube of 1–1·5 mm. bore. Only practice will enable the operator to know the requisite degree of softening and the correct amount of tension to apply. After cooling, the centre portion is cut or broken into approximately 8 cm. lengths, retaining only those which are uniform and of suitable bore. One end is closed by holding it in the edge of a bunsen flame, continually rotating it until it is sealed. Avoid the production of a thick "blob" of glass at the end.

The dried, finely powdered solid is introduced into the capillary tube by thrusting the open end of the tube into a small heap of the substance, and it is consolidated by gently tapping the sealed end of the tube on the bench until a column about 0·5 cm. long is formed. Some materials are of a light or "fluffy" character, and with these a very thin glass "ramrod" may be called for as an aid to charging the tube. The vibration produced by drawing the edge of a blunt file *very lightly* across the tube held vertically is also useful if the substance does not pack down easily.

Attach the tube to a thermometer by a thin rubber band in such a way that the end of the tube is in contact with the thermometer bulb. (The band should not be covered by liquid when tube and thermometer are placed in the bath.) Various patterns of heating bath have been proposed. In the one shown in fig. 1 the thermometer is held in position by passing through the centre of a cork in which a V notch has been cut lengthwise to allow for expansion and escape of vapour. Here convection currents are relied on to maintain a uniform temperature throughout the liquid, and correction for "emergent stem" is apt to be difficult. A "tall form" beaker of 150 ml. capacity is quite satisfactory as a container for the heating liquid, and in this case a length of thin glass rod can be bent in the form shown in fig. 2 and placed so that the loop surrounds the thermometer bulb, when a gentle "up and down" movement will give efficient stirring and a uniform bath

temperature. Violent agitation should be avoided. The complete arrangement is shown in fig. 2.

As heating liquid, high-boiling-point liquid paraffin is undoubtedly best. It has a fairly high specific heat enabling the rate of temperature rise to be easily controlled and is not readily ignited if the container breaks or is upset during a determination. Most grades of high-boiling-point liquid paraffin can be safely used in determining melting-points up to about 220° C. (though they smoke and smell rather badly as this temperature is approached), but the student

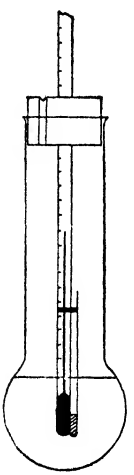


Fig. 1

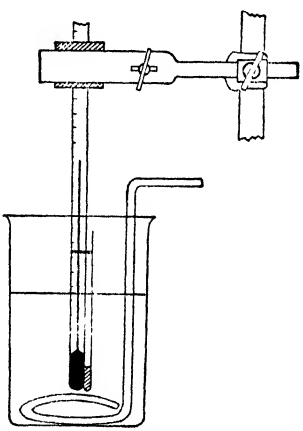


Fig. 2

should always inquire as to the safe maximum before using a new heating bath. Great care must be taken to avoid introducing water into the bath or violent "spitting" will occur at temperatures much above 100° C. With thermometer, melting-point tube and stirrer in position, the bath temperature is raised, at a rate not exceeding 2° C. per minute with gentle stirring, and heating continued until the substance shows signs of softening (i.e sinters). At this stage the temperature should be held as nearly steady as possible to see if *complete* fusion occurs, and if it does the temperature reached is recorded as the melting-point. If complete fusion does not occur, the temperature is raised by 1° C. and again held steady, this procedure being repeated as often as necessary till the melting-point is reached. The most common error in melting-point determinations is a too rapid rate of heating when, owing

to "lag" on the part of the thermometer, the recorded figure is lower than the true one.

In the case of substances of fairly high melting-point the above method will take an undue amount of time and it is better to make a rough determination using a fairly rapid rate of heating, then allow the bath to cool through some 20–30° C., and make a second and accurate determination using this bath, a fresh capillary tube, and the standard rate of heating in the final stage. The temperature at which the molten material solidifies is not of necessity the melting-point, owing to the possibility of supercooling and the fact

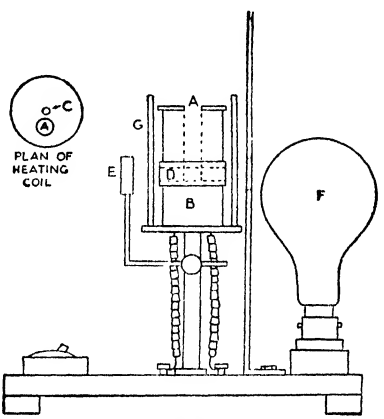


Fig. 3

that decomposition or other chemical change may have occurred on fusion. For the second reason a final determination of the melting-point must never be made on re-solidified material.

If the melting-point of the substance is above 220° C. an electrically-heated melting-point apparatus should be used. The pattern designed by Mason (fig. 3) is very satisfactory in such cases. The thermometer is placed in the hole A in the heating block B and the capillary tube in the smaller central hole C alongside, so that the filled end of the tube which is in contact with the thermometer bulb can be observed through the horizontal hole D with the aid of the lens E and the lamp F. The heating block is wound with a lagged heating coil which is in series with a switch and variable resistance controlling the rate of heating. A cylinder of heat-resisting glass G surrounding the coil and block reduces radiation

loss. The determination of the melting-point is carried out as previously described.

The apparatus is apt to be rather unsatisfactory when used for melting-points below 100° C., because the hygroscopic nature of the lagging on the heating coil causes the glass cylinder G to become coated inside with condensed moisture when the heating current is switched on. Observation of the capillary is then difficult. Also it is not easy for the inexperienced student to secure the essential slow rate of heating.

Mixed melting-points.—Since the melting-point of a pure substance is depressed by the addition of impurity, determination of a mixed melting-point provides useful and simple confirmation of the identity of a given compound.

A small quantity of the compound (whose melting-point has previously been determined) is mixed with rather less than its own weight of authentic substance believed to be identical with it, and the melting-point of the mixture is determined. If the melting-point is sharp and the same as the figure first obtained, identity is established. If the melting-point is indefinite or definitely lower than the first figure, the two substances are not identical.

Determination of the boiling-point

Although a perfectly pure liquid has a sharp boiling-point (constant for a given atmospheric pressure), the difficulties attendant on the commercial production of pure liquids are such that the majority of liquid compounds given for the purpose of identification contain at least traces of impurities, causing them to boil over a range of a few degrees. The boiling-point must therefore be regarded as less definite evidence of identity than the melting-point.

Furthermore, the fact that a liquid has a sharp boiling-point does not prove that it is a single pure substance since azeotropic or constant-boiling mixtures have this same property.

If sufficient material is available, straightforward distillation under atmospheric pressure is the simplest method for determining the boiling-point, and this, at the same time, enables a purer sample of the substance to be obtained as " head and tail " fractions may be collected separately and rejected. The normal precautions must be taken; i.e. (*a*) the bulb of the thermometer must be opposite the opening of the side tube, (*b*) small fragments of porcelain should always be added to prevent " bumping ", (*c*) low-

boiling inflammable liquids must be distilled from a water-bath and (*d*) an air condenser should replace the water condenser if the liquid boils above 150° C.

Most laboratory suppliers will (on request) make small scale distillation apparatus, and this will be found very convenient for qualitative work. In the case of distillation flasks of capacity 10–20 ml., a slightly modified neck (fig. 4) is necessary to accommodate the thermometer, which should be as thin as possible.

The following methods may also be used, but while they require much less of the liquid they are less accurate as they give

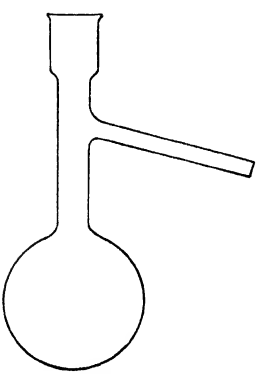


Fig. 4

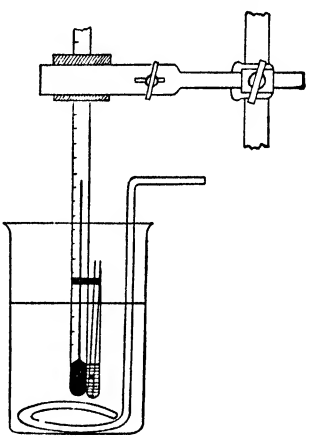


Fig. 5

the lower figure only of the boiling-point range and can be used only for liquids boiling below 220° C. if high-boiling-point liquid paraffin is used in the heating bath:

1. A capillary tube as for melting-point determination is prepared sealed about 1 cm. from the end,* and placed with the short open limb downward in a small narrow test-tube (3″ × ¼″) which contains about 1 ml. of the liquid under investigation. This tube is then attached to the thermometer by a small rubber band so that the lower end is in contact with the thermometer bulb (fig. 5), and the whole placed in a heating bath containing a stirrer as used in melting-point determinations (see p. 5). The bath temperature is raised fairly rapidly and observation kept on the lower open end of the capillary. When the temperature is just above the boiling-

* A capillary tube sealed at the end, and placed with the open end downward in the 3″ by ¼″ tube, will give approximately correct results.

point of the liquid a continuous stream of small bubbles will emerge. Heating is stopped, and the temperature *at which the stream of bubbles ceases* is noted. This is the boiling-point of the liquid.

2. *Method of Emich.*—Take a capillary tube as in Method I above and draw out one end to form a fine capillary. Break this off so as to leave about 1·5 cm. of the fine tube and dip it into the liquid under test. Liquid will rise in the tube by capillarity. Hold the partially filled tube with the wider open end pointing slightly downwards and seal the fine end with a small flame. A small bubble of air will be imprisoned below the liquid. This tube is attached to the thermometer in the usual way (or better with both thermometer and tube backed by a microscope slide) and placed in the heating bath, the temperature of which is raised *slowly*, particularly when the liquid in the capillary shows signs of moving. When the boiling-point is reached, the column of liquid will rise in the capillary to the level of the surrounding bath liquid. Record this temperature.

CHAPTER II

Detection of the Elements

It is impossible to over-emphasize the importance of a correct determination of the elements present in a compound. Any error will lead to the placing of the compound under investigation in the wrong group and render its correct identification impossible.

Students should take advantage of every opportunity to practise the identification of elements until they can obtain consistently correct results. In any case where the result of a test is doubtful it should be repeated without hesitation.

Carbon and hydrogen are almost invariably present in organic compounds, and tests for their presence are seldom carried out. Oxygen, too, is not usually tested for directly, though an indication of its presence may be obtained by the use of " ferrox " paper, i.e. filter paper soaked in a strong solution of ferric thiocyanate in pure methyl alcohol and subsequently dried (see p. 290). When a small piece of such paper, about 1 sq. cm., is immersed in an organic liquid or a solution of a solid in dry benzene, a pink colour is imparted to the liquid or solution if oxygen is present. Obviously the liquid must be perfectly dry for this test to be effective.

Beilstein's test for halogens

Take a piece of stout copper wire, insert one end into a cork for convenience in handling, and hammer out the other end to form a flat surface. Heat this end in the bunsen flame till no colour is imparted to the flame. Place a little of the substance on the flattened end and heat in the lower outer edge of the flame. Wait until the yellow colour due to the burning substance has disappeared, and look for a green flame.

Absence of a green flame means absence of halogens. A green flame usually denotes presence of halogens, though urea, thiourea and some pyridine and quinoline derivatives give a strong green flame due to the formation of cuprous cyanide. The test should always be confirmed by the silver nitrate test (see below).

Fusion with potassium as a test for nitrogen, sulphur, fluorine, chlorine, bromine and iodine

Take a small ignition tube ($3'' \times \frac{1}{2}''$) and clamp lightly in a vertical position. Prepare a small pellet of potassium about the size of a pea, by removing the adhering film of liquid with filter paper, and introduce it into the tube. Warm gently until the potassium is just molten and then drop in the substance in small quantities until the bulk added is about equal to that of the potassium. If a liquid is under examination it must be added dropwise from a fine dropping tube. Now heat the tube and contents *as strongly as possible* for about one minute. While still hot bring a porcelain dish containing about 10 ml. of distilled water up under the tube and allow the lower part of the tube to crack off and fall into the water. Crush the fragments with a flat-ended glass rod and boil well. Filter. The filtrate has now to be examined for cyanide, sulphide and halides, these having possibly been formed by interaction of the potassium with carbon, nitrogen, sulphur and the respective halogens.

Test for nitrogen

To a little of the filtrate add a few drops of sodium hydroxide solution, to ensure that it is alkaline, followed by ferrous sulphate solution. If a black precipitate forms at this stage, the presence of sulphur is indicated and an additional amount of ferrous sulphate should be added. In the absence of sulphur a dark greenish-black precipitate of "ferrous hydroxide" results. Boil well. This converts any cyanide present into ferrocyanide.

$$6KCN + FeSO_4 = K_2SO_4 + K_4[Fe(CN)_6].$$

Add a few drops of ferric chloride solution (though in the absence of sulphur this is not essential) and sufficient dilute hydrochloric acid to render the solution definitely acid. If nitrogen is present, a precipitate of prussian blue, or a green solution due to finely divided particles of this compound, will be formed. If in doubt as to whether prussian blue has been formed, filter through a small filter paper. The precipitate will then be visible on the paper in those cases where nitrogen is present.

$$4FeCl_3 + 3K_4[Fe(CN)_6] = Fe_4[Fe(CN)_6]_3 + 12KCl$$

If sulphur is present, there is a possibility of potassium thiocyanate

being formed which will give a red colour with ferric chloride and hydrochloric acid.

It occasionally happens that a substance, known from the results of the preliminary tests to contain nitrogen, fails to give a positive result in the potassium fusion. This is the case with urea and some of its derivatives and is due mainly to a deficiency of carbon in the compound. This can be corrected either by mixing the original substance with a little pure cane sugar before fusion, or by use of Middleton's mixture (see p. 16).

It may also be noted that failure to obtain a sufficiently high temperature in the fusion often leads to incorrect conclusions.

Test for sulphur

To another portion of the filtrate from the potassium fusion add a few drops of sodium hydroxide solution and then a little freshly prepared solution of sodium nitroprusside. The appearance of a violet-red colour denotes the presence of sulphur in the original substance.

$$Na_2[Fe(CN)_5NO] + Na_2S = Na_4[Fe(CN)_5SNO].$$

To confirm this, place a little of the filtrate in a dish and acidify with dilute hydrochloric acid. Cover immediately with a filter paper, the centre of which has been moistened with sodium plumbite solution (made by adding sodium hydroxide solution to a solution of lead acetate until the precipitate first formed just redissolves). If sulphur is present, a dark stain due to lead sulphide will be visible on the upper surface of the paper. If a very faint stain, visible on the lower surface only, is formed, it is probably due to a trace of sulphur present as impurity.

Further proof of the presence or absence of sulphur in the compound may be obtained by the examination of the aqueous solution obtained from the oxidation fusion (see p. 15).

Test for halogens

Take about 3 ml. of the filtrate from the potassium fusion, acidify with acetic acid and add a few drops of calcium chloride solution. An opalescent solution which deposits gelatinous calcium fluoride on standing indicates *fluorine* in the original compound.

The slowness with which the above precipitate appears may

cause a negative result to be returned for fluorine even when it is present in the original substance, and the above test should be supplemented by the following:—

One ml. of the filtrate from the potassium fusion is made acid with glacial acetic acid and added to an equal volume of cerous nitrate solution (0·2 g. of cerous nitrate dissolved in 5 ml. of water containing two drops of glacial acetic acid). Formation of a milky white gelatinous precipitate indicates that a fluoride is present in the solution. (Phosphates interfere with this test.)

Acidify a portion of the filtrate from the potassium fusion with dilute nitric acid and boil in an open dish till the bulk is reduced to half the original. This destroys cyanide and sulphide, the removal of which is necessary since both give precipitates with silver nitrate in nitric acid solution. Add silver nitrate solution. The formation of a white or yellow precipitate indicates the presence of chlorine, bromine or iodine in the original substance. If a positive result is obtained take a fresh portion of the filtrate, *acidify with dilute hydrochloric acid*, add 1 ml. of carbon tetrachloride and a few drops of chlorine water (a large excess must be avoided). Shake well

A *colourless* carbon tetrachloride layer indicates that *chlorine* is present in the original compound.

A *brown* carbon tetrachloride layer indicates that *bromine* is present in the original compound.

A *violet* carbon tetrachloride layer indicates that *iodine* is present in the original compound.

In the two latter cases, chlorine may also be present, but the small amount of alkali halides present in the filtrate from the potassium fusion makes the application of inorganic methods of separation somewhat difficult. Larger amounts of the original substance can safely be used if lime is substituted for potasssium.

Mix about 0·5 g. of substance with halogen-free slaked lime (As. T. grade is suitable) in an ignition tube, cover with a layer of lime and heat from the top downwards. Cool, extract with boiling water, add sodium carbonate solution and filter off the precipitated calcium carbonate. Take 10 ml. of the filtrate, make acid with dilute sulphuric acid and add a little sodium or potassium nitrite solution. Development of a brown colour indicates the presence of *iodine* in the original compound. Confirm by shaking a small portion of the solution with carbon tetrachloride. A violet carbon tetrachloride layer proves that iodine is present. Boil the re-

mainder of the solution till free from iodine. Test for complete removal of iodine by adding a little more acid and nitrite and boiling again if necessary. Cool, and shake a small portion with carbon tetrachloride. The lower layer should remain colourless. To this solution together with the carbon tetrachloride add a *few drops* of chlorine water and shake well. A brown colour in the carbon tetrachloride layer proves *bromine* present in the original compound. If bromine is present remove it from the main portion of the solution by adding 2 ml. of concentrated sulphuric acid and 0·5 g. of potassium or ammonium persulphate and boiling. Do not evaporate to too small a bulk or hydrogen chloride may be driven off. Cool and test a portion for freedom from bromine with chlorine water and carbon tetrachloride. If free, add silver nitrate solution to the remaining portion. A white precipitate of silver chloride proves that the original substance contains *chlorine*. If no bromine is present, proceed to test for chloride after removal of iodine.

Test for phosphorus and arsenic

Take a mixture of equal parts of potassium nitrate and dry potassium carbonate (oxidation fusion mixture), and mix about 0·2 g. of the organic substance with about 1 g. of this in a clean crucible or test-tube. Since the reaction is sometimes explosive, heat *very gently* at first and then more strongly till a clear colourless melt results. Phosphorus will be converted to potassium phosphate and arsenic to potassium arsenate. Cool and extract with boiling water, filtering if necessary. Make a portion of the filtrate acid with dilute hydrochloric acid and boil off carbon dioxide. Make alkaline with ammonia, add magnesia mixture and shake well. The formation of a white crystalline precipitate indicates the presence of phosphate and/or arsenate. Filter, and dissolve the precipitate in a little dilute hydrochloric acid, saturate the solution with sulphur dioxide, boil off sulphur dioxide and pass in hydrogen sulphide. A yellow precipitate of arsenious sulphide, which must be identified as such, proves that *arsenic* is present in the original substance. Filter off this precipitate, boil off the hydrogen sulphide from the filtrate, add 1 ml. of concentrated nitric acid and about 6 ml. of ammonium nitromolybdate solution (see p. 290) and warm gently. A bright yellow powdery precipitate of ammonium phosphomolybdate proves that *phosphorus* is present in the original compound. The formation of a creamy-white pre-

cipitate is due to the separation of molybdic acid and is not proof of the presence of phosphate.

To confirm the results of this test take the second portion of the filtrate from the oxidation fusion, acidify with dilute nitric acid and boil off carbon dioxide. Neutralize with ammonia and add silver nitrate solution. If phosphorus is present in the original substance a yellow precipitate will be formed. If arsenic is present a reddish-brown precipitate will appear.

If chlorine, bromine or iodine have been previously detected, acidify the filtrate from the oxidation fusion as above and add excess silver nitrate. Filter off the precipitated silver halide and neutralize the filtrate carefully with ammonia. Precipitates as mentioned above will be obtained if phosphorus or arsenic is present in the given compound.

A portion of the solution obtained from the oxidation fusion may be tested for sulphate by acidifying with dilute hydrochloric acid and adding barium chloride solution. A white precipitate of barium sulphate proves that *sulphur* is present in the original.

The alkali-zinc test for nitrogen

The reagent (Middleton's mixture) consists of an intimate mixture of zinc dust and half its weight of anhydrous sodium carbonate. It gives a non-violent reaction except with picric acid and picrates; sulphur does not interfere, no sulphide or thiocyanate being present in the filtrate and a deficiency of carbon in the original is not detrimental. It may be used in testing for sulphur or halogens (chlorine, bromine and iodine) if a comparison " blank " is carried out on the reagent. In view of the variable quality of zinc dust the last use is not recommended.

For a solid mix about 0·4 g. of it with about five times its bulk of mixture, introduce into an ignition tube and add mixture to form a column about one inch in length. *For a liquid* introduce about 3–4 drops of it into an ignition tube and add mixture to fill about two-thirds of the tube. Heat from the top downwards, so that the upper part of the column becomes red-hot before the substance is vaporized. Finally, heat to redness for a minute or more and then plunge into 10 ml. of distilled water in a dish, breaking the tube by force if necessary. Boil for half a minute and filter. The filtrate must be colourless. To 2 ml. of the filtrate add 2–3 drops of sodium hydroxide solution and one or two small crystals of ferrous sulphate. Boil for half a minute and cool. Make just

acid with concentrated hydrochloric acid, heat to boiling and cool. A blue precipitate or a green solution, leaving a blue residue on filtration, proves *nitrogen* present in the original substance.

To the residue on the filter paper add about 10 ml. of dilute hydrochloric acid and cover with a filter paper on the centre of which a drop of sodium plumbite solution has been placed. A dark brown stain visible on the upper surface of the paper indicates the presence of *sulphur* in the original compound.

CHAPTER III

Summary of Classification Tests, Derivatives, etc., for Compounds containing Carbon, Hydrogen, and possibly Oxygen and a Metal

Preliminary examination

1. Physical characteristics.
2. Ignition on a crucible lid.
3. Solubility in water.
4. Reaction of solution in water to litmus.
5. Soda-lime test.
6. Action of hot dilute sulphuric acid.
7. Action of concentrated sulphuric acid.
8. Action of cold and hot sodium hydroxide.

Class	Classification Tests	Additional Tests	Derivatives, &c.
Metallic salts of acids and phenols (p. 23)	Non - combustible residue on ignition		
Carbohydrates **Glycosides** (p. 26)	Molisch's reagent	Fehling's solution Barfoed's solution Specific tests for certain carbohydrates	Osazone Specific rotatory power Acetates
Aldehydes **Ketones** **Polymerized aldehydes** **Keto-Acids** **Acetals** **Some quinones** (p. 35)	2 : 4-Dinitrophenylhydrazine	Schiff's reagent Tollen's reagent Angeli-Rimini test Dimedone	2 : 4-Dinitrophenylhydrazone Phenylhydrazone Semicarbazone Oxime Dimedone derivative Arylidene derivative
Quinones (p. 48)	Appearance	Separate tests	Quinoxaline
Carboxylic acids **Acid anhydrides** **Easily hydrolysable esters** (p. 50)	0·1N Sodium hydroxide and phenolphthalein	Aniline for anhydrides Alkaline potassium permanganate and bromine for unsaturation Ferric chloride	Equivalent weight Amide Anilide *p*-Toluidide *p*-Nitrobenzyl ester *p*-Bromo phenacyl ester S-benzylthiuronium salt 2-Alkylbenziminazole picrate Phenylhydrazide

Class	Classification Tests	Additional Tests	Derivatives, &c.
Phenols (p. 61)	Ferric chloride	Diazotized *p*-nitroaniline Mercurous nitrate test	Aryloxyacetic acid Phenyl carbamate α-Naphthyl carbamate *p*-Nitrobenzyl ether Benzoate 3 : 5-Dinitrobenzoate Bromo derivative *p*-Toluenesulphonyl ester *p*-Nitrobenzoate Acetate
Esters **Lactones** (p. 67)	Alcoholic potash and phenolphthalein	Isolation and identification of hydrolysis products	Equivalent weight Amide of the acid constituent
Alcohols (p. 77)	Metallic potassium	Hexanitrato ceric acid Lucas' test Oxidation	3 : 5-Dinitrobenzoate Phenyl carbamate (urethane) α-Naphthyl carbamate *p*-Nitrophenyl carbamate S-benzylthiuronium derivative 3-Nitrophthalate Benzoate Acetate
Ethers **Cylic ethers** (p. 86)	Cold concentrated sulphuric acid	" Ferrox " paper	3 : 5-Dinitrobenzoate Bromo derivative Nitro derivative Picric acid derivative 1 : 3 : 5-Trinitro benzene derivative
Hydrocarbons (p. 89)	Cold concentrated sulphuric acid and 30 per cent oleum	Bromine, potassium permanganate and Nessler's solution for unsaturation	Physical constants for saturated aliphatic hydrocarbons and paraffins Nitro derivative Addition compound with picric acid, picrolonic acid or 1:3:5-trinitrobenzene Sulphonamide Aroylbenzoic acid Styphnic acid derivative Oxidation of side chain Oxidation to quinone

GROUP I

COMPOUNDS CONTAINING CARBON, HYDROGEN AND POSSIBLY OXYGEN AND A METAL

Preliminary examination

1. *Physical characteristics*

Note physical state, whether crystalline or amorphous (if a solid), odour and colour.

If crystalline and strongly coloured	Probably a quinone.
If intensely red	Probably alizarin or other hydroxy anthraquinone.
If pale yellow	Benzil or anthraquinone.
If pale yellow with a bluish fluorescence	Anthracene.

Note.—Many compounds which are colourless when quite pure are often met with showing colour due to presence of impurities, e.g. cresols.

2. *Effect of ignition on a crucible lid*

Substance burns with a non-smoky flame and leaves no residue	Probably an aliphatic compound.
Substance burns with a luminous smoky flame and leaves no residue	Probably an aromatic compound.
If a non-combustible residue of metal oxide, or carbonate remains	The compound is a metallic salt of an acid or substance containing an acidic hydrogen atom.

3. *Solubility in water*

(*a*) Soluble	All carbohydrates except cellulose, most glycosides; alcohols, acids, aldehydes and ketones containing less than five carbon atoms; some simple phenols; most polyhydric phenols.
(*b*) Sparingly soluble or insoluble	All hydrocarbons; most esters; simple ethers; many aliphatic compounds of high molecular weight; most cyclic compounds.

4. *Reaction to litmus*

(*a*) Strongly acid	Simple carboxylic acids; most aliphatic and many aromatic hydroxy acids; acid anhydrides (these react slowly with water); some easily hydrolysable esters of low molecular weight.
(*b*) Faintly acid	Phenols.

5. *Soda-lime test*

(*a*) *For solids.*—Grind about 2 g. of freshly ignited soda-lime with about 0·5 g. of substance and place in a 3″ × ½″ ignition tube; cover with a 1″ layer of soda-lime and heat gently, beginning at the top and working downwards.

(*b*) *For liquids.*—Introduce about 4–5 drops of liquid into an ignition tube, add dry soda-lime to fill about two-thirds of the tube and heat as above.

A grey sublimate forming metallic globules on rubbing with a glass rod	Presence of a mercury compound.
Vapours evolved turn moist red litmus blue	*Nitrogen* is present in the original compound. If (as is sometimes the case) this has not been found in the elements test, this test must be repeated with the necessary precautions (see p. 12), and proof of the presence of the element obtained. Examination is then continued according to the scheme for Group II.
Phenolic odour (not apparent in the original compound)	Phenolic acid or salt or ester of a a phenolic acid.
Odour of bitter almonds	A derivative of benzaldehyde.
Odour of a hydrocarbon	A carboxylic acid or salt of such an acid. Thus methane is obtained from acetates, ethylene from succinates and benzene from benzoates by decarboxylation.
Odour of burnt sugar	Carbohydrates; tartaric, citric acids and their salts.
Evolution of hydrogen	Formates and oxalates.

6. *Effect of warming with dilute sulphuric acid*

Acid vapours evolved	Volatile acid or derivative of such an acid, e.g. acetic or formic acid.
Odour of an alcohol	Ester of a non-volatile acid derived from a lower aliphatic alcohol.

7. *Action with cold and hot concentrated sulphuric acid*

(*a*) *Cold*

Insoluble	Paraffins; aromatic hydrocarbons.
Soluble	Ethers.
Red or yellow-brown colour	Some glycosides; benzilic acid; salicylic aldehyde.
Intense colours	Triaryl carbinols.

(*b*) *Hot*

No charring but carbon monoxide evolved	Formates.
No charring but carbon monoxide and carbon dioxide evolved	Oxalates.
No charring but pungent acid vapours evolved	Acetates; benzoates.
Slowly darkens, irritating acid fumes evolved	Succinic acid and its salts.
Chars rapidly, carbon dioxide and sulphur dioxide evolved	Carbohydrates; tartaric acid and its salts.
No charring but turns yellow, carbon monoxide and dioxide being evolved	Citric acid and its salts.
Chars but no gases evolved	Aldehydes; some ketones; most polyhydric phenols; many hydroxy aromatic acids and their derivatives.

8. *Action with cold and hot* 30 *per cent sodium hydroxide*

Soluble in the cold even if insoluble in water	Acids; phenols; keto-enolic esters.
Soluble in the cold (but insoluble in sodium bicarbonate solution)	Phenols other than water-soluble phenols.
Soluble on warming	Acid anhydrides; some esters; lactones.
Liquid sets to a white solid in the cold	Some esters of oxalic acid, salicylic acid, &c.
Odour of alcohol on warming	Esters derived from lower aliphatic alcohols.
Solution turns yellow or brown on warming	Sugars, other than sucrose; some phenols.
Resin formed	Aliphatic aldehydes.
An intensely coloured solution	Phthaleins; alizarin derivatives.

GROUP I—CLASS I

METALLIC SALTS OF ACIDS AND PHENOLS

The presence of the metal will be apparent from the residue of metal oxide or carbonate remaining when the substance is burned in air on a crucible lid.

Dissolve the residue in dilute mineral acid (dilute nitric acid in the case of Group I metals) and examine the solution as in inorganic analysis. If the residue is insoluble in mineral acid, e.g. alumina or ferric oxide, treat it as for an insoluble substance in inorganic analysis.

Note that mercury salts may leave no residue, but their presence will have been indicated in the preliminary examination with soda-lime. Identification of mercury is best effected by boiling with strong sodium carbonate solution, filtering and examining the residue for mercury.

Identification of the acid or phenol

1. *If the salt is soluble in water* (as is generally the case with the alkali metal salts) the *p*-nitrobenzyl ester and the S-benzylthiuronium salt (see pp. 53, 54) of the acid may be prepared directly from the original compound.

Preparation of the silver, calcium, barium or lead salt will also serve for the determination of the equivalent weight of the acid (see pp. 70, 71).

Note.—If the preliminary test with litmus shows the compound to be an acid salt, e.g. potassium hydrogen phthalate or potassium hydrogen tartrate, the determination of the equivalent weight of the salt by titration with standard alkali, using phenolphthalein as an indicator, will be a useful aid to identification.

With a soluble salt of a phenol the given compound may be used for the preparation of the corresponding aryl-oxyacetic acid and the *p*-nitrobenzyl ether (see pp. 62, 63).

Isolation of the acid or phenol (if this is desired)

If the acid is volatile, distil about 2 g. of the salt with dilute sulphuric acid and collect the aqueous distillate.

If the acid is not readily volatile, treat one gram of the given

compound with 5 ml. of hot concentrated hydrochloric acid (or dilute nitric acid if Group I metals are present) and cool. Sparingly soluble acids will be precipitated. Filter, wash and treat as for carbon, hydrogen and oxygen containing acids (see pp. 51–4).

If no precipitation occurs, extract the acid liquid with an organic solvent in a separating funnel. Separate the two layers. Wash the solvent layer with a little water, dry over anhydrous sodium sulphate and remove the solvent on a water-bath. Identify the residual acid (see pp. 51–4) or phenol (see pp. 62–6).

If no acid is extracted the given compound is probably a salt of a water-soluble acid more soluble in water than in the organic solvent, e.g. oxalic, tartaric or citric. In addition to the preparation of the derivatives indicated above, further proof of the presence of salts of such acids may be obtained by applying some of the tests given on pp. 25–6.

2. *If the salt is not readily soluble in water* mix one gram of the given compound with one gram of anhydrous sodium carbonate and 10 ml. of water. Boil for about 10 min., then filter. The filtrate will contain the sodium salt of the organic acid with excess sodium carbonate. Make the filtrate just acid with dilute hydrochloric acid, add ammonium hydroxide till just alkaline and boil off excess ammonia. Evaporate the resulting solution to a low bulk then proceed as in 1 above for the preparation of derivatives and the free acid.

Confirmatory tests for salts of the more common water-soluble acids

For water-soluble salts the tests may be carried out on the original compound. If this be acid, neutralize with ammonium hydroxide.

For water-insoluble salts some of the tests may be carried out on the original solid, but it is generally more convenient to prepare a solution of the sodium salt of the acid by boiling some of the substance with sodium carbonate solution and filtering. Make the filtrate just acid with dilute sulphuric, hydrochloric or nitric acid (depending on the test to be applied), add ammonium hydroxide till just alkaline and boil till neutral.

Formates.—1. On warming with *concentrated sulphuric acid* in an ignition tube carbon monoxide is evolved. The gas burns with a blue flame at the mouth of the tube.

2. In neutral solution *silver nitrate* gives a white precipitate of the silver salt which, on warming, is rapidly reduced to a black precipitate of silver.

3. In neutral solution *ferric chloride* gives a red coloration, discharged by hydrochloric acid. If the red solution be diluted and boiled, a brown precipitate of a basic ferric formate is produced.

4. On warming with a solution of *mercuric chloride* a white precipitate of mercurous chloride is produced which in the presence of excess formate is reduced to grey metallic mercury.

Acetates.—1. Treat about 1 g. of the solid with 1 ml. of concentrated sulphuric acid and 2 ml. of ethyl alcohol and warm gently for several minutes. Cool, dilute with water and transfer to a clock-glass. The ethyl acetate formed may be recognized by its pleasant fruity odour.

Iso-amyl alcohol may be used instead of ethyl alcohol as the resulting *iso*-amyl acetate is more readily distinguished from the alcohol itself than is the case with ethyl alcohol.

2. In neutral solution *ferric chloride* gives a deep red coloration destroyed by dilute hydrochloric acid. On diluting the red solution containing ferric acetate and boiling, brown basic ferric acetate is precipitated.

3. To 0·5 ml. of the acetate solution add 0·5 ml. of a 5 per cent *lanthanum nitrate* solution, 0·5 ml. of iodine solution and a few drops of dilute ammonium hydroxide solution. Heat slowly to the boiling-point when a blue colour is produced.

Propionates give a similar reaction while sulphates interfere.

Oxalates.—1. In neutral solution *calcium chloride* gives a white crystalline precipitate of calcium oxalate, insoluble in acetic acid but soluble in dilute mineral acid.

2. Oxalates discharge the colour from *potassium permanganate* acidified with dilute sulphuric acid and heated to 60° C., carbon dioxide being evolved. Chlorides interfere with the test.

3. *Aniline blue test.* Place a very small amount of the substance in an ignition tube, mix with a very little diphenylamine, add a few drops of syrupy phosphoric acid and heat gently over a small flame. A blue colour develops, disappearing on cooling. Dissolve in alcohol when the blue colour reappears.

Tartrates.—1. On adding *calcium chloride* to a concentrated solution, a white crystalline precipitate is formed (precipitation is slow if the solution is dilute). This precipitate is soluble in dilute acetic acid and in dilute mineral acids.

2. *Silver mirror test.* In a perfectly clean test-tube place a few ml. of silver nitrate solution, add 2–3 drops of sodium hydroxide solution followed by dilute ammonia added dropwise until the solution is almost clear. Add a small amount of the tartrate in solution and heat in a water-bath. A silver mirror is formed.

3. *Fenton's test.* To a few ml. of the neutral tartrate solution add one drop of a saturated solution of ferrous sulphate and then 2–3 drops of 10 vol. hydrogen peroxide. Add excess caustic soda solution when an intense violet coloration develops.

4. To a solution of the tartrate add a few ml. of a 5 per cent solution of ammonium vanadate and acidify with acetic acid. An intense orange coloration is formed.

Citrates.—1. *Calcium chloride* gives no precipitate in the cold, but on boiling a white crystalline precipitate is slowly formed.

2. *Denigès' test.* To 5 ml. of the citrate solution add 1 ml. of Denigès' reagent (see p. 290), heat to boiling and add a few drops of a 2 per cent potassium permanganate solution. The colour of this is discharged and a heavy white precipitate suddenly formed.

Succinates.—1. In neutral solution, neutral *ferric chloride* solution gives a pale brown precipitate of basic ferric succinate and the solution becomes acid due to the formation of free succinic acid.

2. Heat gently a mixture of about 0·5 g. of the succinate, 2–3 drops of concentrated sulphuric acid and 1 g. of resorcinol. Cool and pour into water. An orange solution with green fluorescence is obtained. On making alkaline with caustic soda, the solution becomes red and the fluorescence more intense.

GROUP I—CLASS II

CARBOHYDRATES, GLYCOSIDES

Carbohydrates

Strictly speaking the term *carbohydrate* covers all compounds containing only carbon, hydrogen and oxygen in which the H : O ratio is 2 : 1 and which might therefore be written as $C_n(H_2O)_y$. For purposes of identification the class is regarded as embracing the sugars, common glycosides, starch, dextrin, inulin and cellulose. Other compounds which conform to the above definition are known,

e.g. glyceric aldehyde, glycollic aldehyde, formaldehyde and acetic acid, the first of which gives all the main reactions characteristic of the sugars. Such substances are, however, best placed in the class corresponding to their main functional groups and are not therefore included in the *carbohydrate* class. Rhamnose, a methyl pentose ($C_6H_{12}O_5$), although not conforming to the formula requirement of the class, is a typical sugar so far as reactions are concerned and its inclusion here seems justified.

Placing the above limitations on the term *carbohydrate*, it may be stated that all common members of this class are solids and consequently if the substance under examination is a liquid, the classification test for this class may be omitted.

Classification test. Dissolve about 0·1 g. of the substance in 2 ml. of water, add 2 to 3 drops of a 10 per cent solution of α-naphthol in alcohol (Molisch's reagent) and shake. Carefully pour 2 ml. of concentrated sulphuric acid down the side of the tube, so as to form a separate layer at the bottom, and allow to stand for 2 min. If a red-violet ring forms at the junction of the two layers and, on shaking, the whole mixture becomes red-violet and a dull blue precipitate forms, the compound belongs to this class. (Note that benzilic acid also gives the test but is distinguished by its acidic nature.)

If Molisch's test is positive (and the substance is not acidic) place a small amount of the original substance in a dry test-tube and add one drop of concentrated sulphuric acid. The development of a definite colour in a few minutes indicates the presence of a naturally occurring glycoside.

Amygdalin—carmine	Salicin—crimson
Arbutin—yellow	Saponin—red brown
Digitalin—red brown	Strophanthin—green
Digitonin—brown	

Further tests for glycosides will be found on p. 34.

If the substance is not a glycoside, proceed as follows:—

(*a*) Prepare 2 ml. of Fehling's solution (see p. 290), add 1 ml. of an aqueous solution of the original compound and heat in a boiling-water bath for one minute. If the whole of the mixture becomes reddish, due to suspended cuprous oxide, a reducing sugar is present, i.e.

d-glucose	*d*-fructose	*d*-galactose
lactose	*d*-maltose	*d*-mannose
d-xylose	*l*-arabinose	*l*-rhamnose

A subdivision of these may be effected by applying the following test:—

To 2 ml. of Barfoed's solution (13 g. of neutral crystalline copper acetate in 200 ml. of 1 per cent acetic acid) add an equal volume of an aqueous solution of the substance and stand the test-tube in briskly boiling water for 2 min. If no reduction to cuprous oxide occurs, lactose or *d*-maltose is present.

(*b*) If there is no reduction of the Fehling's solution in the above test (*a*), or only a slight yellowish turbidity is produced, the substance is a non-reducing saccharide, i.e.

cellulose	starch	dextrin
inulin	raffinose	sucrose

The following properties are useful as an aid to identification:—

Cellulose is insoluble in hot water but dissolves in Schweitzer's reagent (see p. 291), in warm 85 per cent phosphoric acid catalysed by zinc chloride and in 30 per cent zinc chloride in concentrated hydrochloric acid. Water yields precipitates with all these solutions.

Starch gives a blue colour with iodine, discharged by heating to about 80° C., restored on cooling. Microscopic examination will often enable the particular variety of starch (potato, rice, &c.) to be identified. Soluble starch dissolves in water. Note that some samples of dextrin contain starch.

Dextrin gives a red-violet to brown-violet with iodine. With Nylander's reagent (see p. 291) the alkalinity of which has been partly neutralized by hydrochloric acid it gives an amber solution changing to a white colloidal precipitate, finally becoming black.

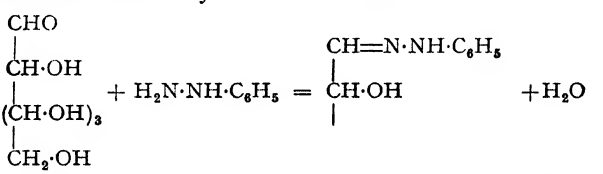
Inulin with 0·5 per cent potassium ferricyanide solution gives a green colour on adding ferric chloride solution. Note that dextrin also gives a green colour. It gives a yellow colour with iodine or on boiling with sodium hydroxide.

Raffinose on heating to 100° C. for 15 to 20 minutes with orcinol gives an amber colour. It is oxidized by 25 per cent nitric acid.

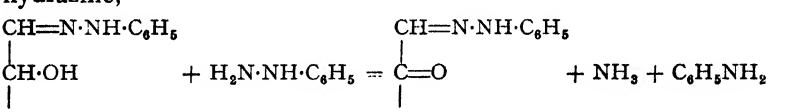
Sucrose.—To a mixture of 1 ml. of saturated nickel ammonium sulphate solution and a few mg. of solid sucrose add about 0·5 ml. of concentrated hydrochloric acid and boil. Sucrose gives a green colour changing to yellow and finally to brownish-red.

Derivatives, &c.

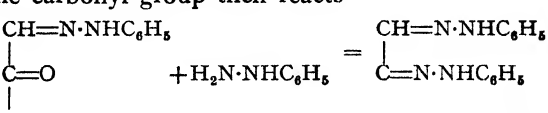
1. **Osazone.**—Although the reducing sugars are now formulated as cyclic compounds, they are capable of reacting with phenylhydrazine, as though they contained free aldehydic or carbonyl groups, to yield phenylhydrazones which by the further action of phenylhydrazine produce osazones. These have, in many cases, characteristic crystalline structures, which make them valuable as an aid to identification. The melting-points are, however, too close to one another to make this property of any use. The phenylhydrazones are formed by the usual reaction:—



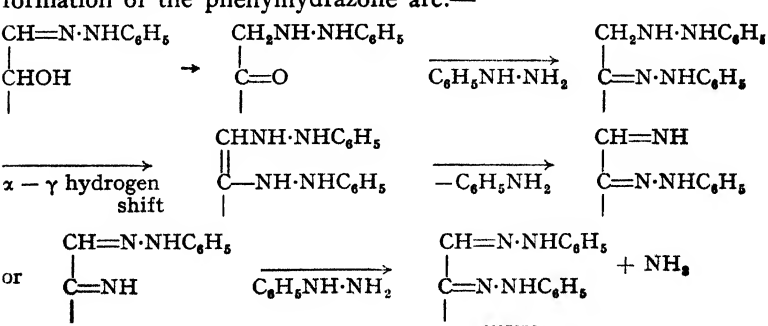
Oxidation of the CH·OH group adjacent to the phenylhydrazine group then occurs at the expense of a second molecule of phenylhydrazine,



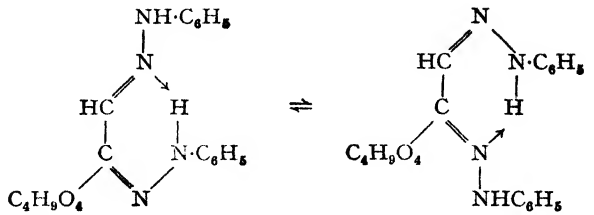
and the carbonyl group then reacts



According to Weygand (1940) the stages subsequent to the formation of the phenylhydrazone are:—



The osazone structure may, however, be one of the tautomeric chelate ring structures.



To prepare the osazone take 1 g. of the sugar in 5 ml. of water and add one drop of a saturated solution of sodium bisulphite (to prevent the formation of tarry impurities) followed by phenylhydrazine acetate solution (1 ml. phenylhydrazine in 1 ml. of glacial acetic acid and water added to 5 ml.). Heat in a loosely corked test-tube in boiling water for 30 min. If a precipitate forms in the hot solution, note the time required for its formation (see Table I, p. 33). Allow the tube to cool slowly to avoid distortion of the crystals. Filter and recrystallize from 50 per cent alcohol. Examine a drop of the liquid plus crystals under a low-power microscope, care being taken to avoid breaking up the crystals, and compare either with photographs (see Frontispiece) or an osazone prepared from an authentic specimen of the sugar.

Note 1.—If conditions are carefully standardized, the time taken for the formation of the osazone is characteristic of the sugar. Otherwise time is merely a rough indication of identity.

Note 2.—Different sugars will give the same osazone, e.g. *d*-glucose, *d*-mannose, *d*-fructose.

2. Specific Rotatory Power

The specific rotation $[\alpha]^t_D$ of a pure liquid observed by the D line of sodium light at the temperature $t°$ C., is calculated from the formula

$$[\alpha]^t_D = \frac{100\alpha}{lc},$$

where α = observed angle of rotation, l = length in *decimetres* of the column of liquid in the polarimeter tube, and c = the number of grams of active substance in 100 ml. of solution.

Since there is considerable variation in the pattern of polarimeters a precise description of the method for determining the

angle of rotation is impracticable, and the procedure is best learnt by a demonstration. Some general principles may, however, be set down relating to the two-field type of instrument. The general arrangement of the optical parts is as shown (fig. 6):—

S—source of monochromatic light.
L_1—lens producing parallel beam of rays.
N_1—polarizing Nicol.
Q—half wave-length plate.
A—glass tube (usually 2 dcm. long) containing solution under test.
N_2—analysing Nicol.
L_2—object glass, H—eye-piece } forming low-power telescope.

Provision is made for rotating completely either N_1 or N_2, the extent of the rotation being measured on a divided circular scale fitted with a vernier.

Fig. 6

Fill the tube A with distilled water, avoiding the inclusion of a bubble of air and being careful not to screw up the end-cap too tightly, as this would produce strain on the end-glass with consequent elliptic polarization and a patchy field. Place the tube in the instrument and rotate N_1 or N_2 till the two halves of the field appear uniformly bright. The scale now gives the zero reading of the instrument. Repeat twice and take the mean. Prepare 100 ml. of exactly 10 per cent solution of sugar, adding a drop of ammonia before finally making up to bulk (see *Note* 1). Wash out tube A with this solution, fill and rotate N_1 or N_2 till the two halves of the field are again uniformly bright. The scale reading corrected for any zero error gives α the angle of rotation. Repeat the reading twice and take the mean.

It should be noted that two settings of the instrument, differing by 180°, will give even illumination of the field, but if it is borne in mind that α for a 10 per cent solution of sugar is usually small, rotation of the Nicol through too great an angle can be avoided.

Convention of sign. It is agreed that optically active substances which rotate the plane of polarized light clockwise shall be regarded as producing +ve rotation and vice versa. If the polarimeter be one in which the polarizing Nicol is rotated, clockwise rotation of the Nicol is required by anti-clockwise rotation of the plane of polarization and α is —ve. Anti-clockwise rotation of the Nicol indicates a +ve value for α. These rotations are considered from the viewpoint of an observer looking towards the light source S.

If the analysing Nicol is rotated the sign of α is the same as the direction of rotation, i.e. clockwise rotation of the Nicol means +ve; anti-clockwise means —ve. For a 10 per cent sugar solution contained in a 2-decimeter tube

$$[\alpha]'_D = \frac{100\alpha}{2 \times 10} = 5\alpha.$$

Note 1.—Most sugars show the property of mutarotation, i.e. the value of α changes on standing in solution and becomes constant after a few hours. This constant value is attained immediately on addition of a trace of ammonia (0·1 per cent).

Note 2.—The figures for specific rotation given in textbooks refer to pure sugars, usually in the anhydrous state. The specimen under examination may not be quite pure; also allowance must be made for water of crystallization. Glucose, maltose, lactose and raffinose may contain one molecule, galactose x molecules, of water of crystallization.

3. Acetate

In the case of some sugars this derivative is often difficult to isolate.

Mix 3 grams of sugar with about 2 grams of fused anhydrous sodium acetate and 15 ml. of acetic anhydride. Reflux for 30 min. Cool, but before solidification occurs, pour into 50 ml. of cold water and allow to stand to hydrolyse the excess of acetic anhydride. Filter, wash with water and recrystallize from alcohol.

Maltose, sucrose and lactose and cellobiose give octa-acetates while dextrose and galactose give penta-acetates.

Table I.—Carbohydrates

	Decomposition Temp. (°C.)	Specific Rotatory Power	Time for formation of osazone (in min.)	M.P. of osazone (°C.)	M.P. of acetyl deriv. (° C.)	
Raffinose (hydrated)	80	+104·5	—	—	100	Exhibits no mutarotation
(anhydrous)	119	+123				
Glucose (hydrated)	90		4–5	205	112α* 134β	
(anhydrous)	146	+ 52				
d-Ribose	95	− 21·5		166		
Maltose (hydrated)	100	+129	—	208	125α 158β	Osazone separates only on cooling after 1½ hr. heating
(anhydrous)	165	+136				
Laevulose (Fructose)	104	− 92	2	204–5	70α 109β	
Rhamnose	105	+ 9·4	7	185		
Lyxose	105	− 13·5		163	141	
Mannose	132	+ 14·5	0·5	205	64α 115β	Same osazone as *d*-glucose. With $C_6H_5NH{\cdot}NH_2{\cdot}HCl$ and sodium acetate in the cold → mannose phenylhydrazone. M.P. 199*d*
Xylose	145	+ 19	7	163		
l-Arabinose	160	+105	10	166		
Galactose (anhydrous)	170	+ 81·7	19		95α 142β	Oxidized by 1 hr. heating on W.B. with HNO_3 (S.G. 1·2) to mucic acid M.P. 213° C.
Sucrose	185	+ 66	30	205	70	Exhibits no mutarotation. Gives glucosazone after hydrolysis
Lactose (hydrated)	203	+ 52·5	1·5 hr.	200*d*	152α 100β	Osazone separates only on cooling. Sugar becomes anhydrous at 130° C.
Cellobiose	225	+ 35	—	198	228α 202β	
Gentiobiose		+ 10		162	188α 192β	
Melibiose		+143		178	177α	
Trehalose (anhydrous)		+197			97	Exhibits no mutarotation

* Acetyl derivatives of sugars often exist in two forms, denoted by α and β. It is the latter which is usually obtained directly from the sugar.

Glycosides

If Molisch's test and the colour reaction with cold concentrated sulphuric acid (see p. 27) indicate the presence of a naturally-occurring glycoside, apply the following colour tests (Jackson and Dehn, *J. Ind. Chem. Eng.* (Anal. Ed.), 1934, 362):—

1. A 0·5 per cent aqueous solution of ferric chloride.
2. A 0·5 per cent solution of ammonium vanadate in concentrated sulphuric acid.
3. Glacial acetic acid containing a trace of ferric chloride.
4. 25 per cent nitric acid in water.
5. Acetic anhydride.
6. 85 per cent phosphoric acid.
7. A 3 per cent solution of zinc chloride in 15 per cent hydrochloric acid.

In all cases a few milligrams of the substance is treated at room temperature with the reagent.

In tests 3 and 5 addition of the reagent is followed by concentrated sulphuric acid in such a manner as to form a separate lower layer. Test 6 requires one hour's standing.

TABLE II

	1	2	3	4	5	6	7	
Arbutin	Bl	Br	Br.G	Or	Y	Y	—	M.P. *c.* 200° C.; $[\alpha]_D$ — 64·3
Digitonin	—	Y	—	—	Y	Y	—	M.P. 235° C. Gives a cryst. ppt. with cholesterol in alcohol
Amygdalin	—	Dk.G	—	—	—	—	—	M.P. 214° C.; $[\alpha]_D$ — 40·5
Salicin	—	Br.R	Car	Y	R	—	—	M.P. 201° C.; $[\alpha]_D$ — 62·6
Digitalin	—	Blood R	Ch.R	—	R	P	Y	M.P. 217° C. d.
Strophanthin	—	Br.Bk	Y	—	R.Br	Br	Y	
Saponin *	—	Br	—	—	Car	R	—	* Refers to the tri-terpene glycosides from soapwort and allied plants

Bl—blue. Bk—black. Car—carmine. Ch—cherry. G—green. Or—orange. P—purple. R—red. Y—yellow. Br—brown.

The melting-points of naturally occurring glycosides vary considerably according to their purity.

α-Methyl glycoside (M.P. 165° C., $[\alpha]_D^{20} + 159°$) does not occur naturally.

Additional evidence of identity can be obtained in some cases by refluxing about 1 g. of the substance with dilute sulphuric acid till hydrolysis is complete.

Distil off a few ml. and test the distillate for methyl alcohol by the tests on p. 68. If present, the original substance is a methyl glycoside.

Cool the residual liquid in the flask, extract with ether and after drying and removing the ether, examine the residue for

(*a*) hydroquinone, arising from arbutin;

(*b*) saliretan (formed by polymerization of salicyl alcohol arising from salicin) by oxidation to salicylic aldehyde with chromic/sulphuric acids;

(*c*) benzaldehyde arising from amygdalin.

Note.—Digitonin forms digitogenin (M.P. 253° C.) on hydrolysis, whilst digitalin gives no simple product.

Make the aqueous layer from the ether extraction alkaline with sodium hydroxide and test for the presence of a reducing sugar with Fehling's and Barfoed's reagents.

In the case of arbutin, amygdalin, salicin or α-methyl glycoside, determine the specific rotatory power.

GROUP I—CLASS III

ALDEHYDES, KETONES, ACETALS, POLYMERIZED ALDEHYDES, KETO-ACIDS, MANY QUINONES

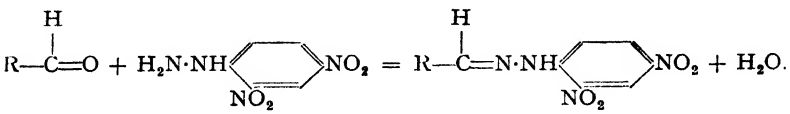
Aldehydes are among the most reactive of organic compounds. In general the polymerized aldehydes and acetals only give reactions for aldehydes after boiling with dilute mineral acid to hydrolyse and then cooling, e.g.

$$\underset{\text{acetal}}{CH_3{\cdot}CH(OC_2H_5)_2} + H_2O \rightleftharpoons CH_3{\cdot}CHO + 2C_2H_5OH$$

and

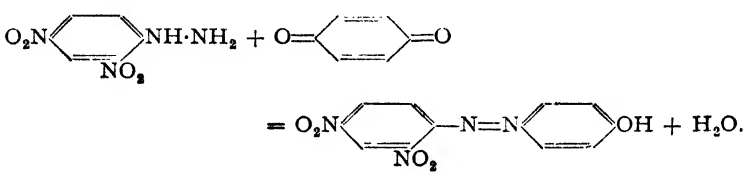
$$\underset{\text{metaldehyde}}{(CH_3{\cdot}CHO)_3} \rightleftharpoons 3CH_3{\cdot}CHO.$$

Classification test.—Take 0·1 g. or 1 drop of the original compound in a dry test-tube and add 1 ml. of 2 : 4-dinitrophenylhydrazine reagent prepared as on p. 290. The formation of a yellow or orange precipitate indicates a substance of this class.



If the original substance is insoluble in alcohol an attempt should be made to dissolve it in cold concentrated sulphuric acid and to apply the above test to the resulting solution.

Quinones react abnormally with the reagent.



To distinguish between aldehydes and ketones

(*a*) To a few ml. of Schiff's reagent (see p. 291) add a few drops of the original substance, but do not heat, as this alone would be sufficient to restore the colour of the original fuchsine. The development of a magenta colour (rather bluer than the fuchsine) within one minute indicates the presence of an aldehyde. Some aromatic aldehydes react abnormally with Schiff's reagent and give yellow or red precipitates. This depends partly on the amount of free sulphur dioxide in the reagent.

Owing to their low solubility in water, aromatic aldehydes react more slowly than aliphatic aldehydes. This may be overcome, however, by dissolving the substance in aldehyde-free alcohol or pure dioxan. In such cases a comparison " blank " on the solvent should be made.

Polymerized aldehydes and acetals do not give this reaction unless previously boiled with a little dilute hydrochloric acid. Since Schiff's test is very sensitive for water-soluble compounds, traces of aldehyde, present as impurity in the original substance, may give a positive reaction.

(*b*) Prepare fresh Tollens' reagent by mixing equal volumes of 10 per cent silver nitrate and 10 per cent caustic soda, and adding

concentrated ammonia drop by drop until the silver oxide first formed *just* redissolves. A small quantity of the original substance is shaken in the *cold* with the reagent. A black precipitate of metallic silver, or a silver mirror, is produced if an aldehyde is present.

Of those compounds not yet eliminated, quinones and formic acid give a positive reaction.

(*c*) In the Angeli-Rimini test for aldehydes a few drops of the substance dissolved in aldehyde-free alcohol are added to 5 ml. of an alcoholic solution of benzenesulphohydroxamic acid (see p. 291). Add, while keeping cool and shaking, 2N caustic soda till definitely alkaline. Allow to stand for 15 min. then acidify to Congo-red (test-paper) and add one drop of ferric chloride. An intense red colour is given by aldehydes only.

Note.—The test fails with aldehydes having hydroxyl or carbonyl groups in the γ or δ position.

A comparison " blank " should be carried out on the reagent in case the alcohol used in its preparation contains aldehyde. Usually only a faint colour results. In the case of salicylic aldehyde, ferric chloride alone will give a violet colour, and bromine water should be added to destroy this.

$$C_6H_5SO_2\cdot NH\cdot OH \xrightarrow[NaOH]{} C_6H_5\cdot SO_2H + O{:}NH$$

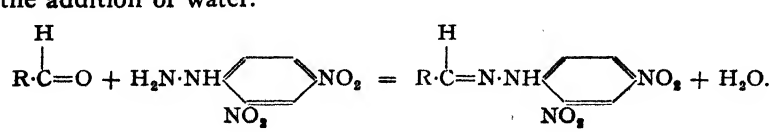
$$C_6H_5\cdot CHO + HN{:}O = C_6H_5C(OH){:}NOH$$

(hydroxamic acid)
(red colour with ferric chloride)

(*d*) Dimedone (see derivative 5 below) may be used as a specific test for aldehydes, as ketones react only under exceptional conditions.

Derivatives

1. 2 : 4-**Dinitrophenylhydrazone.**—Mix about 0·1 g. of 2 : 4-dinitrophenylhydrazine with 2 ml. of pure alcohol and heat to boiling. Add concentrated hydrochloric acid drop by drop, keeping at the boil, until the liquid just clears. Add 0·1 g. of the original compound dissolved in a little pure alcohol, heat to boiling and cool. Filter, and recrystallize from hot alcohol without the addition of water.

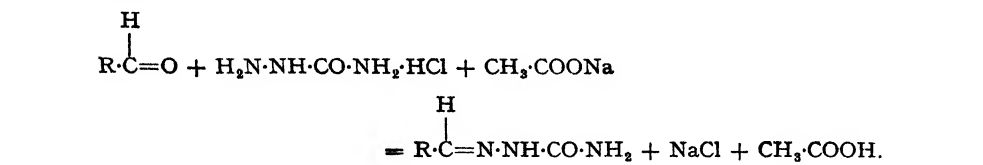


2. Phenylhydrazone.—Equal quantities (about 5 drops) of the carbonyl compound and phenylhydrazine are heated in a test-tube over a small flame for 2 min. One ml. of alcohol is then added followed by water, drop by drop, until crystallization occurs.

3. **Semicarbazone.**—This is not always an ideal derivative for identification purposes as, in some cases, the semicarbazone takes some hours to prepare. Theoretically, for aldehydes and some ketones, it should exist in two forms, *syn* and *anti*.

(*a*) *For water-soluble compounds.*—Add one ml. of the aldehyde or ketone to a cold solution of 1 g. of semicarbazide hydrochloride and 4·5 g. of crystalline sodium acetate in 10 ml. of water. Shake well, and if a crystalline solid separates do not heat but filter it off and recrystallize as below. (It is particularly important to avoid rise of temperature in the case of crotonic aldehyde). If no derivative separates in the cold, place the tube in a beaker of boiling water for about 15 min., then cool in ice. Scratch the sides of the tube, if necessary, to induce crystallization. Filter, and recrystallize from water or 25–50 per cent alcohol.

(*b*) *For water-insoluble compounds.*—Dissolve 1 g. of the aldehyde or ketone in 10 ml. of alcohol. Add water until faintly turbid and remove the turbidity with a few drops of alcohol. Add 1 g. of semicarbazide hydrochloride and 1·5 g. of crystalline sodium acetate. From this point follow procedure (*a*).



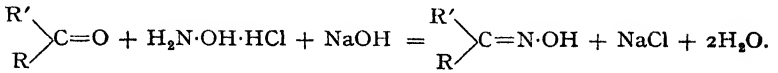
$$R\cdot\overset{H}{\underset{|}{C}}=O + H_2N\cdot NH\cdot CO\cdot NH_2\cdot HCl + CH_3\cdot COONa$$

$$= R\cdot\overset{H}{\underset{|}{C}}=N\cdot NH\cdot CO\cdot NH_2 + NaCl + CH_3\cdot COOH.$$

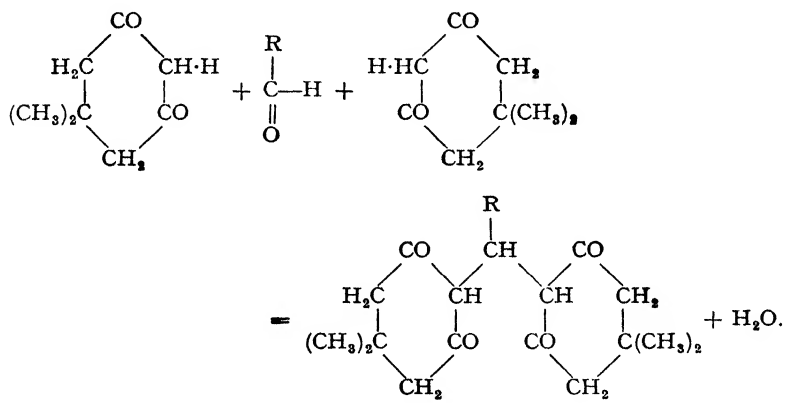
4. Oxime.—(*a*) *For aldehydes.*—Dissolve 0·5 g. of hydroxylamine hydrochloride in a slight excess of caustic soda solution using phenolphthalein as an external indicator. Then add about 0·5 g. of the aldehyde and, if this is water-insoluble, just sufficient alcohol to give a clear solution. Warm on a steam-bath for 15 min., cool and filter off impurities if necessary. Neutralize with hydrochloric acid to phenolphthalein, cool in ice and scratch the sides of the test-tube to induce crystallization. Occasionally the addition of a few ml. of distilled water will facilitate the separation of the oxime. Recrystallize from water or dilute alcohol.

(*b*) *For ketones.*—In the case of ketones use 1 g. of hydroxylamine hydrochloride, 15 ml. 2N caustic soda, 0·5 g. of ketone, and

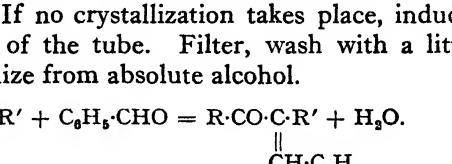
alcohol sufficient to give a clear solution plus 10 ml. in excess of this. Reflux for 30 min. and from this point proceed as in (*a*).



5. **Dimedone derivative** (for aldehydes only). Add 0·2 g. of the aldehyde to a solution of 0·6 g. dimedone in 30 ml. of 50 per cent alcohol or more accurately in the ratio of one gram-molecule of aldehyde to 2 gram-molecules of dimedone. Warm the solution and allow to stand for 2 or 3 hours. If the derivative be colloidal in character, shake vigorously to coagulate. Recrystallize from dilute alcohol.



6. **Arylidene derivative** (for those compounds containing the keto-methylene group $R{\cdot}CH_2{\cdot}CO{\cdot}R'$ or $R{\cdot}CH_2{\cdot}CO{\cdot}CH_2R'$). Dissolve 1 g. of the ketone in 10 ml. of alcohol and add one or two molecular proportions of benzaldehyde according as to whether one or two keto-methylene groups are present. Add 0·5 ml. of 5N sodium hydroxide and allow to stand for an hour or more at room temperature. If no crystallization takes place, induce it by scratching the sides of the tube. Filter, wash with a little cold alcohol and recrystallize from absolute alcohol.



7. **Hydrolysis of acetals.**—Reflux 5 g. of the substance with 20 ml. of 2 per cent hydrochloric acid for 5 min. in the case of

compounds of low molecular weight, and for up to 60 min. in the case of high molecular weight compounds. With substances that are hydrolysable only with difficulty, the use of 2 per cent hydrochloric acid in dioxan is advisable.

If an oil is present in the cooled solution, separate it and identify it by the preparation of a suitable derivative. It will probably be benzaldehyde.

If the cooled solution is homogeneous, divide it into two parts. From (1) prepare a derivative of the aldehyde and from (2) a derivative, e.g. a xanthate (see p. 81), of the alcohol.

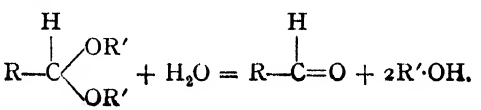


Table III.—Aldehydes

	B.P. °C.	Oxime	Semi-carbazone	Phenyl-hydrazone	2:4-dinitro-phenyl-hydrazone	Dimedone deriv.	
Liquids							
Formaldehyde	−21	—	169d	—	168	189	
Acetaldehyde	21	47	162	63 / 99	168	140	
Propionaldehyde	50	40	89 / 154	—	154	155	
Glyoxal	50	178	>270	170	328	186(m)	(m) = mono derivative
Acrolein	52	—	171	52*	165	192	* Phenylhydrazine yields phenylpyrazoline
iso-Butyric aldehyde	64	—	125	—	182	154	
α-Methyl acrolein	73	—	198	74 †	206		† 4-Me-phenyl pyrazoline
n-Butyraldehyde	74	—	104	—	126	134	
iso-Valeraldehyde	92	48	132	—	123	155	
n-Valeraldehyde	103	52	—	—	107	105	
Crotonaldehyde	103	119	201	56	190	183	Sol. cpd. with $NaHSO_3$. Not regenerated by Na_2CO_3
Paraldehyde	124	As for Acetaldehyde after warming with a trace of conc. H_2SO_4					
n-Caproaldehyde	131	51	106	—	104	108	
n-Heptaldehyde (Oenanthol)	156	57	109	—	108	103	
Furfural	161	89 / 74	203	97	ca. 200	162	
n-Octaldehyde (Caprylic aldehyde)	172	59	98	—	106	90	

[Contd. over

TABLE III—(*contd.*)

	B.P. °C.	Oxime	Semi-carbazone	Phenyl-hydrazone	2:4-dinitro-phenyl-hydrazone	Dimedone deriv.	
Liquids							
Benzaldehyde	179	35α	*c.* 227	158	237	195	
5-Me furfural	187	112s / 58a	211	148	—	—	
n-Nonaldehyde (Pelargonic aldehyde)	191	63	100	—	100	86	
Phenylacetaldehyde	194	100	156	58	121	165	
Salicylaldehyde	196	57	231	142	252d	211	Tri-acetyl deriv. 100° C.
Acetaldol	77 / 16 mm	—	194	—	—	147	
m-Toluic aldehyde	199	60	224	91	194	172	
o-Toluic aldehyde	200	49	212	105	194	167	
p-Toluic aldehyde	204	80 / 110	234	113	234	—	
Citronellal	206	—	83	—	77	78	Optically active; $[\alpha]_D$ + 13°
Capric aldehyde (*n*-Decaldehyde)	208	69	102	—	104	92	
Hydrocinnamaldehyde	224	94	127	—	149	—	
Citral	228d	143 / 12 mm	164	—	116	—	
Cuminaldehyde	235	52 / 112	210	129	241	171	
p-Methoxy benzaldehyde (Anisaldehyde)	247	92	210	120	254d	145	

Cinnamaldehyde	252d	138s 65a	215	168	255d	219	
	M.P.						
n-Undecylic aldehyde	−4	72	103	—	104	—	Oxidizes in air to undecylic acid
	B.P.						
α-Naphthaldehyde	292	98	222	80	—	—	
Solids	M.P.						
o-Methoxy benzaldehyde	36	92	215d	—	253	188	
Piperonal	37	110	234	103	266	178	
Lauric aldehyde (*n*-Duodecaldehyde)	44	77	106	—	106	—	
Phthalaldehyde	56	—	—	191	—	—	
Veratric aldehyde (3:4-Di-methoxy benzaldehyde)	58	95	177	121	264		
β-Naphthaldehyde	60	156	245	206	270		
Vanillin	80	117	240d	105	271	197	
m-Hydroxybenzaldehyde	104	88	199	130	260		
p-Hydroxybenzaldehyde	115	72*	224	177	280d	189	* Hydrate. Anhyd. 112
Terephthalaldehyde	116	200	—	154 278	—		
2:4-Di-hydroxy benzaldehyde	135	191	—	159	286d	226	
3:4-Di-hydroxy benzaldehyde	153	157	230d	176	275d	145d	
Metaldehyde	subl. >150	As for Acetaldehyde after warming with a trace of conc. H_2SO_4					
Paraformaldehyde (Trioxymethylene)	d	As for Formaldehyde					

[Contd. over

Table IV.—Ketones

	B.P. °C.	Oxime	Semi-carbazone	Phenyl-hydrazone	2 : 4-dinitro-phenyl-hydrazone	Benzal-dehyde (Arylidene) deriv.	
Liquids							
Acetone	56	60	188	42	126	112	
Methyl ethyl ketone	80	—	148	—	115		
Methyl vinyl ketone	80	—	141				
Diacetyl	88	238*(d) 74(m)	278	245	315	52(m)	* Dimethyl glyoxime Polymerizes with ice-cold HCl
Methyl *iso*-propyl ketone	94	—	113	—	117		
Diethyl ketone	101	69	139	—	156	31	
Methyl *n*-propyl ketone	102	58	108	—	143		
Pinacolone	106	79	158	—	125	41	
Methyl *tert*-butyl ketone	105	77	157				
Ethyl *iso*-propyl ketone	114	—	80	—	112		
Methyl *iso*-butyl ketone	118	58	130	—	95		
Ethyl *n*-propyl ketone	123	—	110	—	130		
Di-*iso*-propyl ketone	124	34	159	—	98	—	Does not form bisulphite cpd.
Methyl *n*-butyl ketone	128	49	122	—	106		
Mesityl oxide	130	49	164	—	203		
Cyclopentanone	131	56	205	55	146		mono anil. M.P. 52° C.
Ethyl *iso*-butyl ketone	136	129	152	—	75		$NH_2OH \cdot HCl \rightarrow$ di-methyl
n-Propyl *iso*-propyl ketone	136	—	119				*iso*-oxazole B.P. 141° C.
Acetylacetone	139	149(di)	—	—	209		and dioxime
Methyl *iso*-amyl ketone	144	—	143	—	95		$Ph \cdot NH \cdot NH_2 \rightarrow$ 3:5-di-methyl 1-phenyl pyra-zole B.P. 273° C.
Di-*n*-propyl ketone	145	—	133	—	75		
Hydroxyacetone (Acetol)	146	71	196	103	129		

[Contd. over

Acetoin	148	—	185				
Methyl *n*-amyl ketone	151	—	123	207	89		
n-Propyl *iso*-butyl ketone	155	—	122				
Cyclohexanone	155	90	166	77	162		
2-Methyl cyclohexanone	163	43	195	—	137		
Diacetone alcohol	164	57	—	—	203		
Pyruvic acid	165d	—	222	192	218		
Di-*iso*-butyl ketone	166	—	126	—	92		
3-Methyl cyclohexanone	168	—	191	94	155	122	
4-Methyl cyclohexanone	169	39	198	110	134	99	
Methyl *iso*-hexyl ketone	171	—	155	—	77		
Methyl *n*-hexyl ketone	172	—	122	—	58		
Hexahydro acetophenone (Me-cyclohexyl ketone)	180	60	177	—	140		*p*-nitrophenylhydrazone M.P. 154° C.
Ethyl aceto acetate	181	—	133		96		$Ph{\cdot}NH{\cdot}NH_2 \rightarrow$ methyl phenyl pyrazolone M.P. 127° C.
Di-*n*-butyl ketone	187	—	90				
Acetonyl acetone	188	134(di)	220	120(di)	257		
Methyl *n*-heptyl ketone	191		120				
Fenchone	193	165	183	—	140		
Cyclo-octanone	196	—	167	—	163	—	M.P. 25° C.
Phorone	198	48	186	—	112	—	M.P. 28° C.
α-Thujone	200	—	186				
β-Thujone	202	55	174	—	114		Picrate M.P. 53° C.
Acetophenone	202	60	198	105	250	58	*p*-nitrophenylhydrazone M.P. 184° C.
Ethyl levulate	206	—	150	103	101		
l-Menthone	207	59	184	53	146		
Methyl *n*-octyl ketone	209	—	121				
Ethyl *n*-heptyl ketone	211	—	101				
o-Methyl acetophenone	214	61	203	—	159		
iso-Phorone	214	76	191	68	130		
Benzyl methyl ketone	216	70	198	87	156	—	M.P. 27° C.
Propiophenone	218	53	176	—	190		

TABLE IV—(*contd.*)

	B.P. °C	Oxime	Semi-carbazone	Phenyl-hydrazone	2:4-dinitro-phenyl-hydrazone	Benzal-dehyde (Arylidene) deriv.	
Liquids							
m-Methyl acetophenone	220	57	197	—	207		
Phenyl *n*-propyl ketone	220	50	184	200			
Methyl *p*-tolyl ketone	222	85	205	94	248		
n-Butyrophenone	222	50	188		190		
Pulegone	224	119	174	—	147		
d-Carvone	225	72	163	110	190		
Benzyl ethyl ketone	226	—	135				
o-Methoxy acetophenone	245	83	183	114			
Levulinic acid	250–3	96	—	108	206	123(m)	
α-Ionone	$\frac{127}{12}$ mm	90	142	—	150		
o-Hydroxy acetophenone	$\frac{96}{10}$ mm	117	210	112			
Solids	M.P.						
Methyl *n*-undecyl ketone	29	57	123	—	69		
β-Ionone	33	—	149	—	—	—	B.P. $\frac{134°\text{ C.}}{12\text{ mm}}$
Di-benzyl ketone	34	125	146	120	100	162(m)	
Methyl α-naphthyl ketone	34	136	235	136	—	126	Picrate M.P. 116° C.
p-Methoxy acetophenone	38	87	198	142	220		
Benzal acetone	41	115	186	156	227	112	
α-Hydrindone	41	144	233	126	258	113	B.P. 244° C.
Benzophenone	48	141	164	138	238		

Methyl β-naphthyl ketone	53	145	237		262		Picrate M.P. 85° C.
Phenyl *p*-tolyl ketone	59	{154 / 136}	122	109	200		
Phenyl benzyl ketone (Desoxy benzoin)	60	98	148	116	204	102	
Benzoyl acetone	61	—	—	—	151	99(m)	$NH_2OH \rightarrow$ 3Me5Ph *iso*-oxazole M.P. 43° C.
Benzalacetophenone	62	{ 73 / 75}	{168 / 180}	118	244d		
p-Methoxy benzophenone	62	{116 / 138}	—	{132 / 90}			
Cyclo pentadecanone	63	75	187	—	105		
Cinnamalacetone	68	153	186	180	222		
Laurone	69	40					
Fluorenone	83	195	—	151	284		
Di-*p*-tolyl ketone	92	163		100	229		
Benzil	95	137(m) 237(di)	182(m) 244(di)	225(di)	189		
m-Hydroxyacetophenone	95	—	195				
p-Hydroxyacetophenone	110	145	199	151	261		
Di-benzal acetone	112	144	190	153	180		
Benzoin	133	151	206d	106(m) 225(di)	245	—	Benzoyl deriv. M.P. 125° C.
Furoin	139	161	—	80	216		
Furil	162	—	—	184	215		
Xanthone	173	161	—	152			
Gallacetophenone	173	163	225				
d-Camphor	179	118	237	233	177	98	
Cinnamalacetophenone	235	135	—	157	218		
Alizarin	289						

(m) = mono deriv. (di) = di deriv

TABLE V.—ACETALS

	B.P. °C.	Hydrolysis products
Dimethoxymethane (Methylal)	45	Formaldehyde, methyl alcohol
1 : 1-Dimethoxyethane	64	Acetaldehyde, methyl alcohol
2-Methyl-1 : 3-dioxolane	82	Acetaldehyde, ethylene glycol
Diethoxymethane (Ethylal)	89	Formaldehyde, ethyl alcohol
1 : 1-Diethoxyethane (Acetal)	102	Acetaldehyde, ethyl alcohol
1 : 1-Diethoxy-2-propene (Acrolein acetal)	126	Acrolein, ethyl alcohol
Di-*n*-propoxymethane	140	Formaldehyde, *n*-propyl alcohol
Benzaldehyde dimethylacetal	198	Benzaldehyde, methyl alcohol
Benzaldehyde diethylacetal	222	Benzaldehyde, ethyl alcohol

GROUP I—CLASS IV

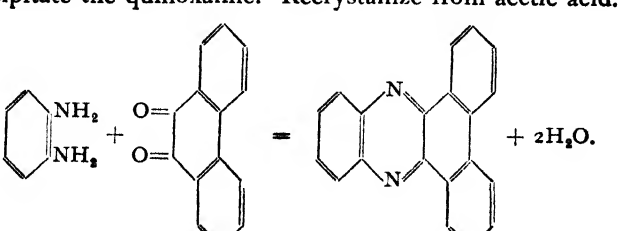
QUINONES

The quinones are *coloured* compounds. Although they contain the carbonyl group, e.g. benzoquinone O=  =O, they do not always react in the same way with the usual reagents for this group. Thus they sometimes form addition compounds with hydrazine and substituted hydrazines.

Although the quinoxaline may be used as a derivative in some cases, each quinone should be identified by applying separate tests.

Derivatives

1. **Quinoxaline.**—Dissolve separately equal weights of the quinone and *o*-phenylene diamine in the minimum quantity of boiling acetic acid and mix the solutions. Cool, or add water, to precipitate the quinoxaline. Recrystallize from acetic acid.



phenanthraquinone

2. **Semicarbazone.**—Method as for ketones (p. 38).

TABLE VI.—QUINONES

	M.P. °C.	Colour	Semi-carbazone	Miscellaneous
Thymoquinone	45	Yellow	202	Reduced by SO_2 to hydrothymoquinone, M.P. 139° C.
p-Toluquinone	68	Yellow	179	Reduced by SO_2 to toluhydroquinone, M.P. 124° C. Hydroxylamine HCl → monoxime, M.P. 134° C.
Benzoquinone	115	Deep Yellow	243 (bis) 165 (mono)	$FeSO_4$ in dil. H_2SO_4 → quinhydrone, M.P. 171° C. Conc. HCl on warming → chlorohydroquinone, M.P. 106° C. Hydroxylamine HCl → *p*-nitrosophenol, M.P. 144° C.
β-Naphthoquinone	115–120d	Red	184	SO_2 (on boiling) → β-hydronaphthoquinone, M.P. 60° C. Hydroxylamine HCl in alcohol → β-nitroso-α-naphthol, M.P. 163° C.
α-Naphthoquinone	125	Yellow	247d (mono)	Zn and HCl → α-hydronaphthoquinone, M.P. 173° C. Phenylhydrazine HCl in 50 per cent HOAc → benzene azo-α-naphthol, M.P. 206° C.
Quinhydrone	171	Dark Green		Zn and HCl → hydroquinone, M.P. 169° C.
Camphorquinone	198	Bright Yellow	236 mono 147 (bis)	Zn and HCl → α-hydroxycamphor, M.P. 203° C. Phenylhydrazine → monophenylhydrazone, M.P. 170° C.
Phenanthraquinone	208	Orange	—	CrO_3 in glacial HOAc → diphenic acid, M.P. 229° C. Dist. with soda-lime → diphenyl M.P. 70° C. SO_2 in warm alc. → hydrophenanthraquinone, M.P. 147° C. Quinoxaline, M.P. 222° C.
Acenaphthenequinone	261	Yellow	271 (bis) 192 (mono)	Quinoxaline, M.P. 241° C.
Anthraquinone	280	Pale Yellow	—	Heating with Zn dust → anthracene, M.P. 216° C. Zn dust and NH_4OH on warming → dihydroanthranol, M.P. 76° C. $(Ac)_2O$ + AcONa + $ZnCl_2$ → diacetate, M.P. 260° C.
Alizarin	289	Orange-red	—	NaOH → violet colour $(Ac)_2O$ + NaOAc → mono acetyl deriv., M.P. 205° C.

GROUP I—CLASS V

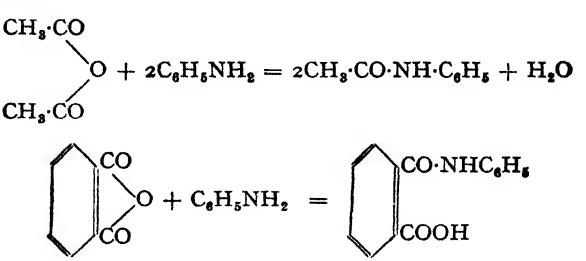
CARBOXYLIC ACIDS, ACID ANHYDRIDES, EASILY HYDROLYSABLE ESTERS

Classification test.—Dissolve 0·1 g. or 3 drops of the given compound in water or neutral alcohol, add phenolphthalein followed by 0·1N caustic soda drop by drop. If more than three to four drops are required to give a permanent pink colour, and the colour change is sharp, the substance belongs to this class and is probably a carboxylic acid. The other two types included here sometimes give fading end-points.

Reference must now be made to the preliminary examination in which the substance was treated with 30 per cent sodium hydroxide solution. Carboxylic acids are easily soluble in the cold, while acid anhydrides dissolve gradually on warming, generally with evolution of heat.

Esters giving the above classification test are usually derived from methyl or ethyl alcohol and a weak acid such as formic or oxalic. They will liberate the corresponding alcohol in the caustic soda test, and should be treated as for esters (see p. 67).

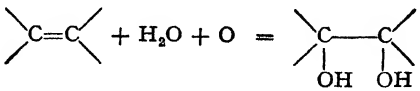
Test for anhydrides.—Dissolve a little of the original compound in benzene and add aniline. Warm gently for one minute and then cool. If a precipitate is formed the substance is an anhydride. With the anhydrides of monobasic acids it is the anilide which separates out, while anhydrides of dibasic acids, the carboxyl groups of which are attached to adjacent carbon atoms, yield anilic acids.



They form useful derivatives when filtered, washed with dilute hydrochloric acid, recrystallized from alcohol and dried.

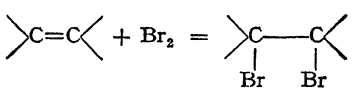
Tests for unsaturation.—(*a*) Dissolve 0·1 g. of the original substance in 10 per cent sodium carbonate solution and add 0·1N

potassium permanganate solution drop by drop. If the solution turns green or brown, due to reduction of the permanganate, the acid is possibly unsaturated.



Certain easily oxidizable substances such as formic acid, malonic acid, some aliphatic hydroxy-acids and many of the phenolic acids will also reduce permanganate in the presence of sodium carbonate.

(*b*) The original compound (dissolved in carbon tetrachloride or chloroform in the case of a solid) is treated with a few drops of a solution of bromine in the same solvent. If the bromine solution is instantly decolorized *without evolution of hydrobromic acid*, as tested by exposing the vapours to a solution of silver nitrate in nitric acid held on the end of a glass rod, the acid is unsaturated. If no discharge of colour occurs in the cold, warm the solution. Rapid decolorization, without evolution of hydrobromic acid, indicates that the unsaturated linkages are either conjugated with aromatic or similar residues, e.g. cinnamic acid, or are largely surrounded by substituents.



Ferric chloride test.—To a neutral solution of the ammonium salt of the acid, prepared by dissolving the acid in dilute ammonia and boiling off the excess of the latter, add a few drops of neutral * ferric chloride solution.

(*a*) Aromatic acids and certain aliphatic dibasic acids, e.g. succinic and adipic acids, give a buff coloured precipitate.

(*b*) Aliphatic monocarboxylic acids give a reddish brown colour.

(*c*) Many aromatic hydroxy acids, especially those with the hydroxyl group in the *ortho* position to the carboxyl group, give a violet or bluish colour.

(*d*) α-Hydroxy acids give an intense yellow colour. This last test may usefully be modified by taking the violet coloured solution prepared by adding a few drops of neutral ferric chloride to a solution of phenol and adding to it a solution of the α-hydroxy acid

* The laboratory solution of ferric chloride is acid due to hydrolysis. Add just sufficient ammonia to produce a *faint* precipitate, filter and use the filtrate.

in water. The violet coloration is removed and a deep yellow tint takes its place.

Derivatives, etc.

1. **Equivalent weight.**—Weigh out accurately about 0·2 g. of the acid and dissolve in water or neutral alcohol, add 2–3 drops of phenolphthalein and titrate with approximately 0·1N caustic soda solution of known strength.

$$\text{Equivalent weight} = \frac{1000 \times \text{Weight of acid}}{\text{Titration} \times \text{Normality of caustic soda}}.$$

For all anhydrides, and for those acids which are insoluble in alcohol, dissolve a known weight in an accurately measured excess of standard sodium hydroxide, boil, cool, and titrate the unneutralized alkali with standard acid to phenolphthalein.

2. **Amide.**—This derivative is more suitable for aromatic acids than for aliphatics, as the amides of the latter are fairly soluble in water and somewhat difficult to isolate.

(*a*) *For acids.*—Heat 1 g. of the acid with 3 ml. of thionyl chloride for 30 min. under a reflux condenser. Cool gradually and add, drop by drop, 15 ml. of concentrated ammonia (*care*, since the initial reaction is very vigorous). Filter and recrystallize from hot water or dilute alcohol. If the amide does not separate from the ammoniacal solution on cooling, evaporate the solution to dryness on a water-bath and extract the amide with absolute alcohol.

Note.—Powdered ammonium carbonate (10 g.) may be used in place of concentrated ammonia.

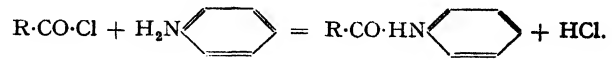
$$\text{R·COOH} + \text{SOCl}_2 = \text{R·CO·Cl} + \text{SO}_2 + \text{HCl}.$$
$$\text{R·CO·Cl} + 2\text{NH}_3 = \text{R·CO·NH}_2 + \text{NH}_4\text{Cl}.$$

(*b*) *For acid anhydrides.*—Shake the anhydride with 10 ml. of concentrated ammonia in a small glass-stoppered bottle until a solid is formed. Filter and wash with a little water. Recrystallize from water or dilute alcohol. If no solid is formed treat as in (*a*) above.

$$\begin{matrix}\text{R·CO}\\ \quad\rangle\text{O}\\ \text{R·CO}\end{matrix} + 2\text{NH}_3 = 2\text{R·CO·NH}_2 + \text{H}_2\text{O}.$$

3. **Anilide.**—(*a*) *For acids.*—Prepare the acid chloride as for the amide (derivative 2(*a*) above), cool and add 1–2 g. of aniline dissolved in benzene. Warm. Cool and separate the benzene

layer. Wash this with 5 ml. of water, 5 ml. of dilute hydrochloric acid, 5 ml. of dilute caustic soda and 5 ml. of water in this order. Dry the benzene solution, evaporate off the benzene and recrystallize the anilide from alcohol or petroleum ether containing a little benzene.

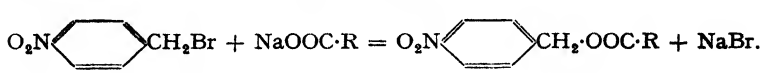


(*b*) *For acid anhydrides.*—Dissolve 0·5 g. of the anhydride in 1 ml. dry benzene and add a few drops of aniline. Warm, allow to stand and filter off the crystalline product. Wash with a little dilute hydrochloric acid and recrystallize as in (*a*). See test for acid anhydrides p. 50.

4. ***p*-Toluidide.**—(*a*) Prepared as above for the anilide (derivative 3(*a*)), substituting *p*-toluidine for aniline.

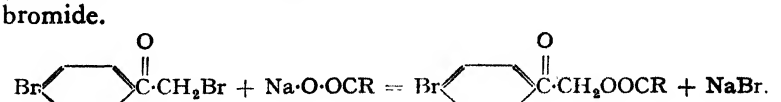
(*b*) Heat one part of the acid or anhydride and five parts of *p*-toluidine in an oil-bath at 220° C. for 20 min. Cool and digest with dilute hydrochloric acid. Wash the precipitate with water and dilute alcohol. Recrystallize from glacial acetic acid.

5. ***p*-Nitrobenzyl ester.**—Dissolve 0·5 g. of the acid in 2·5 ml. of water or alcohol. Neutralize with sodium hydroxide using phenolphthalein as an external indicator, then add 2–3 drops of dilute hydrochloric acid. Add this solution to 10 ml. of alcohol containing 0·5 g. of *p*-nitrobenzyl bromide. Reflux for 1 hour if the acid is monobasic, 2 hours if dibasic and 3 hours if tribasic. If a solid separates during refluxing, add just sufficient alcohol to redissolve it. Cool, filter and recrystallize from alcohol.



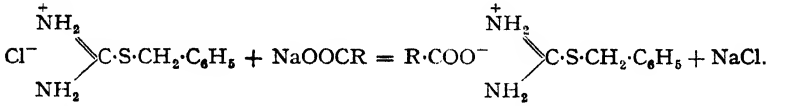
Important.—*p*-nitrobenzyl bromide is a vigorous skin irritant, and should not be allowed to get on the hands or face. Washing with alcohol is the best method of removal.

6. ***p*-Bromophenacyl ester.**—The method is the same as for the *p*-nitrobenzyl ester except that *p*-bromophenacyl bromide (*p*-bromo-ω-bromoacetophenone) is substituted for *p*-nitrobenzyl bromide.



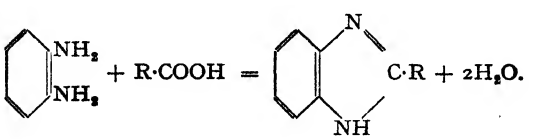
Important.—*p*-bromophenacyl bromide is a strong lachrymator.

7. **S-benzylthiuronium salt.***—Neutralize about 1 g. of the acid by titrating with standard alkali using phenolphthalein as indicator. Concentrate the solution until it is almost saturated and then add 1·5 ml. of a hot alcoholic solution of S-benzylthiuronium chloride (containing 15 g. in 100 ml. of alcohol) for each ml. of *normal* caustic soda used in the first place. On cooling, the S-benzylthiuronium salt of the acid usually crystallizes out, though a few acids may require further concentration of the solution. The presence of water should be avoided as much as possible to avoid hydrolysis of the salt.

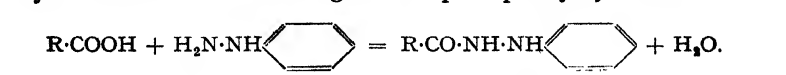


8. **2-Alkyl-benziminazole picrate.**—This derivative is useful for the rapid identification of aliphatic acids.

Reflux 0·5 g. of the acid, 0·5 g. of *o*-phenylenediamine and 4 ml. of 4N hydrochloric acid for 15 min. Cool and add concentrated ammonia until the alkylbenziminazole separates out. Filter and wash well with water. Prepare a saturated solution of it in alcohol and add to 0·5 g. of picric acid dissolved in the minimum quantity of boiling alcohol. Purify the picrate by crystallization from alcohol.



9. **Phenylhydrazide.**—Heat equal quantities of the acid and phenylhydrazine in a test-tube *above* a small flame until a clear solution is obtained, then place the test-tube in a boiling water bath for an hour. On cooling a pasty mass is usually obtained. Crystallization from alcohol gives the pure phenylhydrazide.



* The M.P. of S-benzylthiuronium salts is affected by rate of heating, rapid heating giving slightly higher figures than those shown in Tables VII and VIII which are for a temperature rise of 2° C. per minute.

TABLE VII.—CARBOXYLIC ACIDS (SATURATED)

	B.P. °C.	Equivalent weight	Amide	Anilide	*p*-Toluidide	*p*-Nitrobenzyl ester	*p*-Bromophenacyl ester	Phenylhydrazide	2-Alkylbenzimidazole picrate	S-benzylthiuronium salt	Miscellaneous
Liquids											
Formic	101	46	3	50	53	31	140	145	230	146	
Acetic	118	60	82	112	145	78	85	129	214	134	
Propionic	141	74	79	105	124	31	59	157	120	148	
iso-Butyric	155	88	129	105	104	—	77	142	136	143	
n-Butyric	163	88	114	96	75	35	63	103	124	146	
Pivalic (Trimethylacetic)	164	102	—	129	120		76				
Pyruvic	165d	88	125	104	109	—	—	—	—	158d	2 : 4-Dinitrophenylhydrazone, M.P. 218° C.
Ethyl methylacetic	176	102	—	110	93		55				
iso-Valeric	176	102	135	110	107	—	68	—	—	153	
n-Valeric	186	102	104	63	74	—	75				
Di-ethyl acetic	193	116	—	124	116						
iso-Caproic (*iso*-Hexoic)	195	116	—	111	63		77				
Tiglic	198	100	—	77	71		68				
Methoxyacetic	203	90	96	58							
n-Caproic (*n*-Hexoic)	205	116	100	92	73	—	72	—	282		
Ethoxyacetic	206	104	82	—	32		105				

[Contd. over

TABLE VII—(*contd.*)

	B.P. °C.	Equivalent weight	Amide	Anilide	*p*-Toluidide	*p*-Nitrobenzyl ester	*p*-Bromophenacyl ester	Phenylhydrazide	2-Alkylbenzimidazole picrate	S-benzylthiuronium salt	Miscellaneous
Liquids											
Heptoic (*n*-Heptylic)	224	130	96	71	80	—	72				
Hexahydrobenzoic	232	128	186	144							
n-Caprylic (*n*-Octoic)	237	144	110	55	70	—	67				
Pelargonic (*n*-Nonoic)	253	158	99	57	84	—	68				
Ethylglycollic	—	104	82	—	—	—	105				
Solids	M.P.										
dl-Lactic	18	90	74	59	107	—	112	—	131	153	Generally a syrupy liquid
n-Undecanoic	28	338	103	71	80	—	68				
Capric (Decanoic)	31	162	99	70	78	—	67			150	
Levulic	33	116	108	102	109	61	84	—	—	—	2 : 4-Dinitrophenylhydrazone, M.P. 206° C.
Lauric	44	200	98	76	87	—	76	—	—	141	
***n*-Tridecanoic**	44	214	100	80	88	—	75				
Hydrocinnamic	48	150	105	98	135	36	104				
Myristic	54	228	102	84	93	—	81	—	—	139	

Margaric	60	270	106	—	—	49	83			
Palmitic	62	256	106	90	98	42	84	111	—	141
Stearic	69	284	108	94	102	—	90	113	—	143
Arachidic	76	312	109	—	—	—	89			
Phenylacetic	78	136	154	117	136	65	89	175	—	160
α-Hydroxy-*iso*-butyric	79	104	98	136	133	80				
Glycollic	80	76	120	96	143	107	138	—	214	141
Phenoxyacetic	96	152	101	99	—	—	148			
Glutaric	97	66	174	224	217	69	137	219		
l-Malic	100	67	102 (mon) 156 (di)	197	207	124	179	—	—	159
Citric (hydrated)	100	70	210	192	189	102	148			
o-Methoxybenzoic	100	152	128	131	—	—	113			
Oxalic (hydrated)	101	63	419d	246	268	204	242d	—	—	193
o-Toluic	102	136	142	125	144	91	57	—	—	145
Pimelic	105	80	—	155	206	—	137			
Azelaic	107	94	175	185	200	44	131	—	—	163
m-Toluic	110	136	97	126	118	86	108	—	—	164
Ethylmalonic	111	66	214	150	—	75				
β-Benzoylpropionic	116	178	—	150						
p-iso-Propylbenzoic	116	164	133							
dl-Tropic (α-Phenyl-β-hydroxybenzoic)	117	166	169							
Benzylmalonic	117d	150	225	217	—	119				
dl-Mandelic	118	152	133	151	172	124	—	—	209	166
Methylethylmalonic	122	73	183	—	—	66				
Benzoic	122	122	128	164	158	89	119	—	—	166

[Contd. over

TABLE VII—(*contd.*)

	M.P. °C.	Equivalent weight	Amide	Anilide	*p*-Toluidide	*p*-Nitrobenzyl ester	*p*-Bromophenacyl ester	Phenylhydrazide	2-Alkylbenzimidazole picrate	S-benzylthiuronium salt	Miscellaneous
Solids											
Di-ethylmalonic	125	80	224	—	—	91					
o-Benzoylbenzoic	126	226	165	195	—	100					
2 : 5-Dimethylbenzoic	132	150	186	104							
Sebacic	133	101	210	198	201	72	147				
Malonic	133d	52	170	224	250	85				145d	
Acetylsalicylic	135	180	138	136	—	90	—	—	—	144	
Methylmalonic	135d	59	217	182							
Suberic	140	79	216	187	219	85	144				
Diphenylacetic	145	212	167	180	172	104	—	—	—	145	
p-Hydroxyphenylacetic	148	152	167								
Benzilic	150	228	154	175	—	99	152			125	
Adipic	151	73	220	240 (di)	238	106	154	206		159	
Citric (anhydrous)	153	64	210	192	189	102	148				
2:4:6-Trimethylbenzoic	155	164	188								
Salicylic	158	138	139	134	—	96	140	—	—	146	15 per cent HNO_3 → 5-Nitrosalicylic acid, M.P. 226° C.
α-Naphthoic	162	172	205	160	—	—	135			151	

3:4-Dimethylbenzoic	164	150	130	**104**							
Mesitylenic (3:5-Dimethylbenzoic)	166	150	133								
d- or *l*-Tartaric	170	75	195	180	264	163	216	240			
p-Toluic	178	136	158	147	161	104	153	—	—	190	
Anisic (*p*-Methoxybenzoic)	184	152	162	168	186	132	152	—	—	174	
Succinic	185	59	260d	226	255	88	211	—	—	149	
β-Naphthoic	186	172	192	170	197						
d-Camphoric	187	100	192 (di)	226	—	66					
Dimethylmalonic	192	66	269	—	—	84					
Protocatechuic	194d	154	212	166	—	188					
Phthalic	195d	83	220 (di)	250	201	155	153	—	—	157	
m-Hydroxybenzoic	201	138	170	155	163	106	168				
dl-Tartaric	204	75	—	—	—	147					
Vanillic	207	168	—	—	—	140					
Mucic	213d	105	—	—	—	>310	225	—	—	194	
p-Hydroxybenzoic	213	138	162	197	204	198	184	—	—	143	
2-Hydroxy-3-naphthoic	222*	188	—	249	222	—	—	—	—	—	* Cryst. from water, M.P. 239° C.
Gallic	263	170	245	207							
Naphthalic	—	108									
iso-Phthalic	>300	83	280	—	—	264	179	—	—	215	
Terephthalic	subl. >300	83	—	—	—	—	225	—	—	202	

TABLE VIII.—CARBOXYLIC ACIDS (UNSATURATED)

	B.P. °C.	Equivalent weight	Amide	Anilide	*p*-Toluidide	*p*-Nitrobenzyl ester	*p*-Bromophenacyl ester	S-benzylthiuronium salt	Miscellaneous
Liquids									
Acrylic	140	72	84	104	141				
Crotonic (cis)	165d	86	—	102	132		81		
Oleic	285	282	72	41	43	—	46	—	M.P. 14° C.
Solids	M.P.								
Methacrylic	16	84	106						
Erucic	34	—	—	55	58	—	61		
Elaidic	51	282	92				65		
Brassidic	65	338							
Crotonic (trans)	72	86	160	118	132	67	96	162	
Citraconic	—	65	187d	175		71			
Maleic	130	58	153	187	142	89	168	175	
Cinnamic	133	148	147	151	168	116	145	175	
Furoic	133	112	141	123	108	133	138	211	
Sorbic	134	112	—	153	—	—	129		
Phenylpropiolic	136	146	102	126	142	83			
Itaconic	165d	65	192	190	—	91	117		
Aconitic (trans)	191	58	250d	—	—	76	186		
Fumaric	200 subl.	58	270	314	—	151	—	178	
Mesaconic (Methylfumaric)	202	65	176	185	212	134			
p-Coumaric	206	164	194						
o-Coumaric	207	164	209d	—	—	152			
Piperic	216	218	—	—	—	145			

TABLE IX.—ACID ANHYDRIDES

	B.P. °C.	Acid	Amide	Anilide	Equivalent weight	Miscellaneous
Liquids						
Acetic	138	—	82	112	51	
Propionic	168	—	79	105	65	
n-Butyric	191	—	115	96	79	
Citraconic	213	—	187d	175	56	
n-Valeric	215	—	104	63	93	
Crotonic	248	—	160	102	77	
n-Heptoic	258	—	96	71	121	
Solids	M.P.					
Benzoic	42	122	128	164	113	
Maleic	56	130	153	187	49	
Itaconic	68	165d	192	190	56	
Succinic	116	185	260d	226	50	
Cinnamic	130	133	147	151	139	
Phthalic	131	195d	149 mono 220 di	250 di	74	Fusion with resorcinol and one drop of conc. H_2SO_4 → fluorescein
1 : 2-Naphthalic	169	175d	265d	—	99	
d-Camphoric	221	187	192	226	91	
2 : 3-Naphthalic	266	241d	—	—	99	
α-Naphthoic	274	162	205	160	163	
1 : 8-Naphthalic	274	—	—	—	99	

GROUP I—CLASS VI

PHENOLS

Classification test.—Dissolve 0·1 g. of the given compound in 2 ml. of water or alcohol and add 3 drops of a *dilute* neutral solution of ferric chloride. A violet, blue or green colour, which may be permanent or transient, indicates the possible presence of a member of this class.

Since ferric chloride gives a coloration or precipitate with compounds containing the $\begin{matrix}-C-OH\\ \|\\ C\end{matrix}$ group, the test is not specific for phenols, and production of colour may be due to keto-enolic compounds such as acetoacetic ester. With the latter type of compound, however, the addition of a dilute solution of bromine

discharges the colour which reappears on standing. In the case of a phenol the colour is discharged but does not return on standing, in some cases a precipitate of the bromo derivative being formed.

The following may be used as a test for a phenol or keto-enolic compound:—

Prepare a *very dilute* solution of the phenol, and make alkaline with caustic soda. To this solution add a small quantity of a cold diazotized solution of *p*-nitro-aniline in dilute hydrochloric acid. A red colour is produced.

Furthermore, all simple water-insoluble phenols are insoluble in sodium bicarbonate solution, but soluble in caustic soda often with production of a coloured solution.

A definite distinction between phenols and keto-enolic compounds is afforded by the following reaction:—

To a cold solution of mercurous nitrate in dilute nitric acid add some of the given substance. The immediate formation of a grey precipitate of metallic mercury indicates the presence of an enolic compound. For the complete identification of such compounds see esters, pp. 67–70, and the determination of equivalent weight.

Derivatives

1. **Aryl-oxyacetic acid.**—To a mixture of 1 g. of the phenol and 5 ml. of 33 per cent caustic soda add 1·5 g. of chloroacetic acid. If a precipitate of the sodium salt of the phenol is formed, add water until it dissolves. Heat in a water-bath for one hour. Cool, dilute with 10 ml. water and make acid with dilute hydrochloric acid to Congo red indicator. Extract immediately with petrol-ether or ether. Wash the ether layer once with water and then shake with 20 ml. of sodium carbonate solution. Run off the alkaline layer and acidify it with dilute hydrochloric acid. Filter off the precipitated aryl-oxyacetic acid and recrystallize from water.

Its equivalent weight may be found by dissolving in aqueous alcohol and titrating with standard alkali using phenolphthalein as indicator.

$$CH_2Cl{\cdot}COOH + Ar{\cdot}ONa = Ar{\cdot}O{\cdot}CH_2{\cdot}COOH + NaCl.$$

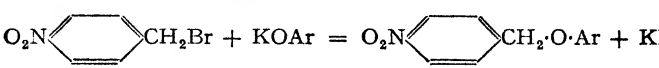
2. **Phenyl or α-naphthyl carbamate (urethane).**—The α-naphthyl compound is preferable because of the greater stability towards water, and lower cost of the reagent, and the fact that the derivatives often have a higher melting-point than those of phenyl

isocyanate. Both phenyl and α-naphthyl isocyanates have slight lachrymatory properties.

Place 1·0 g. of the phenol in a *dry* test-tube and add 0·5 g. of phenyl or α-naphthyl isocyanate. Warm in an oil-bath to 100° C. Dissolve in hot carbon tetrachloride or petrol-ether B.P. 80°–100°. Filter and cool.

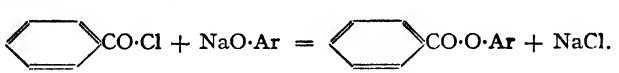
$$Ar{\cdot}OH + C_{10}H_7N{=}C{=}O = C_{10}H_7{\cdot}NH{\cdot}COOAr.$$

3. ***p*-Nitrobenzyl ether.**—To 25 ml. of 0·2N alcoholic potash add 1 g. of the phenol (or a larger amount if the equivalent weight be suspected to exceed 200) and 1·0 g. of *p*-nitrobenzyl bromide (see p. 53). Heat under reflux for one hour. Cool, and purify the derivative as in the case of the *p*-nitrobenzyl ester of a carboxylic acid (see p. 53).



4. **Benzoate.**—(*a*) In a glass-stoppered bottle place 2 g. of the phenol, 2 ml. of benzoyl chloride and 10 ml. of 20 per cent sodium hydroxide. Shake vigorously. If the smell of benzoyl chloride persists, add sodium carbonate and continue shaking until the smell disappears. The solution must be kept alkaline to litmus. Filter off the derivative, wash with water, and recrystallize from alcohol.

(*b*) Dissolve 1·0 g. of the phenol in 3 ml. of pyridine and add 0·5 g. of benzoyl chloride. Warm gently for a few minutes or allow to stand for 24 hours. Pour into water, wash with dilute hydrochloric acid to remove excess pyridine, then with sodium carbonate to remove benzoic acid, and finally with water. Recrystallize from alcohol.



5. **3 : 5-Dinitrobenzoate.**—Mix 0·5 g. of 3 : 5-dinitrobenzoyl chloride with 1 g. of the phenol and warm gently for 10 min. Add 10 ml. of water, cool and filter off the derivative. Wash with sodium carbonate solution followed by water and recrystallize from 60 per cent alcohol.

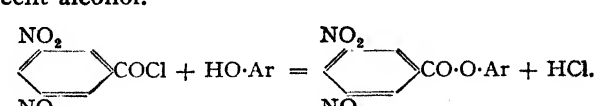


TABLE X.—PHENOLS

	B.P. °C.	Acetyl	Benzoyl	Aryl-oxy-acetic acid	3 : 5-Dinitro-benzoate	*p*-Nitro-benzoate	α-Naphthyl *iso*-cyanate deriv.	Phenyl *iso*-cyanate deriv.	*p*-Toluene sulphon-chloride deriv.	*p*-Nitrobenzyl ether	Bromo-deriv.
Liquids											
m-Cresol	203	—	55	103	165	90	128	125	51	51	84 (tri)
o-Ethyl phenol	207	—	39	141	108	57	—	141			
m-Ethyl phenol	214	—	52	75	—	68	—	139			
p-Ethyl phenol	218	—	60	97	132	81	128	120			
Carvacrol	237	—	—	151	76	51	116	135	—	—	46
Resorcinol mono-methyl ether (*m*-Methoxy phenol)	243	—	—	117	—	—	129	—	—	—	104 (tri)
Eugenol	250	29	70	100	131	81	122	96	85	54	118 (tetra)
iso-Eugenol	267	80	104	94	158	109	150				
Solids	M.P.										
p-*n*-Butyl phenol	22	—	27	81	—	68	—	114			
1 : 3-Xylen-4-ol (2 : 4-Dimethyl phenol)	26	—	38	142	165	105	135	102			
Guaiacol (*o*-Methoxy phenol)	28	—	57	116	141	104	118	136	85	64	116 (tri)
o-Cresol	31	—	—	152	134	94	142	144	55	89	56 (di)
m-Phenyl phenol	34	—	61	—	—	—	—	—	53		
p-Cresol	36	—	70	136	188	98	146	115	70	88	108 (tetra)
Phenol	42	—	69	99	146	127	133	126	96	91	93 (tri)
1 : 3-Xylen-2-ol (2 : 6-Dimethyl phenol)	49	—	—	140	159	—	176	133	—	—	79
Thymol	50	—	32	148	103	70	160	108	71	86	55
p-Methoxy phenol	53	32	87	111							

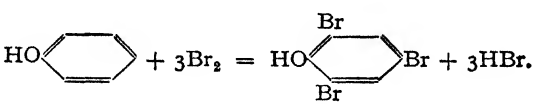
Orcinol (hydrated)	58	25	88	217	190	214	160	154	—	—	104 (tri)
o-Phenyl phenol	58	63	76	—	—	—	—	—	65		
1 : 2-Xylen-4-ol (3 : 4-Dimethyl phenol)	63	—	58	163	182	—	142	120	—	—	171 (tri)
Homocatechol	65	—	58	—	—	—	—	166			
iso-Homocatechol	68	—	—	—	—	—	—	174			
1 : 3-Xylen-5-ol (3 : 5-Dimethyl phenol)	68	—	24	111	195	109	—	150	83	—	166 (tri)
Mesitol	69	—	62	139	—	—	—	142			
Pseudo-cumenol	71	34	63	132	—	—	—	111	—	—	35
Saligenin	87	with Aniline			gives	*o*-hydroxy		benzyl-aniline, M. P. 108			
α-Naphthol	94	46	56	192	217	143	152	178	88	140	105 (di)
p-Tert butyl phenol	95	—	83	86	—	—	—	149	110	—	50
p-Tert amyl phenol	96	—	61	—	—	—	126	108	54		
Catechol	104	64	84	—	152	169	—	169	—	—	192 (tetra)
Orcinol (anhyd.)	107	As for Orcinol (hyd.)									
Resorcinol	110	—	117	195	201	182	—	164	80	—	112 (di)
β-Naphthol	122	72	107	154	210	169	157	155	125	107	84
1 : 3-Dihydroxy naphthalene	124	55									
Toluhydroquinone (2 : methyl-1 : 4 dihydroxy benzene)	124	52									
p-Cyclo-hexyl phenol	132	35	118	—	168	137	—	146			
Pyrogallol	133	165	90	198	205	230	—	173	—	—	158
1 : 8-Dihydroxy naphthalene	140	155	175								
p-Phenyl phenol	165	88	149	—	—	—	—	168	179		
Hydroquinone (Quinol)	169	123	205	250	317	258	—	224	159	—	186 (di)
1 : 4-Dihydroxy naphthalene	176	128	169								
2 : 7-Dihydroxy naphthalene	186	136	139	—	—	—	—	—	150		
Phloroglucinol (hyd.) (1 : 3 : 5-Trihydroxy benzene)	218	105	174	—	162	283	—	191	—	—	151 (tri)
1 : 5-Dihydroxy naphthalene	258	160	235								
Phenolphthalein	254	143	169					135			

6. **Bromo-derivative.**—The presence of the hydroxyl group in a ring facilitates the introduction of halogens into the nucleus, the number and position of the substituent atoms varying with the nature of the phenol. Bromo-derivatives are often difficult to prepare, particularly in the case of polyhydroxy phenols which oxidize easily.

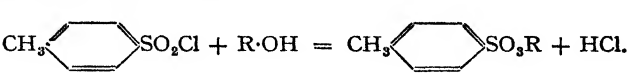
(*a*) Dissolve or suspend 1 g. of the phenol in glacial acetic acid and add a solution of bromine in glacial acetic acid until the colour of bromine persists. Warm gently, adding more bromine if necessary and allow to stand for 15 min. or longer if possible. If no precipitate separates, add water drop by drop till precipitation occurs. Filter, wash with dilute sodium carbonate solution or sulphurous acid, and then with water. Recrystallize from alcohol.

(*b*) Dissolve 1 g. of the phenol in carbon tetrachloride or chloroform and add a solution of bromine in the same solvent. If no derivative separates, remove the solvent by evaporation and recrystallize as in (*a*).

(*c*) Bromination in aqueous solution may also be effected by adding a solution of bromine in aqueous potassium bromide.



7. ***p*-Toluene sulphonyl ester.**—To a suspension, or solution, of 1 g. of the phenol in 2·5 ml. of pyridine add 2 g. of *p*-toluenesulphonyl chloride. Heat on a water-bath for 15 min. Pour into 25 ml. of water and shake vigorously until solid. Filter, wash with cold dilute caustic soda, and then finally with cold water. Recrystallize from alcohol.



8. ***p*-Nitrobenzoate.**—Dissolve 1 g. of the phenol in a small amount of pyridine and add the equivalent, or a slight excess, of *p*-nitrobenzoyl chloride. Reflux for ten minutes, cool and add water. Filter and wash the derivative with a little cold dilute sodium hydroxide, followed by water. Recrystallize from alcohol.

9. **Acetate.**—To 1 ml. of acetic anhydride add *one drop* of concentrated sulphuric acid and about 0·5 g. of the phenol. Warm for 2 min. and pour into water. Scratch the side of the test-tube to

induce crystallization. Filter and recrystallize from dilute alcohol.

Many of the derivatives are liquids and consequently of little value for identification purposes.

GROUP I—CLASS VII

ESTERS, LACTONES

Classification test.—Dissolve about 1 g. of the original substance in 3 ml. of neutral alcohol. Add three drops of approximately N/2 alcoholic potassium hydroxide and one drop of neutral phenolphthalein.* Heat the test-tube and contents in boiling water and observe whether the colour of the test solution fades compared with a blank. If fading occurs, an ester or lactone is present.

Hydrolysis of the ester or lactone.—Reflux about 10 g. of the ester with 50 ml. of 20 per cent sodium or potassium hydroxide until hydrolysis is complete. In most cases one hour's boiling is sufficient. Some esters, e.g. those derived from *ortho*-substituted benzoic acids, are very resistant to the action of alkali. In these cases 50 per cent aqueous potash is a better hydrolysing agent, the time being extended to 1½ to 2 hours, or the alternative procedure using diethylene glycol as a hydrolysing medium (see p. 71) may be used. With phenolic esters which resist attack, 20 per cent alcoholic potassium hydroxide may be used, the bulk of the alcohol being distilled off before proceeding with the examination.

It is essential that complete hydrolysis be achieved, and it is sometimes difficult to know when this has been done, for the persistence of an oily upper layer may be due to formation of one of the higher alcohols. This is probably the case, if it remains after increasing the concentration of alkali to about 50 per cent by the addition of solid (cool and use care in making this addition) and refluxing for a further hour.

The hydrolysis products may be a soluble or insoluble, volatile or non-volatile alcohol or phenol, and an acid, or a hydroxy acid from a lactone, the last three being present as alkali salts. Cool the mixture. If an oil or precipitate forms, it may be due to an insoluble alcohol or a sparingly soluble alkali salt of the acid.

$$R{\cdot}COOR' + NaOH = R{\cdot}COONa + R'{\cdot}OH$$

$$CH_3{\cdot}CH\begin{matrix}O\text{——}CO\\ |\quad\quad|\\ CH_2\text{—}CH_2\end{matrix} + NaOH = CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}COONa.$$

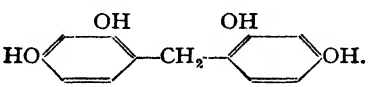
* If the solution remains colourless, add water dropwise until a pink colour develops.

A. Isolation and identification of the alcohol or phenol

1. Distil off about 25 ml. from the alkaline solution. If a steam volatile alcohol is present, it will be found in the distillate. Note any distinctive odour. To small separate portions of the distillate apply the following tests:

(*a*) *For methyl alcohol*

To 3 ml. of the distillate in a test-tube or crucible, add a trace of resorcinol and then plunge a red-hot copper spiral into it. Repeat this three times. Formaldehyde is formed, which with resorcinol gives methylene resorcinol:



Cool and pour on to a few drops of concentrated sulphuric acid. A white turbidity which soon turns red and gives a flocculent white precipitate shows that methyl alcohol is probably present. Tertiary butyl alcohol also gives this test; ethyl alcohol gives a yellow colour.

(*b*) *For ethyl alcohol and those which contain the* $CH_3 \cdot \underset{|}{CH} \cdot OH$ *group*

To about one ml. of the distillate add 2 drops of 10 per cent iodine solution and just enough sodium hydroxide solution to discharge the colour. An immediate precipitate of iodoform indicates the presence of *iso*-propyl alcohol. If no precipitate is formed, warm to 60° C., add another drop of caustic soda and enough iodine to give a permanent yellow colour. Formation of a precipitate of iodoform indicates the presence of an alcohol containing the above grouping.

Acetone, and those ketones containing the group $CH_3 \cdot \underset{|}{CO}$, formed by the hydrolysis of keto-enolic esters, will also give this test.

(*c*) If the distillate from the hydrolysed ester be homogeneous or slightly turbid (due to the presence of a sparingly soluble volatile alcohol) saturate the whole of the distillate with potassium carbonate. If an upper layer of alcohol separates, remove it, warm very gently with a granule of fused sodium acetate to dry it, decant, and from the dry alcohol prepare a derivative. Since the amount of alcohol obtained is usually small, either the 3 : 5-dinitrobenzoate

or α-naphthyl carbamate is the most convenient (see Derivatives of Alcohols, p. 79).

2. High-boiling alcohols, e.g. benzyl alcohol, may be removed by extracting the hydrolysed solution with ether, and after drying and distilling off the ether, a derivative may be prepared.

3. Take a small portion of the alkaline solution free from alcohol, and acidify with moderately concentrated hydrochloric acid. If there is a *brisk effervescence* due to liberation of carbon dioxide (as indicated by the usual lime-water test), the original compound is an ester of carbonic acid. Some indication of the presence of such compounds will have been obtained in the preliminary examination when carbon dioxide is evolved on warming with concentrated sulphuric acid. Furthermore, the equivalent weight of the ester (see p. 72) will be abnormal, namely twice the theoretical value.

4. If tests A1 and A2 above yield negative results, then the hydrolysate may contain a phenoxide. Just acidify the solution with dilute sulphuric acid and saturate with sodium bicarbonate. If a fair amount of the phenol is precipitated, filter it off, wash with a little water, dry, determine its melting-point and prepare a derivative (see p. 62). Whether a precipitate be formed or not, extract the filtrate or solution with ether to remove any water-soluble phenol remaining. If no precipitate was formed, dry the ethereal extract and distil off the ether. Any residue will be a phenol. Use it for the preparation of a derivative (see p. 62).

5. In the absence of a positive result from tests A1, A2 or A4, defer tests for polyhydric alcohols until the acid has been removed or definitely identified (see C, p. 71). If no alcohol or phenol is formed by hydrolysis, the substance is a lactone.

B. Isolation and identification of the acid

1. If a carbonate has been proved absent (see A3 above), acidify the solution from which alcohol or phenol has been removed, with dilute sulphuric acid. If a precipitate or oily suspension is produced, this indicates the presence of an aromatic acid, or a sparingly soluble aliphatic acid. Filter or extract with ether and prepare a derivative (see p. 52). Also determine the equivalent weight if possible (see pp. 52 and 70).

2. If no precipitate or emulsion forms in B1, distil the acidified solution and examine the distillate for those organic acids which

are volatile in steam. Make a neutral solution of the distillate by adding a slight excess of ammonia and boiling off the excess.

To separate portions add:—(*a*) mercuric chloride solution, when a white precipitate of mercurous chloride on warming indicates the presence of formic acid, (*b*) neutral ferric chloride solution—see corresponding tests for acids, p. 25. (Ammonium acetate gives an immediate white precipitate, soluble in acetic acid.)

3. In the absence of a positive result in tests B1 or B2, extract the acidified solution with ether. The ethereal layer may contain a non-volatile, water soluble acid, which is more soluble in ether than in water. Separate the ethereal layer, dry over anhydrous sodium or magnesium sulphate, filter free from the drying agent, evaporate off the ether and identify the residual acid.

4. If no acid has yet been isolated, tests are finally applied for non-volatile acids more soluble in water than in ether.

Take some of the acid solution remaining after test B3 and add ammonia till alkaline. Boil off excess ammonia and carry out the following tests on separate portions of the neutral solutions:—

(*a*) Acidify with acetic acid and add calcium chloride solution. A white precipitate indicates the presence of oxalate. Filter off the precipitate, dissolve in hot dilute sulphuric acid and add potassium permanganate which should be decolorized.

(*b*) Add silver nitrate solution in excess. If a silver salt is precipitated, filter, wash with water until the washings give no test for silver ions. Wash twice with alcohol, twice with ether and dry at 100° C., protecting the salt from light. Weigh accurately in a tared crucible about 0·5 g. of the dry salt. Heat gently at first, to avoid loss by spirting, and finally to redness. Cool in a desiccator and weigh the metallic silver.

$$\text{Equivalent weight of acid} = \frac{\text{weight of silver salt} \times 107{\cdot}9}{\text{weight of silver}} - 106{\cdot}9.$$

If (*b*) gives no result, attempt the determination of the equivalent weight of the acid through the calcium, barium or lead salt thus:

Calcium salt.—To the neutral solution from the hydrolysis, add a concentrated solution of calcium chloride and boil. If a precipitate forms, filter, wash free from chloride, and dry at 130° C. to remove any possible water of crystallization. Weigh out accurately about 0·5 g. of the calcium salt in a tared crucible and moisten with 50 per cent sulphuric acid. Heat gently at first and then quite strongly till the residue is white. Cool in a desiccator

and weigh the calcium sulphate. Repeat the ignition until constant weight is attained.

$$\text{Equivalent weight of acid} = \frac{\text{weight of calcium salt} \times 68{\cdot}05}{\text{weight of calcium sulphate}} - 19{\cdot}04.$$

Barium salt.—As for calcium salt, using barium chloride in place of calcium chloride.

$$\text{Equivalent weight of acid} = \frac{\text{weight of barium salt} \times 116{\cdot}7}{\text{weight of barium sulphate}} - 67{\cdot}68.$$

Lead salt.—As for the calcium salt, using lead acetate solution as a precipitant.

$$\text{Equivalent weight of acid} = \frac{\text{weight of lead salt} \times 151{\cdot}6}{\text{weight of lead sulphate}} - 102{\cdot}6.$$

Deduce the above formulæ.

Some few acids, e.g. lactic acid, do not give any of the above tests, and special tests should be applied. Lactic acid is best isolated by acidifying the hydrolysate and absorbing the solution in powdered plaster of Paris. The mass is broken up and extracted with ether in a Soxhlet. Evaporate off the ether and prepare a derivative of the acid.

C. Isolation and identification of a polyhydric alcohol

Some indication of the presence of these will be given by the physical properties of the ester. After the removal of acids soluble in ether or sparingly soluble in water, evaporate the neutralized solution to dryness either on a water-bath or preferably under reduced pressure. Extract with ethyl acetate and prepare a suitable derivative of the alcohol.

Rapid saponification of esters by potassium hydroxide in diethylene glycol

Introduce into a 25 ml. distilling flask 3 ml. of diethylene glycol, 0·5 g. of potassium hydroxide in the form of pellets, and 10 drops of water. Heat the mixture gently over a small flame until all the potash has dissolved. Cool the mixture and add 1 g. of the ester or double this amount if the molecular weight is known to be high. Close the neck of the flask with a cork carrying a thermometer of suitable temperature range. Fit the side arm of the flask with

a cork of suitable size to connect to a small water-cooled condenser. Heat the mixture over a small flame during which time the contents should be thoroughly shaken. When the system has become homogeneous or only consists of a solid suspended in a liquid, connect the flask to the condenser and distil off the alcohol. Prepare a suitable derivative of the latter (see p. 79).

The residue in the flask consists of either a solution or a suspension of the potassium salt of the acid in diethylene glycol. Add about 10 ml. of water, 10 ml. of ethyl alcohol, and 1 drop of phenolphthalein. While shaking, add 6N sulphuric acid drop by drop until the solution is just acid. Set aside the resulting solution to allow as complete a precipitation of potassium sulphate as possible. Filter, divide the filtrate into two portions and use them to prepare suitable derivatives of the acid, e.g. *p*-nitrobenzyl and *p*-bromophenacyl esters (see p. 53).

Derivatives, &c.

It is clear that any derivatives prepared from the original ester give information only with regard to the acid from which the ester is derived, and generally speaking, isolation and identification of the alcohol and acid obtained by hydrolysis, together with an equivalent weight determination, is all that is necessary to identify an ester.

1. **Equivalent weight.**—This value provides a reliable check on the identity of the alcohol (or phenol) and acid already characterized. It is particularly useful in those cases where the acid is difficult to isolate and gives few characteristic reactions. It must always be carried out if the ester is derived from a polyhydric alcohol in order that the number of acid groups in the molecule may be determined.

Weigh into a clean dry 150 ml. flask about 1·5 g. of the ester. Introduce 25 ml. of approximately normal alcoholic caustic potash and 3 ml. of water. Carry out a duplicate experiment but without the ester present. Reflux both solutions on a water-bath for about half an hour. Wash down each condenser with 10 ml. of water. Cool the contents of the flasks, add a few drops of phenolphthalein, and titrate the excess alkali with normal hydrochloric acid.

For those esters which are only hydrolysed with difficulty the following procedure may be used:

Prepare an approximately normal solution of caustic potash

in diethylene glycol by dissolving 3 g. of potassium hydroxide in 50 ml. of diethylene glycol (do not heat above 130° C.). Pipette out two 10 ml. portions of this solution into two separate flasks. Weigh out accurately about 0·5 g. of the ester and introduce into one of the flasks. Heat both flasks so that a temperature of 70°–80° C. is reached in about 3 min. Shake the mixture and raise the temperature to about 120° C. After 3 min. cool, wash down each condenser and flask with about 20 ml. of water, add a few drops of phenolphthalein and titrate with N/5 hydrochloric acid.

$$\text{Equivalent weight of ester} = \frac{\text{weight of ester} \times 1000}{\text{difference in titrations} \times \text{normality of HCl}}$$

Note.—The figure obtained in the case of an ester of carbonic acid will be twice the theoretical value, as in the back titration of the hydrolysed ester, the end-point—using phenolphthalein—is not reached until the carbonate present has been converted to bicarbonate. Thus the figure, titration on blank minus titration on hydrolysed solution, is half the expected value and the equivalent weight is accordingly doubled.

2. **Amide.**—In some cases, e.g. methyl oxalate, the amide of the corresponding acid may be obtained directly by adding 10 ml. of concentrated ammonia to 0·5 g. of the ester in a stoppered bottle and shaking well. Occasionally, overnight standing is necessary to produce a result. Filter off the amide, wash with a very little water and recrystallize from aqueous alcohol. (Note that oxamide cannot be recrystallized.)

$$\begin{matrix}\text{CO·OCH}_3\\ |\\ \text{CO·OCH}_3\end{matrix} + 2\text{NH}_3 = \begin{matrix}\text{CO·NH}_2\\ |\\ \text{CO·NH}_2\end{matrix} + 2\text{CH}_3\text{·OH}.$$

TABLE XI.—ESTERS

Liquids	B.P. °C.	E.W.
Methyl formate	32	60
Ethyl formate	54	74
Methyl acetate	57	74
iso-Propyl formate	68	88
Vinyl acetate	72	86
Ethyl acetate	77	88
Methyl propionate	79	90
n-Propyl formate	81	88
Allyl formate	83	86
Methyl acrylate	85	86
Methyl carbonate	90	90*
iso-Propyl acetate	91	102
Methyl *iso*-butyrate	92	102
sec-Butyl formate	97	102
iso-Butyl formate	98	102
Ethyl propionate	98	102
n-Propyl acetate	101	102
Ethyl acrylate	101	100
Methyl orthoformate	101	106
Methyl *n*-butyrate	102	102
Allyl acetate	103	100
n-Butyl formate	107	102
Ethyl *iso*-butyrate	110	116
sec-Butyl acetate	111	116
iso-Propyl propionate	111	116
iso-Butyl acetate	116	116
Methyl *iso*-valerate	116	116
Ethyl *n*-butyrate	120	116
n-Propyl propionate	122	116
iso-Amyl formate	123	116
n-Butyl acetate	125	116
Ethyl carbonate	126	118*
iso-Propyl *n*-butyrate	128	130
Methyl *n*-valerate	130	116
n-Amyl formate	130	116
Ethyl *iso*-valerate	134	130
Methyl pyruvate	136	102
iso-Butyl propionate	137	116
Ethyl crotonate	138	114
iso-Amyl acetate	142	130
n-Propyl *n*-butyrate	143	130
n-Butyl propionate	144	130
Methyl lactate	145	94
Ethylene glycol mono-methyl-ether acetate	144	106
Ethyl *n*-valerate	145	130
Ethyl ortho-formate	145	148
n-Amyl acetate	146	130
iso-Butyl *iso*-butyrate	147	143
Methyl *iso*-butyl carbinol acetate	148	131
Methyl *n*-caproate	150	130
Ethyl ethoxy acetate	152	132
Ethyl lactate	154	108
Ethyl pyruvate	155	116
Ethylene glycol mono-ethyl-ether acetate	156	120
iso-Butyl *n*-butyrate	157	144
iso-Amyl propionate	160	144
Ethyl glycollate	160	104
Cyclo hexyl formate	162	128
n-Butyl *n*-butyrate	165	144
n-Amyl propionate	166	144
Ethyl *n*-caproate	166	144
n-Propyl *n*-valerate	167	144
n-Propyl carbonate	168	146*
iso-Propyl lactate	168	122
Methyl aceto acetate	169	116
Methyl *n*-heptoate	173	144
Cyclo hexyl acetate	175	142
Furfuryl acetate	176	140
iso-Amyl *n*-butyrate	178	158
Methyl furoate	181	126
Methyl malonate	181	66
Ethyl aceto acetate	181	130
β-Hydroxy ethyl acetate	182	104
n-Amyl *n*-butyrate	185	158
n-Propyl *n*-caproate	186	158
Ethyl oxalate	186	73
Ethylene glycol di-acetate	187	61
Ethyl methyl aceto-acetate	187	144
n-Butyl lactate	188	136
Ethyl *n*-heptoate	189	158
iso-Propyl oxalate	190	87
iso-Butyl carbonate	190	174*
iso-Amyl *iso*-valerate	190	172
Methyl levulinate	191	130
n-Heptyl acetate	192	158
Methyl caprylate	193	158
Tetra - hydro furfuryl acetate	194	144
Methyl succinate	195	73
Ethyl methyl malonate	196	87·5
Phenyl acetate	196	136
Ethyl malonate	198	80

* Indicates abnormal equivalent weights.

TABLE XI—(*contd.*)

Liquids	B.P. °C.	E.W.
Methyl benzoate	198	136
Ethyl ethyl aceto-acetate	198	158
Benzyl formate	203	136
n-Amyl valerate	204	172
γ-Butyrolactone	204	86
Ethyl levulinate	205	210
Ethyl caprylate	206	172
n-Butyl carbonate	207	174*
γ-Valerolactone	207	100
o-Cresyl acetate	208	150
Trimethylene glycol di-acetate	210	80
Phenyl propionate	211	150
n-Propyl furoate	211	154
Ethylene glycol di-propionate	212	87
m-Cresyl acetate	212	150
p-Cresyl acetate	212	150
n-Propyl oxalate	213	87
Methyl pelargonate	213	172
Ethyl benzoate	213	150
Methyl *o*-toluate	213	150
Methyl *m*-toluate	213	150
Ethyl fumarate	215	86
Benzyl acetate	216	150
Ethyl succinate	216	87
Methyl *p*-toluate	217	150
Diethylene glycol mono-ethyl-ether acetate	218	178
iso-Propyl benzoate	218	164
Methyl phenyl acetate	218	150
n-Propyl levulinate	221	158
n-Amyl *n*-caproate	222	186
Methyl salicylate	224	152
Ethyl maleate	225	86
Ethyl pelargonate	227	186
Phenyl *n*-butyrate	227	164
l-Menthyl acetate	227	198
iso-Amyl carbonate	228	202*
Benzyl propionate	228	164
iso-Butyl oxalate	229	101
Ethyl phenyl acetate	229	164
n-Propyl benzoate	230	164
Allyl benzoate	230	162
Methyl caprate	232	186
Ethyl salicylate	234	166
iso-Propyl salicylate	237	180
Benzyl *n*-butyrate	238	178
n-Propyl salicylate	239	180
Ethyl *n*-butyl malonate	240	108
iso-Butyl benzoate	241	178
n-Butyl oxalate	243	101
Thymyl acetate	244	192
Ethyl adipate	245	101
Ethyl caprate	245	200
n-Propyl succinate	246	101
iso-Butyl phenyl acetate	247	192
Methyl undecylenate	248	200
n-Butyl benzoate	249	178
Ethyl acetonedicarboxylate	250	101
n-Butyl phenylacetate	254	192
Ethyl pimelate	255	108
Ethyl benzoyl formate	257	178
Glyceryl tri-acetate (tri-acetin)	258	73
Glyceryl di-acetate (di-acetin)	260	109
iso-Amyl oxalate	262	115
iso-Amyl benzoate	262	192
iso-Butyl succinate	265	115
Methyl laurate	268	214
n-Butyl salicylate	268	194
Ethyl anisate	269	180
Ethyl laurate	269	228
Ethyl benzoyl acetate	270	192
Ethyl cinnamate	271	176
iso-Amyl salicylate	277	208
Resorcinol diacetate	278	97
Ethyl *d*-tartrate	280	103
Methyl phthalate	282	97
Ethyl suberate	282	115
Glyceryl tri-propionate	289	87
Ethyl azelate	291	122
Ethyl citrate	294	92
Methyl myristate	296	242
iso-Amyl succinate	297	129
Ethyl phthalate	298	111
Ethyl benzyl malonate	300	125
Ethyl *iso*-phthalate	302	111
iso-Propyl phthalate	302	125
Ethyl myristate	306	256
Ethyl sebacate	307	129
o-Cresyl benzoate	307	212
Glyceryl tri-butyrate	318	101

* Indicates abnormal equivalent weights.

TABLE XI—(*contd.*)

Liquids	B.P. °C.	E.W.
Benzyl phenyl-acetate	318	226
Benzyl salicylate	320	228
Benzyl benzoate	323	212
n-Butyl phthalate	338	139
iso-Amyl phthalate	349	153
Glyceryl mono-acetate (monacetin)	d	218
n-Butyl *d*-tartrate	d	131
n-Butyl citrate	d	120

Solids	M.P.	B.P.	E.W.
Cetyl acetate	22		284
n-Butyl *d*-tartrate	22		131
Ethyl palmitate	24		284
Bornyl acetate	29	221	196
Methyl palmitate	30		270
Methyl *p*-toluate	33	217	150
Thymyl benzoate	33		254
Ethyl stearate	33		312
Ethyl furoate	33		140
Methyl cinnamate	36	263	162
Ethyl mandelate	37	254	180
Methyl sebacate	38	288d	115
Methyl stearate	38		298
Benzyl cinnamate	39		238
Benzyl phthalate	42		173
Phenyl salicylate	42		214
Benzyl succinate	42		149
Cyclohexyl oxalate	42		127
Ethyl terephthalate	44		111
Cinnamyl cinnamate	44		255
Methyl anisate	45	255	166
Methyl *d*-tartrate	48 (61)	280	89
α-Naphthyl acetate	49		187
Methyl oxalate	51	163	59
m-Cresyl benzoate	54		212
Methyl mandelate	58		166

Solids	M.P.	B.P.	E.W.
o-Cresyl carbonate	60		242*
Methyl *iso*-phthalate	67		97
Coumarin	67	290	146
Phenyl benzoate	68	299	198
Phenyl phthalate	70		159
Methyl *m*-hydroxy benzoate	70		152
β-Naphthyl acetate	70		187
Glyceryl tristearate	71		297
p-Cresyl benzoate	71		212
Phenyl cinnamate	72		224
Ethyl *m*-hydroxy benzoate	72		166
Ethylene glycol dibenzoate	73		135
Phthalide	73	290	134
Phenyl carbonate	78	306	214*
Methyl citrate	79	285d	78
Benzyl oxalate	80		135
Guaiacol carbonate	86		274*
β-Naphthyl salicylate	95		265
β-Naphthyl benzoate	107		249
m-Cresyl carbonate	115		242*
Ethyl *p*-hydroxy benzoate	116		166
Resorcinol dibenzoate	117		159
Hydroquinone di-acetate	123		97
Lactide	128	255	70
Methyl *p*-hydroxy benzoate	131		152
Methyl terephthalate	140		97
Pyrogallol triacetate	161		84

* Indicates abnormal equivalent weights.

GROUP I—CLASS VIII

ALCOHOLS

Classification test.—If the original compound be a liquid, add a small piece of freshly cut metallic potassium to a one ml. portion which has been previously dried over anhydrous sodium sulphate. If the original substance be a solid, dissolve it in *dry* benzene, xylene or ether, and add a small piece of potassium. In either case a brisk and well sustained effervescence indicates a substance of this class.*

$$2R{\cdot}OH + 2K = 2R{\cdot}OK + H_2.$$

Confirm the conclusion drawn from the above test by the use of a solution of pernitrato ceric acid $H_2Ce(NO_3)_6$, or perchlorato ceric acid $H_2Ce(ClO_4)_6$. The former is readily prepared by dissolving 40 g. of hexanitrato ammonium cerate $(NH_4)_2Ce(NO_3)_6$ in 100 ml. of 2N nitric acid.

One ml. of the reagent is diluted with 2 ml. of water and 1–2 drops of the original substance, or a saturated solution of it in water is added. Formation of a red colour indicates the presence of an alcohol. For compounds insoluble in water, dissolve in the minimum amount of dioxan, and add to one ml. of the cerate reagent diluted with 2 ml. of dioxan.

Note.—Dioxan may not be used with the perchlorato reagent.

To distinguish between primary, secondary and tertiary alcohols which are soluble in water, i.e. alcohols containing less than seven carbon atoms:

(*a*) *Lucas' test*

This depends on the rate of formation of the alkyl chloride from the alcohol when this is treated at about 25° C. with zinc chloride in hydrochloric acid.

To one ml. of the alcohol add 10 ml. of a saturated solution of zinc chloride in concentrated hydrochloric acid (136 g. of anhydrous zinc chloride in 105 g. of concentrated hydrochloric acid). Shake and allow to stand. The immediate formation of an emulsion or insoluble layer indicates a *tertiary alcohol.* If a distinct layer forms in 10 min. a *secondary alcohol* is present. No visible reaction

* Disposal of potassium used in this test is effected by adding methylated spirit until all the metal has reacted, before pouring away.

occurs in the case of a *primary alcohol.* (If impurities are present in a primary alcohol, some cloudiness may be observed, but no separate layer will be formed on standing.*)

(*b*) To one ml. of the alcohol add 6 ml. of concentrated hydrochloric acid. Shake and allow to stand. A *tertiary alcohol* reacts to form the alkyl chloride which separates out as a surface layer in a few minutes. Solutions containing primary or secondary alcohols usually remain clear.

(*c*) *Oxidation*

Mix a small quantity of the alcohol with a little more than its own volume of chromic acid mixture (1 g. CrO_3, 6 ml. water and 0·8 ml. concentrated sulphuric acid), in a small distilling flask. Distil a small quantity, without the use of a condenser, allowing the side tube to dip into a few ml. of water in a test-tube. Test the distillate for (*a*) aldehyde, (*b*) ketone (see p. 36); (*a*) arises from the oxidation of a *primary alcohol,* (*b*) from the oxidation of a *secondary alcohol.*

By delivering the distillate directly into an alcoholic solution of 2 : 4 dinitrophenylhydrazine (see p. 37, derivative 1), crystalline derivatives from primary and secondary alcohols may be obtained.

Test for poly-hydroxy compounds of the aliphatic series (Feigl and Zappert)

One ml. of 5 per cent potassium periodate solution and 0·5 ml. of 2N sulphuric acid are mixed, and a little of the original compound added. Allow to stand for 5 minutes. Sulphur dioxide is then passed through the solution until it becomes faintly yellow. One ml. of Schiff's reagent is added and the solution allowed to stand, when the violet colour slowly appears at a rate dependent on the type of alcohol.

The test is based on Malaprade's reaction,

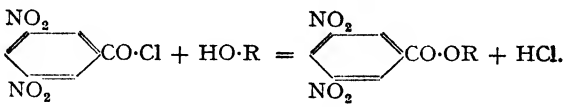
$$CH_2OH[CH(OH)]_nCH_2OH + (n + 1)HIO_4 = 2H{\cdot}CHO + nH{\cdot}COOH + (n + 1)HIO_3 + H_2O,$$

which uses excess periodic acid in the cold. After removing the excess of iodic and periodic acids with sulphur dioxide, the aldehyde is readily detected with Schiff's reagent.

* Allyl alcohol reacts within 7 min. as a secondary alcohol; *iso*-propyl alcohol does not react as a secondary alcohol.

Derivatives

1. 3 : 5-**Dinitrobenzoate.**—(*a*) Mix 0·5 g. of 3 : 5-dinitrobenzoyl chloride with one ml. of the alcohol and allow to simmer under a reflux condenser for 10 min. or until there is no further evolution of hydrochloric acid fumes. Add 10 ml. of water, cool and filter off the derivative. Wash with sodium carbonate solution, followed by water, and recrystallize from 60 per cent alcohol.



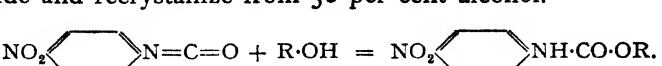
(*b*) Mix a few drops of the alcohol with a solution of 3 : 5-dinitrobenzoyl chloride in benzene and add a little anhydrous pyridine. In the case of primary and secondary alcohols heat to boiling or allow to stand at room temperature for some hours; with tertiary alcohols reflux for half an hour. Cool and dilute with dry ether. Wash the ethereal solution in a separating funnel with dilute hydrochloric acid, followed by dilute caustic soda, and finally with a large volume of water. Evaporate off the ether and recrystallize the ester from benzene or petrol ether.

If a derivative sparingly soluble in organic solvents is formed, as is the case with polyhydric alcohols, filter off after washing with water.

2. **Phenyl- or α-naphthyl carbamate (urethane).**—Prepare as in the case of the corresponding derivatives of phenols (see Derivative 2, p. 62), avoiding the use of water as far as possible and recrystallizing from carbon tetrachloride or light petroleum.

Primary alcohols usually react vigorously with the reagent, secondary alcohols require heating, while tertiary alcohols give poor yields, owing to the readiness with which they lose water.

3. ***p*-Nitrophenyl carbamate (urethane).**—For alcohols lower than octyl, add some *p*-nitrophenyl isocyanate to an excess of the alcohol dissolved in carbon tetrachloride. Filter the hot solution and allow the urethane to crystallize out. In the case of the higher alcohols use petroleum ether instead of carbon tetrachloride and recrystallize from 50 per cent alcohol.



4. **S-benzylthiuronium derivative.**—Alkyl sulphuric acids and their sodium salts form characteristic derivatives with S-

benzylthiuronium chloride and this reaction can be used to identify alcohols after preliminary conversion to their hydrogen sulphates.

Prepare a mixture of eight drops of chlorosulphonic acid and 10 drops of dioxan, and add 10 drops of the alcohol slowly, shaking after each addition. Warm if necessary to cause evolution of hydrochloric acid gas, which shows that the alkyl sulphuric acid has been formed. Allow to stand for 5 to 10 min. Add one ml. of a saturated aqueous solution, or 15 per cent alcoholic solution, of S-benzylthiuronium chloride. If a saturated aqueous solution be used in the preparation of those derivatives marked *, Table XII, cool the solution well and scratch the inside of the tube with a glass rod to induce crystallization.

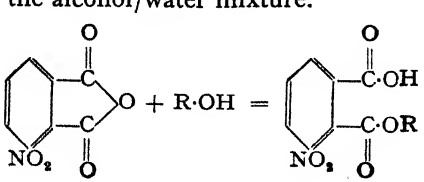
Methyl and ethyl alcohols yield no derivative with the reagent.

$$H{\cdot}SO_3Cl + HO{\cdot}R = H{\cdot}SO_3{\cdot}OR + HCl$$

$$Cl^- \left[\begin{matrix}\overset{+}{N}H_2 \\ \diagdown \\ C{\cdot}S{\cdot}CH_2{\cdot}C_6H_5 \\ \diagup \\ NH_2\end{matrix}\right] + H{\cdot}SO_3{\cdot}OR = SO_3OR^- \left[\begin{matrix}\overset{+}{N}H_2 \\ \diagdown \\ C{\cdot}S{\cdot}CH_2{\cdot}C_6H_5 \\ \diagup \\ NH_2\end{matrix}\right] + HCl.$$

5. **3-Nitrophthalate.** (*a*) *For alcohols boiling below* 150° *C.* Reflux a mixture of 0·4 g. of 3-nitrophthalic anhydride and 0·5 ml. of the alcohol gently in a test-tube fitted with an air condenser, heating being continued for 5 to 10 min. after liquefaction has occurred. Cool, add 5 ml. of water and heat to boiling. If solid remains undissolved add an additional 5 to 10 ml. of hot water. Cool the solution to cause the ester to crystallize, but if an oil separates, allow to stand overnight. Recrystallize from hot water.

(*b*) *For alcohols boiling above* 150° *C.* Reflux 0·4 g. of 3-nitrophthalic anhydride, 0·5 g. of alcohol, and 5 ml. of dry toluene until all the anhydride has dissolved and then for a further 15 min. Remove the toluene by suction. Extract the residue twice with 5 ml. of hot water and dissolve the residual oil by boiling with 10 ml. of 95 per cent alcohol. Filter if not clear. Add water dropwise to the hot solution until it becomes slightly turbid, then a few drops of alcohol to clear. Allow to cool slowly and set aside for some days. Occasionally toluene may be used for recrystallization in place of the alcohol/water mixture.



6. **Benzoate.**
7. **Acetate.** } Method of preparation as for phenols (see p. 63).

Note.—These last two derivatives are not of general value since in the case of the lower alcohols they are liquids.

8. **Potassium alkyl xanthate.**—Take 0·5 to 1·0 g. of the alcohol in 10 to 25 ml. of water, treat with 15 to 37·5 g. of solid potassium hydroxide in a separating funnel and cool to 40° C. Add 5 ml. each of carbon disulphide and acetone (both alcohol-free) and shake, cautiously at first, and then more vigorously at intervals during 15 min.

(*a*) *For monohydric alcohols* add 25 ml. (150 ml. for *iso*-propyl alcohol) of acetone, shake well, discard the lower layer, and filter the acetone solution through glass wool. Precipitate the xanthate by the addition of ether, filter, dissolve the product in the least amount of alcohol and add ether to facilitate crystallization. Wash the crystallized product with ether and dry in a vacuum desiccator.

(*b*) *For polyhydric alcohols* add 25 ml. of acetone, shake well, and filter through a sintered glass crucible. Wash the residue with a little acetone and three 10 ml. portions of *iso*-propyl alcohol. Dissolve the crude xanthate in the least amount of hot methyl alcohol and recrystallize by the addition of *iso*-propyl alcohol. Purify further by recrystallization from water/*iso*-propyl alcohol. Finally wash with *iso*-propyl alcohol and with dry ether and dry in a vacuum desiccator.

In determining the melting-point of the derivative, raise the temperature of the heating bath or coil to within 10° C. of the melting-point before introducing the substance. To avoid decomposition the time of heating should not exceed 4 min.

$$CS_2 + R{\cdot}OH + KOH = S{=}C\begin{matrix}OR\\SK\end{matrix} + H_2O.$$

9. ***p*-Nitrobenzoate.**—See corresponding derivative for phenols (Derivative 8, p. 66).

TABLE XII.—ALCOHOLS

	B.P. °C.	3 : 5-Dinitrobenzoate	α-Naphthyl carbamate	Phenyl carbamate	*p*-Nitrophenyl carbamate	3-Nitrophthalate	*p*-Nitrobenzoate	S-benzylthiuronium salt of alkyl sulphuric acid	Potassium alkyl xanthate	
Liquids										
Methyl alcohol	66	109	124	47	180	153†	96	—	182	† Anhydrous
Ethyl alcohol	78	93	85	52	129	157	56	—	225	Gives iodoform test
iso-Propyl alc.	82	122	106	90	116	153	110	142	278	Gives iodoform test
tert-Butyl alc.	83	142	101	140	—	—	116	—	—	M.P. 25° C.
n-Propyl alc.	97	74	80	58	115	142	35	111	233	
Allyl alc.	97	50	109	67	108	124	28			
sec-Butyl alc.	99	75	97	65	75	131	26	117		
tert-Amyl alc. (Dimethyl ethyl carbinol)	102	117	71	42	—	—	85			
iso-Butyl alc.	108	88	100	82	80	183	69	136	260	
sec-Amyl alc. (Methyl *iso*-propyl carbinol)	113	76	112	69	—	—	—	—	—	Gives iodoform test
sec-Amyl alc. (Diethyl carbinol)	116	101	71	48						
n-Butyl alc.	118	62	71	60	96	147	35	100	255	
sec-Amyl alc. (Methyl *n*-propyl carbinol)	119	61	76	—	—	103				
Amyl alc. (*sec*-Butyl carbinol)	128	70	82	—	—	158				

[Contd. over.

iso-Amyl alc. (*iso*-Butyl carbinol)	130	62	67	55	98	166	—	—	260	
4-Methyl-2-pentanol	131									
Methyl *iso*-butyl carbinol	137	—	—	143						
n-Amyl alc.	138	46	68	46	86	136	—	85*		
Cyclopentanol	140	115	118	132			62			
Acetoin	142									
n-Hexyl alc.	156	61	59	41	103	124	—	85*		
Cyclohexanol	160	112	128	82	—	160	50			
2-Heptanol	160	49	54							
2-Methylcyclohexanol cis	165	99	—	92	—	—	56			
2-Methylcyclohexanol trans		115	—	103	—	—	65			
Furfuryl alc.	170	80	129	45	—	—	76			Polymerizes very rapidly
4-Methylcyclohexanol cis	174	134	—	119	—	—	94			
4-Methylcyclohexanol trans		140	157	123	—	—	67			
3-Methylcyclohexanol cis	175	111	118	—	—	—	65			
3-Methylcyclohexanol trans		98	129	92	—	—	48			
n-Heptyl alc.	176	47	60	59	105	127		77*		
Tetrahydro furfuryl alc.	177	84	90	58	—	—	47			
Capryl alc. (*sec-n*-Octyl alc.)	179	32	63	—	—	—	28			
Propylene glycol	188	—	—	153			127			
n-Octyl alc.	192	61	66	74	111	128	—	42*		
Ethylene glycol	197	169	176	156	—	—	140	180	200	Dibenzoate, M.P. 73° C.
Linaloöl	197	—	53	65	—	—	70			
Phenyl methyl carbinol	203	94	106	94	—	—	43			

TABLE XII—(*contd.*)

	B.P. °C.	3:5-Dinitrobenzoate	α-Naphthyl carbamate	Phenyl carbamate	*p*-Nitrophenyl carbamate	3-Nitrophthalate	*p*-Nitrobenzoate	S-benzylthiuronium salt of alkyl sulphuric acid	Potassium alkyl xanthate	
Liquids										
Benzyl alc.	206	112	134	78	157	183	85	—	178	Oxidation with $KMnO_4$ → benzoic acid, M.P. 122° C.
n-Nonyl alc.	215	52	66	62	104	125				
Trimethylene glycol	216	178	164	137	—	—	119	—	—	Dibenzoate, M.P. 53° C.
m-Methylbenzyl alc.	217	—	116							
β-Phenyl ethyl alc.	219	107	119	79	135	123	62	—	—	Oxidation with $KMnO_4$ → benzoic acid, M.P. 122° C.
Ethylphenyl carbinol	219	—	102	—	—	—	60			
Citronellol	222									
Geraniol	229	62	47	—	—	117	35			
n-Decyl alc.	231	57	71	60	117	123	30	73		
γ-Phenyl-*n*-propyl alc.	235	92	—	45	104	117	46			
Diethylene glycol	245	—	—	—	—	—	—	207		
Glycerol	290d	—	191	180	216	—	188	—	—	Tribenzoate, M.P. 76° C.

Solids	M.P.									
n-Undecyl alc.	19	—	73	62	100	123	30			
Lauryl alc.	24	60	80	74	117	125	45	74		
p-Methoxybenzyl alc. (Anisyl alc.)	25	—	126	90	—	85	—	—	—	Oxidation with $KMnO_4$ → anisic acid, M.P. 184° C.
Tridecyl alc.	30	—	80	70	—	124	37			
Cinnamyl alc.	33	121	114	90	—	—	78			
Pinacol	40	—	—	215	—	—	—	—	—	Warming with H_2O → hydrate, M.P. 46° C.
α-Terpineol	35	78	147	112	—	—	139			
o-Methyl benzyl alc.	36	—	—	79						
Myristyl alc.	39	—	81	71	—	123	—	87		
l-Menthol	42	153	120	111	—	—	62	—	—	Benzoate, M.P. 55° C.
Fenchyl alc.	45	—	148	82	—	—	95	—	—	B.P. 202° C.
Pentadecyl alc.	45	—	85	72	—	123	46			
α-Phenyl *n*-butyl alc.	49	—	99	—	—	—	58			
Cetyl alc.	50	66	82	76	118	122	52			
Heptadecyl alc.	54	—	89	—	—	122	54			
Stearyl alc.	59	—	89	80	115	119	64			
p-Methyl benzyl alc.	60	—	—	79						
Benzhydrol (Diphenyl carbinol)	69	141	136	—	150	—	131	—	—	Conc. H_2SO_4 → red colour
l-Cholesterol	148	—	160	168	205	—	190	—	—	Benzoate, M.P. 150° C.
Triphenyl carbinol	162	—	—	—	—	—	—	—	—	Conc. H_2SO_4 → yellow colour
Ergosterol	165	202	—	—	—	—	—	—	—	Acetate, M.P. 180° C.
d-Mannitol	166	—	—	303	—	—	—	—	—	Hexa-acetate, M.P. 120° C.
d-Borneol	208	154	131	138	—	—	153	174		
iso-Borneol	216	138	130	—	—	—	129			
Pentaerithritol	258	—	—	—	—	—	—	—	—	Tetrabenzoate, M.P. 99° C. Tetra-acetate, M.P. 84° C.

GROUP I—CLASS IX

ETHERS, CYCLIC ETHERS

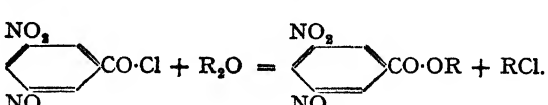
Classification test.—If the given compound is a liquid, dry about 1 ml. of it over anhydrous sodium sulphate. Add to the dried liquid a 0·5 cm. square of " ferrox " paper (see p. 290), and shake gently. If the liquid becomes red, due to dissolved ferric thiocyanate, it is an ether. In the case of a solid, dissolve it in dry benzene and add the " ferrox " paper.

" Ferrox " paper is not a specific test for ethers, but merely indicates the presence of oxygen in the compound. Since only ethers and hydrocarbons have not yet been covered by the various classification tests for carbon, hydrogen and oxygen compounds, it may be used as above.

Confirmatory test.—Mix some of the original substance with an equal quantity of concentrated sulphuric acid. If the substance dissolves in the cold, add carefully an equal volume of water. If the original substance is reprecipitated, it is probably a member of this class, although aromatic and fatty-aromatic ethers will not be precipitated.

Derivatives

1. 3 : 5-Dinitrobenzoate. — *For simple aliphatic ethers only.* Heat a mixture of 1 ml. of the dry ether, 0·15 g. of anhydrous zinc chloride and 0·5 g. of 3 : 5-dinitrobenzoyl chloride under a reflux condenser for one hour. Cool and add 10 ml. of 5 per cent sodium carbonate solution. Heat to 100° C., cool and filter. Wash the solid with 5 per cent sodium carbonate solution and then with water. Dry and extract with hot carbon tetrachloride. Filter and cool the filtrate. Evaporate off the carbon tetrachloride.



In the case of mixed aliphatic-aromatic or simple aromatic ethers one of the following derivatives can generally be prepared:

2. Bromo derivative.—See corresponding derivative for phenols (p. 66).

3. **Nitro derivative.**—See corresponding derivative for hydrocarbons (p. 90).

4. **Picric acid, or 1 : 3 : 5-trinitrobenzene derivative.**—See corresponding derivative for hydrocarbons (p. 91).

TABLE XIII.—ALIPHATIC ETHERS

	B.P. °C.	3 : 5-Dinitrobenzoate	
Methyl ethyl ether	10		
Furan	32		
Diethyl ether	35	93	
Allyl ethyl ether	65		
Di-*iso*-propyl ether	68	121	
Di-*n*-propyl ether	90	74	
Ethyl *n*-butyl ether	92		
Dioxan	102		
Ethylene glycol diethyl ether	121		
Di-*iso*-butyl ether	122	86	
Ethylene glycol mono-ethyl ether	135		
Di-*n*-butyl ether	140	63	
Benzyl methyl ether	167		
Ethylene glycol mono-*n*-butyl ether	171		
Di-*iso*-amyl ether	172	61	
Cineole	176		
Benzyl ethyl ether	189		
Di-*n*-amyl ether	190	43	
Diethylene glycol mono-methyl ether	193		
Diethylene glycol mono-ethyl ether	202		
n-Hexyl ether	208	55	
Benzyl *iso*-butyl ether	212		
Benzyl *n*-butyl ether	212		
Diethylene glycol mono-*n*-butyl ether	231		
Ethylene glycol monophenyl ether	245		
Di-*n*-heptyl ether	260	47	
Di-benzyl ether	298	112	Picrate 78

TABLE XIV.—AROMATIC ETHERS

	B.P. °C.	Picrate	Bromo derivative	Miscellaneous
Liquids				
Anisole	154	81	—	Dinitro deriv., M.P. 88° C.
o-Cresyl methyl ether	171	119	63 (m)	
Phenetole	172	92	—	Nitro deriv., M.P. 58° C.
p-Cresyl methyl ether	176	89	—	Oxidation with alkaline $KMnO_4$ → anisic acid, M.P. 184° C.
m-Cresyl methyl ether	177	114	—	Trinitro deriv., M.P. 91° C.
o-Cresyl ethyl ether	192	118	—	Dinitro deriv., M.P. 51° C.
m-Cresyl ethyl ether	192	115	—	Oxidation → *m*-ethoxybenzoic acid, M.P. 137°C.
p-Cresyl ethyl ether	192	111	—	Oxidation → *p*-ethoxybenzoic acid, M.P. 195° C.
Veratrole	206	57	92 (di)	Nitro deriv., M.P. 95° C.
n-Butyl phenyl ether	210	112		
Resorcinol dimethyl ether	214	58	140 (di)	
Methyl thymyl ether	216	—	—	Trinitro deriv., M.P. 92° C.
n-Butyl *o*-cresyl ether	223			
Safrole	232	75	169 (penta)	1 : 3 : 5-Trinitrobenzene deriv., M.P. 51° C.
Anethole	232	70	108 (tri)	
Resorcinol diethyl ether	235	58		
Eugenol methyl ether	244	—	78 (tri)	
iso-Safrole	246	75	109 (tri)	1 : 3 : 5 - Trinitrobenzene deriv., M.P. 86° C.
Methyl α-naphthyl ether	265	130	46 (m)	1 : 3 : 5 - Trinitrobenzene deriv., M.P. 138° C.
Ethyl α-naphthyl ether	278	119	48 (m)	1 : 3 : 5 - Trinitrobenzene deriv., M.P. 126° C.
n-Propyl α-naphthyl ether	298	99		
Solids	M.P.			
iso-Amyl α-naphthyl ether	—	96		
iso-Amyl β-naphthyl ether	26	91		
Diphenyl ether	28	110	54 (di)	Dinitro deriv., M.P. 135° C.
Apiole	32	—	—	Oxidation → apiolic acid, M.P. 175° C.
o-Methoxydiphenyl ether	32	—	—	Nitro deriv., M.P. 95° C.
iso-Butyl β-naphthyl ether	33	84		
Ethyl β-naphthyl ether	37	101	66 (m)	1 : 3 : 5 - Trinitrobenzene deriv., M.P. 95° C.
n-Propyl β-naphthyl ether	40	81		
iso-Propyl β-naphthyl ether	41	95		
Catechol diethyl ether	43	71	—	Trinitro deriv., M.P. 122°C.

TABLE XIV—(*contd.*)

	M.P. °C.	Picrate	Bromo derivative	Miscellaneous
Solids				
Hydroquinone dimethyl ether	55	119	142 (di)	
Methyl β-naphthyl ether	72	117	62 (m)	1 : 3 : 5 - Trinitrobenzene deriv., M.P. 94° C.
Hydroquinone diethyl ether	72	—	—	Trinitro deriv., M.P. 130°C.
Benzyl α-naphthyl ether	77			
p-Methoxydiphenyl ether	85			
Dibenzofuran	87	94		
Benzyl β-naphthyl ether	100			
ββ-Dinaphthyl ether	105	122		
αα-Dinaphthyl ether	110			
Hydroquinone dibenzyl ether	127	—	—	Nitro deriv., M.P. 83° C.
n-Butyl α-naphthyl ether	—	85		
n-Butyl β-naphthyl ether	—	67		
iso-Butyl α-naphthyl ether	—	105		
sec-Butyl α-naphthyl ether	—	101		
sec-Butyl β-naphthyl ether	—	86		

GROUP I—CLASS X

HYDROCARBONS

Any compound of the carbon, hydrogen and oxygen class remaining unclassified, is likely to be a hydrocarbon.

General tests

1. Mix some of the original compound with an equal bulk of cold concentrated sulphuric acid.

(*a*) If it is ***insoluble*** in the acid it is probably a saturated aliphatic hydrocarbon, a cyclo-paraffin, or an aromatic hydrocarbon. Some of the latter are, however, sulphonated by, and therefore soluble in, cold concentrated sulphuric acid. See (*b*) below.

Mix some of the compound with an equal volume of 30 per cent

oleum. Saturated aliphatic hydrocarbons and cyclo-paraffins are insoluble, aromatic hydrocarbons are soluble.

(*b*) If the original substance is *soluble* in cold concentrated sulphuric acid it is probably an unsaturated aliphatic or alicyclic hydrocarbon, an aromatic hydrocarbon with an unsaturated side-chain, e.g. styrene $C_6H_5 \cdot CH = CH_2$, or one of the more highly methylated hydrocarbons.

2. *Tests for unsaturation*

(*a*) Treat the original compound with a solution of bromine in carbon tetrachloride. Instant decolorization in the cold, without evolution of hydrobromic acid, indicates that the compound is unsaturated.

If the unsaturated linkages are conjugated with aromatic or similar groups, or largely surrounded by substituents, discharge of colour without evolution of hydrobromic acid may only take place on warming.

(*b*) Dissolve about 0·1 g. of the substance in absolute alcohol and add 2 drops of 1 per cent potassium permanganate solution. The rapid appearance of a brown colour or precipitate indicates that a double bond is present in the compound (Baeyer's test).

(*c*) Add Nessler's reagent (see p. 291). Compounds containing the acetylenic linkage, —C≡C—, form mercury derivatives which may be used for identification purposes.

$$2R \cdot C \equiv C \cdot H + K_2HgI_4 + 2KOH = (R \cdot C \equiv C)_2Hg + 4KI + 2H_2O$$

Derivatives, &c.

1. If the original substance has been definitely classified as a saturated aliphatic hydrocarbon or cycloparaffin, it is advisable to rely, for final identification, on such physical constants as the boiling-point, density or refractive index. This last is most conveniently determined with the *Abbé Refractometer* for the use of which a suitable textbook on light should be consulted.

2. **Nitro-compounds.**—There is no general method of nitration applicable to all aromatic compounds, but one of the following will generally give a satisfactory result. *Great care* should always be exercised in carrying out nitration as the reaction may become explosive. It is best to carry out the process in a fume-chamber, and in any event the tube or vessel should always point *away* from the operator or any neighbouring student.

(*a*) Prepare a mixture of 4 ml. of concentrated sulphuric acid and 4 ml. of concentrated nitric acid and cool well. Add *slowly* 1 ml. of the hydrocarbon, shaking well and cooling after each addition. Heat to 50° C. on a water-bath for a few minutes, cool and pour into 25 ml. of cold water. If a solid is precipitated (cooling in ice and water will hasten solidification), filter, wash well with cold water and recrystallize from dilute alcohol. This method generally results in the formation of the mono-nitro-derivative.

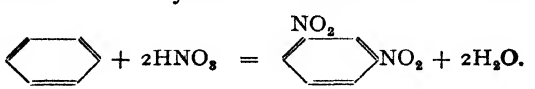
If the nucleus is already mono-substituted a mixture of *ortho*- and *para*-isomerides will be formed, the *ortho*-compound often being liquid at room temperature, while the *para*-compound is solid. In such a case, an oil will separate when the nitration mixture is poured into water. It is often possible to isolate the *para*-compound by decanting off the acid layer, washing the residual oil with water and then treating with petrol ether or alcohol in which the *ortho*-derivative is more soluble. This leaves the solid *para*-compound which may be purified by recrystallization.

Addition of a *very small* amount of acetone to the mixed acids will sometimes prove useful in facilitating nitration.

(*b*) As above, but substitute fuming nitric acid for the concentrated nitric acid.

(*c*) Boil about 0·5 g. of the hydrocarbon with 4 ml. of fuming nitric acid for not more than 30 min. Pour into 10 ml of water, cool and filter off the solid. Wash with water and recrystallize from dilute alcohol.

(*d*) Dissolve about 0·3 g. of the hydrocarbon in 4 ml. of glacial acetic acid and to the cooled solution add, drop by drop, 2 ml. of fuming nitric acid. Heat to boiling. Allow to stand for about 15 min. then pour into 10 ml. of water. Cool, scratch the inside of the tube with a glass rod to induce crystallization, filter the precipitate, wash with water and recrystallize from alcohol or dilute alcohol.



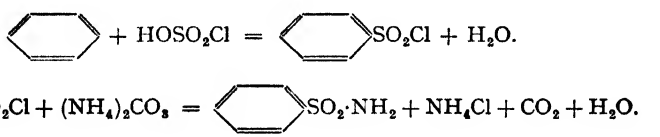
3. Addition compounds with picric acid, picrolonic acid or 1 : 3 : 5-trinitrobenzene.—For aromatic hydrocarbons only.

Dissolve 0·5 g. of the hydrocarbon in the minimum quantity of boiling 95 per cent alcohol, acetone, benzene or acetic acid, and add an equal volume of a clear saturated solution of picric acid, picrolonic acid, or 1 : 3 : 5-trinitrobenzene in the same solvent. Heat in a boiling water-bath and cool the solution.

Do not recrystallize unless from a saturated solution of the reagent in the same solvent as, in some cases, the derivatives are unstable. Only a small quantity of the derivative should be prepared as some are explosive.

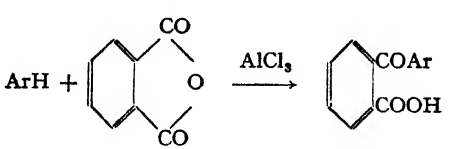
4. **Sulphonamide.**—For aromatic hydrocarbons only.

Add about 1 g. of the hydrocarbon, drop by drop, to 4 ml. of chlorosulphonic acid, shaking and cooling after each addition. Pour the resulting mixture into a little ice-cold water, when the resulting sulphonyl chloride will separate at the bottom as an oil. Separate from the aqueous layer and mix with an equal amount of powdered ammonium carbonate. Heat on a water-bath for half an hour, dilute with water, filter and recrystallize.



5. ***o*-Aroylbenzoic acid.**—For aromatic hydrocarbons only.

To a solution of 0·5 g. of the dry hydrocarbon in 10 ml. of dry carbon disulphide add an intimate mixture of 0·5 g. of phthalic anhydride and 1 g. of anhydrous aluminium chloride. Reflux on a water-bath until hydrochloric acid fumes cease to be evolved. Cool, separate and reject the carbon disulphide layer. While vigorously shaking and keeping the mixture cold, preferably in ice, add 10 ml. of 6N hydrochloric acid drop by drop. If the crude *o*-aroylbenzoic acid be a solid, filter; if an oil, decant off the supernatant liquid. In either case, wash with cold water; then boil the crude product with 20 ml. of 10 per cent ammonium hydroxide and a little decolorizing charcoal. Filter while hot. Cool the filtrate and acidify with hydrochloric acid. Filter off the derivative and recrystallize from 50 per cent alcohol.



6. **Addition compound with styphnic acid (2 : 4 : 6-trinitro-resorcinol).**—For aromatic hydrocarbons only.

Heat 1·25 g. of styphnic acid with 1/200 mol of the hydrocarbon in 5 to 10 ml. of glacial acetic acid until solution is complete. Cool,

filter and wash with acetic acid followed by alcohol. Dry in air and determine its melting-point. Recrystallize a small portion from acetic acid and redetermine the melting-point.

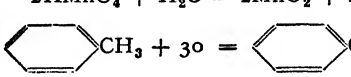
The derivative is highly coloured.

7. **Oxidation of a side chain to a carboxyl group.**—This oxidation is difficult, requires a considerable amount of time, and the yield is often small.

Add 2 g. of the hydrocarbon to a mixture of 7 g. of solid potassium permanganate, 20 ml. of water and 10 ml. of pyridine. Add a few small pieces of porous pot and boil gently under a reflux condenser until the colour of the permanganate has disappeared. If the layer of hydrocarbon still persists, cool, add more permanganate and boil again. Add 10 ml. of 10 per cent caustic soda solution, re-boil for 5 min., filter while still hot and, if necessary, pass sulphur dioxide through the filtrate until it is colourless. Acidify with dilute sulphuric acid. If the organic acid is precipitated at this stage filter it off and recrystallize from water or alcohol. If no precipitation occurs, extract the acid solution with ether, separate and distil off the ether. Purify the acid as above.

Hydrocarbons with one side-chain give rise to benzoic acid; those with two give one of the phthalic acids.

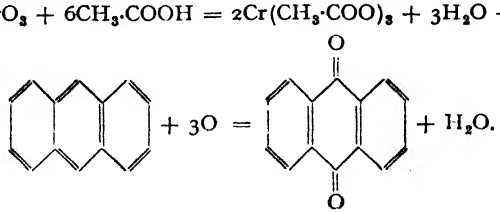
$$2KMnO_4 + H_2O = 2MnO_2 + 2KOH + 3O.$$



8. **Oxidation to quinones.**—This reaction is applicable only to condensed aromatic hydrocarbons.

Add 1 g. of chromium trioxide, dissolved in 2 ml. of water, to a suspension or solution of 0·5 g. of the hydrocarbon in 10 ml. of glacial acetic acid. Heat gently over a small flame for 2 min., cooling the mixture if the reaction becomes too violent. Allow to stand while still hot for 15 min. and then cool. If no precipitate is formed, dilute with water. Recrystallize from glacial acetic acid.

$$2CrO_3 + 6CH_3{\cdot}COOH = 2Cr(CH_3{\cdot}COO)_3 + 3H_2O + 3O.$$



For M.P.s of quinones see Table VI.

TABLE XV.—HYDROCARBONS

(PARAFFINS AND CYCLOPARAFFINS)

	B.P. °C.	$n_D^{20°}$	
Neopentane	9	1·3513 (0°)	
iso-Pentane	31	1·355	
n-Pentane	36	1·3570	
Cyclopentane	50	1·4093	
γ-Methylpentane	64	1·381	
n-Hexane	68	1·3754	
Cyclohexane	81	1·4312	Boiling fuming HNO_3 → adipic acid, M.P. 151° C.
n-Heptane	98	1·385	
2 : 2 : 4-Trimethylpentane	99	1·3916	
Methylcyclohexane	100	1·4235	
Di-*iso*-butyl	108	1·3935 (25°)	
iso-Octane	116	1·3944 (25°)	
n-Octane	125	1·3890	
1 : 3 : 5-Trimethylcyclohexane	138		
n-Nonane	149	1·405	
Di-*iso*-amyl	158	1·408	
p-Menthane	169	1·437	
n-Decane	173	1·415	
Decalin (*trans*) (Decahydronaphthalene)	185	1·4697	
Decalin (*cis*)	194	1·4811	
n-Undecane	194	1·4184	
n-Dodecane	215	1·4209	

Table XVI.—Hydrocarbons (Unsaturated)

	B.P. °C.	$n_D^{20°}$	
Liquids			
3-Methyl-1-butene	21		
2-Pentene	36	1·3789	
Trimethylethylene (Amylene)	38	1·3855	
Cyclopentadiene	42	1·4470	
Cyclopentene	46	1·4218	
Diallyl	59	1·4010	
Tetramethylethylene	72		
Cyclohexene	83	1·4492	Oxidized by HNO_3 → adipic acid, M.P. 151° C.
1-Heptyne	100	1·418	Mercury deriv., M.P. 61° C.
Di-*iso*-butylene	101	1·4082	
Δ^3-Tetrahydrotoluene	103	1·4430	Oxidized by HNO_3 → β-methyladipic acid, M.P. 93° C.
Δ^2-Tetrahydrotoluene	105	1·4426	Oxidized by HNO_3 → α-methyladipic acid, M.P. 64° C.
Δ^1-Tetrahydrotoluene	111	1·4496	
Phenylacetylene	140	1·5524	Mercury deriv., M.P. 125° C.
Styrene	146	1·5485	One drop conc. H_2SO_4 → glassy mass Dibromide, M.P. 73° C. Oxidation (alk. $KMnO_4$) → benzoic acid, M.P. 122° C.
d- or *l*-Pinene	156	1·4653	Dibromide, M.P. 164° C.
Allylbenzene	157		
Limonene	176	1·4727	Tetrabromide, M.P. 104° C.
Sylvestrene	176	1·4774	Tetrabromide, M.P. 135° C.
Propenylbenzene	177	1·5143	
Indene	180	1·5710	1 : 3 : 5-Trinitrobenzene deriv., M.P. 101° C. Picric acid deriv., M.P. 96° C. (explosive)
Dipentene	181	1·4730	Tetrabromide, M.P. 124° C.
Solids	M.P.		
Dihydronaphthalene	15	1·5740	
l-Camphene	42	1·4621	Dibromide, M.P. 89° C.
1 : 4-Diphenylbutadiene (*cis*)	70		
1 : 1 : 2-Triphenylethylene	73		
l-Bornylene	113		
Stilbene	125		Dibromide, M.P. 237° C. Styphnic acid deriv., M.P. 142° C. 1 : 3 : 5-Trinitrobenzene deriv, M.P. 129° C.
1 : 4-Diphenylbutadiene (*trans*)	148		

Table XVII.—Aromatic Hydrocarbons

	B.P. °C.	Nitro deriv. M.P. °C.	Nitro deriv. Method	Nitro deriv. Position of nitro-groups	*o*-Aroylbenzoic acid	Picrate	Sulphonamide	Miscellaneous
Liquids								
Benzene	80	89	b	1, 3	128	84		
Toluene	111	70	b	2, 4	138	88	137	Oxidation → benzoic acid, M.P. 122° C.
Ethyl benzene	135	37	—	2, 4, 6	128	96	109	Oxidation → benzoic acid, M.P. 122° C.
p-Xylene	138	137	b	2, 3, 5	132	90	147	
m-Xylene	139	182	b	2, 4, 6	126	91	137	
o-Xylene	142	71	b	4, 5	178	88	144	
Cumene (*iso*-Propyl benzene)	153	109	b	2, 4, 6	133	—	107	Oxidation → benzoic acid, M.P. 122° C.
n-Propyl benzene	158	—	—	—	125	103	—	Oxidation → benzoic acid, M.P. 122° C.
Mesitylene	164	230	b	2, 4, 6	211	97	141	
pseudo-Cumene	168	185	a	3, 5, 6	—	97	181	
p-Cymene	175	54	a < 15°	2, 6	123	—	115	
Hydrindene	177							
m-Diethylbenzene	182	62	—	2, 4, 6	114			
n-Butylbenzene	182	—	—	—	97			
iso-Durene	195	—	—	—	213			
n-Amylbenzene	202							
Prehnitene	204	—	—	—	—	90		
Tetralin	206	95	—	5, 7	154			
1 : 3 : 5-Triethylbenzene	218	108	—	2, 4, 6	129			
Cyclohexylbenzene	237	58	—	4				

α-Methylnaphthalene	240	71	—	4	169	141	—	1:3:5-Trinitrobenzene deriv., M.P. 154° C.
α-Ethyl naphthalene	251	—	—	—	—	98		1:3:5-Trinitrobenzene deriv., M.P. 113° C.
β-Ethyl naphthalene	251	—	—	—	—	77		1:3:5-Trinitrobenzene deriv., M.P. 88° C.
1 : 7-Dimethyl naphthalene	261	—	—	—	—	121		1:3:5-Trinitrobenzene deriv., M.P. 137° C.
1 : 6-Dimethyl naphthalene	262	—	—	—	—	114		1:3:5-Trinitrobenzene deriv., M.P. 131° C.
1 : 1-Diphenylethane	270							
Solids	M.P.							
Diphenylmethane	26	172	b	2, 2′, 4, 4′				
β-Methyl naphthalene	32	81	—	1	—	115	—	1:3:5-Trinitrobenzene deriv., M.P. 123° C.
β-Benzyl naphthalene	35	—	—	—	—	93		
Pentamethylbenzene	51	154	—	6	—	131	—	1:3:5-Trinitrobenzene deriv., M.P. 121° C.
Dibenzyl	52	180	c cold	4, 4′	—	—	—	1:3:5-Trinitrobenzene deriv., M.P. 102° C. Oxidation → benzoic acid, M.P. 122° C.
α-Benzyl naphthalene	59	—	—	—	—	101	—	Styphnate, M.P. 134° C.
Diphenyl	70	233	c	4, 4′	224			2:2′:4:4′-Tetranitro deriv., M.P. 164° C.
Durene	79	205	—	3, 6	264	95		
Naphthalene	80	61	—	1	172	150	—	Styphnate, M.P. 168° C. 1:3:5-Trinitrobenzene deriv., M.P. 153° C.
m-Diphenylbenzene	85							
Acenaphthylene	92	—	—	—	—	201	—	1:3:5-Trinitrobenzene deriv., M.P. 221° C.
Triphenylmethane	92	206	c cold	4, 4′, 4″				
Acenaphthene	95	101	—	5	198	161	—	Styphnate, M.P. 154° C. 1:3:5-Trinitrobenzene deriv., M.P. 168° C.
2 : 7-Dimethylnaphthalene	96	—	—	—	—	136	—	Styphnate, M.P. 158° C.
Retene	98	—	—	—	—	124	—	Quinone, M.P. 196° C. Styphnate, M.P. 141° C.
Phenanthrene	100	—	—	—	—	143	—	1:3:5-Trinitrobenzene deriv., M.P. 139° C. Quinone M.P. 208° C. Styphnate, M.P. 142° C. 1:3:5-Trinitrobenzene deriv., M.P. 164° C.

[Contd. over.

TABLE XVII—(*contd.*)

	M.P.° C.	Nitro deriv.			*o*-Aroylbenzoic acid	Picrate	Sulphonamide	Miscellaneous
		M.P. °C.	Method	Position of nitro-groups				
Solids								
2 : 3-Dimethyl naphthalene	104	—	—	—	—	124		Styphnate, M.P. 149° C.
Fluoranthrene	110	—	—	—	—	182	—	Conc. H_2SO_4 → greenish blue colour Styphnate, M.P. 151° C. 1:3:5-Trinitrobenzene deriv., M.P. 207° C.
2 : 6-Dimethyl naphthalene	111	—	—	—	—	143		Styphnate, M.P. 159° C.
Fluorene	115	334	d	2, 7	227	77	—	Conc. H_2SO_4 → blue colour Styphnate, M.P. 134° C. 1:3:5-Trinitrobenzene deriv., M.P. 105° C.
Pyrene	149	—	—	—	—	227		Styphnate, M.P. 191° C.
αα′-Dinaphthyl	160	—	—	—	—	145		
Hexamethyl benzene	162	—	—	—	—	170	—	1:3:5-Trinitrobenzene deriv., M.P. 174° C.
ββ′-Dinaphthyl	188	—	—	—	—	184		
1 : 4-Diphenylbenzene (*p*-Terphenyl)	213							
Anthracene	216	—	—	—	—	138	—	Quinone, M.P. 273° C. Styphnate, M.P. 180° C. 1:3:5-Trinitrobenzene deriv., M.P. 164° C.
Chrysene	254	—	—	—	214	273	—	Quinone, M.P. 239° C. 1:3:5-Trinitrobenzene deriv., M.P. 186° C.

CHAPTER IV

Summary of Classification Tests, Derivatives, etc., for Compounds containing Carbon, Hydrogen, Nitrogen, and possibly Oxygen and a Metal

Preliminary examination

1. Physical characteristics.
2. Ignition on a crucible lid.
3. Reaction to litmus of water-soluble compounds.
4. Action of hot dilute sulphuric acid.
5. Action of cold and hot concentrated sulphuric acid.
6. Action of cold and hot 30 per cent sodium hydroxide.
7. Effect of heating with soda-lime.

Class	Classification tests	Additional tests	Derivatives, &c.
Ammonium salts	Moist magnesium or zinc oxide	Schiff's reagent	Isolation of acid or aldehyde and preparation of derivatives as for these compounds (see p. 52 and p. 37)
Aldehyde ammonias (p. 105)		2 : 4-Dinitrophenylhydrazine	
		Murexide test for ammonium urate	
Derivatives of hydrazine and hydroxylamine (p. 106)	Fehling's solution after heating with acid	Hydrolysis and identification of hydrolysis products	Prepared from products of hydrolysis
	Ammoniacal silver nitrate		
Primary aliphatic amines and their salts	Nitrous acid in 75 per cent sulphuric acid	*For primary aliphatic amines and their salts*	Acetyl. Benzoyl
			Benzene or *p*-Toluene sulphonamide
Amides		2 : 4-Dinitrochlorobenzene	Phenyl thiourea
Guanidines			α-Naphthyl or *p*-nitrophenyl isocyanate deriv.
Aliphatic amino-acids		Rimini test	
Some carboxylic esters of amino-acids			2 : 4-Dinitrophenyl derivative
			Dinitroalkyl-*m*-toluidine. Picrate
Urethanes (p. 109)		*For amides*	Hydrolysis products
		" Biuret " test	N-xanthyl amide
		Xanthydrol	Salts (of urea and its alkyl derivs.)
		Potassium permanganate	
		For aliphatic amino-acids	Acetyl. Benzoyl
			p-Toluene sulphonyl
		" Formalin " test	Phenyl or α-Naphthyl isocyanate deriv.
		" Ninhydrin " test for α-amino-acids	Picrate
			Equivalent weight
		For esters of amino-acids and urethanes	β-Naphthyl urea
			Carbanilide
			Benzoyl deriv. (for esters of amino-acids)
Primary aromatic amines and their salts	Nitrous acid in cold dilute acid solution	*For secondary amines*	Acetyl. Benzoyl
			p-Nitrobenzoyl
Secondary amines		Formation of nitrosamines	Benzene or *p*-toluene sulphonyl deriv.
		Liebermann's nitroso reaction	
Some tertiary amines (pp. 124)		Nitroprusside test	
		For o- *or* m-*diamines and tertiary aromatic amines*	(For primary or secondary amines only)
		Coloured solution or precipitate in nitrous acid test	Picrate
			Phenyl thiourea
			Phenyl or α-naphthyl carbamate
		For primary aromatic amines	Formate
		Formation of azo-dye	

Class	Classification tests	Additional tests	Derivatives, &c.
		For diamines Formation of azine Oxidation to quinone Indophenol reaction	
Nitro-paraffins (p. 143)	Konovaloff's reaction	*For primary nitro-paraffins* Formation of nitrolic acid *For secondary nitro-paraffins* Formation of pseudo-nitrole	Reduction to amine and preparation of derivative of this
***N*-Nitroso compounds** (p. 145)	Liebermann's test		Secondary amine and derivative of this
***C*-Nitroso compounds** (p. 145)	Colour		Amine and derivative of this
Tertiary amines	Formation of quaternary ammonium hydroxide	Formation of hydrochloride	Quaternary ammonium iodide Picrate *p*-Nitroso deriv.
Heterocyclic bases (p. 147)			
Alkyl nitrites and nitrates (p. 152)	Diphenylamine test	*For nitrites* 2-Phenyl indole Devarda's alloy	Hydrolysis product Equivalent weight
Purines (p. 153)	Murexide test	Special tests	
Nitriles (cyanides) (p. 155)	Hydroxylamine test	Hydrogen peroxide and sodium hydroxide Carbylamine reaction after reduction to primary amine	Amide. Acid Phloracetophenone derivative
Imides (p. 159)	Alcoholic potash		Acid
Substituted amides (p. 160)	Hydrolysis with phosphoric/hydrochloric acid in diethylene glycol	Tests for (*a*) Primary aliphatic amine (*b*) Secondary amine (*c*) Primary aromatic amine	Hydrolysis products and derivatives of these
Aromatic nitro-compounds	Stannous chloride test	Calcium chloride/zinc dust	Reduction to amines
Azo-, hydrazo- and azoxy-compounds (p. 162)		*For nitro-compounds* Colour reactions with acetone and sodium hydroxide	*For nitro-compounds* Poly-nitro-compounds Oxidation of side chain Addition compounds with naphthalene

GROUP II

COMPOUNDS CONTAINING CARBON, HYDROGEN, NITROGEN AND POSSIBLY OXYGEN AND A METAL

Preliminary examination

1. *Physical properties*

If pale yellow	Probably a nitro-compound.
If red, orange or intense yellow	Azo-compounds; nitranilines; some nitro-phenols; 2 : 4-dinitrophenylhydrazones.
If an intense green	*p*-Nitroso-compounds, e.g. *p*-nitrosodimethyl aniline (they can, however, exist in the colourless dimolecular form, becoming green when fused).
If hygroscopic	Probably a salt of urea or a guanidine derivative.
A fishy ammoniacal odour	Lower aliphatic amines and their salts.
An aniline-like odour	Aromatic amines.
A pyridine-like odour	Heterocyclic bases.
A pungent odour and slight lachrymatory effect	Isocyanates.
A characteristic and intensely disagreeable odour	Isocyanides.

2. *Effect of ignition on a crucible lid*

Substance burns with a non-smoky flame	Probably an aliphatic compound.
Substance burns with a smoky flame	Probably an aromatic compound.
An odour of hydrocyanic acid	Cyanohydrin.
An odour of ammonia	Ammonium salts, uric acid, &c.
A residue of a metallic oxide or carbonate remains after strong ignition	A metallic salt of a nitrogen-containing acid, of a nitro- or amino-phenol.

3. *Reaction to litmus of water-soluble compounds*

Warm the substance with water and test the resulting solution with litmus.

(*a*) Acid	Salts of urea; salts of primary and secondary amines; nitro-acids; some nitro-phenols; a few aromatic amino-acids and simple amides; alkyl nitrates and nitrites; acyl derivatives of amino-acids, e.g. hippuric acid.

(*b*) Neutral	Aliphatic amino-acids; ammonium salts; aromatic amines of high molecular weight; nitrohydrocarbons; nitroso-, azoxy- and hydrazo-compounds; substituted amides of high molecular weight; nitriles; *iso*-cyanides; hydrazones; most oximes.
(*c*) Alkaline	Lower aliphatic primary, secondary and tertiary amines; most of the simple aromatic amines and diamines; amino-phenols; substituted hydrazines; guanidine and its alkyl derivatives.

4. *Action of hot dilute sulphuric acid*

Substance is soluble but insoluble in water	Probably a primary, secondary or tertiary aliphatic or aromatic amine; a heterocyclic base; a substituted hydrazine; a purine; an alkaloid or an oxime, though not all members of these classes are soluble.
An odour of an aldehyde or ketone	Oxime; hydrazone; semicarbazone; aldehyde ammonia; hydrobenzamide. In particular, formaldehyde will be liberated from methylene aniline (yellow-brown solution) or from hexamethylene tetramine, i.e. hexamine (colourless solution). Benzaldehyde (+HCN) from amygdalin.*
Volatile acids evolved	Ammonium salts and amides of such acids.
Evolution of carbon dioxide	Carbonates of strong bases, e.g. guanidine carbonate.

5. *Action of cold and hot concentrated sulphuric acid*

A vigorous reaction and the whole solidifies	Probably a free base.
Substance dissolves without charring and carbon dioxide is evolved (lime-water test)	Probably urea, one of its salts (other than the oxalate) or a related compound, e.g. urethane.
Evolution of carbon monoxide and carbon dioxide	Cyanates; nitrogen derivatives of oxalic acid, e.g. oxamide, oxanilide; salt formed from oxalic acid and a nitrogen containing base.
Evolution of carbon monoxide alone	Formyl derivatives of amines; ammonium formate.
Volatile acids evolved	Ammonium salts, amides and substituted amides of such acids.

* For identification of amygdalin, see Glycosides (p. 34) in the C·H·O group.

Nitrous and nitric acid fumes evolved	Nitrites, nitrates and nitrosamines.
Intense carmine colour	Amygdalin.*

6. *Action of cold and hot 30 per cent sodium hydroxide*

Soluble in the cold but insoluble in water	Probably amino- or nitro-carboxylic acid; nitro-phenol; simple amide or imide; oxime; purine.
Liquid or solid base produced on warming	Salt or acyl derivative of a primary or secondary amine; derivative of hydrazine; amino-acid of high molecular weight. (Some bases which are normally solid at ordinary temperature may only solidify on cooling and scratching.)
Odour of an aldehyde or ketone	Oximes; hydrazones; semicarbazones.
Odour of an alcohol	Esters of nitrogen-containing acids
Solution becomes intensely coloured *immediately* in the cold	Probably a nitro-phenol.
Yellow solution on warming	Some nitro-compounds.
Solution turns black	Simple or substituted aminophenols.
Ammonia (test with moist red litmus paper) evolved *in the cold*	Ammonium salt; aldehyde ammonia.
Ammonia evolved only on warming or boiling	One of the following types is present (arranged in rough order according to the readiness with which ammonia is evolved): (i) Guanidines; (ii) amides and similar compounds, e.g. imides, urethanes, semicarbazides and carbazides; (iii) aromatic amino-compounds with the NO- or NO_2-group in the *ortho-* or *para-*position; (iv) simple ureides; (v) nitriles; (vi) oximes; (vii) purrines. Hydrobenzamide (benzaldehyde also evolved).

7. *Soda-lime test* (*see p.* 21)

Ammonia evolved	Those compounds (listed above) which give off ammonia when treated with sodium hydroxide evolve the same gas, more or less readily, when heated with soda-lime.
A fishy ammoniacal odour due to aliphatic amines	Aliphatic amino-acids.
A liquid or solid base formed on distillation	Aromatic amino-acid; acyl derivative of a primary or secondary amine; derivative of hydrazine. An attempt should be made to isolate and identify such a base by applying tests for such compounds.

* For identification of amygdalin, see Glycosides (p. 43) in the C·H·O group.

GROUP II—CLASS I

AMMONIUM SALTS, ALDEHYDE AMMONIAS

Classification tests.—(*a*) Grind a small quantity of the given compound with zinc oxide or magnesium oxide in a mortar, transfer to a watch glass and moisten with water.

Alternatively, rub some of the substance with zinc or magnesium oxide on the palm of the hand, moisten with water and continue rubbing.

In either case, if ammonia is evolved (indicated by odour and test with moist red litmus paper), a compound of this class is present.

(*b*) To distinguish between the two, take about 0·5 g. of the original substance in a test-tube, add about 2 ml. of dilute sulphuric acid, boil, then cool, and apply to the solution tests for aldehyde, viz. Schiff's reagent or 2 : 4-dinitrophenylhydrazine (see p. 36). If positive results are obtained, treat the original compound as for an aldehyde ammonia (see p. 106).

Ammonium salts

The given compound may be an ammonium salt of a carboxylic acid, a nitrogen-containing carboxylic acid or uric acid. Some indication of the presence of compounds of the second class will have been obtained in the preliminary test with soda-lime as:

ammonium salts of aliphatic amino acids ⟶ ammonia + alkyl amines
" " aromatic " " ⟶ " + aromatic amines
" " nitro-acids ⟶ " + nitro-compounds.

The presence of a nitrogen-containing acid should be confirmed by boiling about one gram of the original substance with sodium hydroxide until all the ammonia has been driven off, acidifying with hydrochloric acid, evaporating to dryness, and applying the alkali-zinc test for nitrogen (see p. 16) to the residue.

(*a*) *If nitrogen is proved absent in the residue.*—Treat the ammonium salt as in the isolation and identification of the acid from hydrolysis of esters (see p. 69).

(*b*) *If nitrogen is proved present in the residue.*—Apply tests for

aliphatic amino- (see p. 109), aromatic amino- (see p. 124) and nitro- (see p. 162) groups, and prepare derivatives of the acid directly from the original compound.

Test for ammonium urate as follows:

1. "*Murexide*" *test.*—Treat a small quantity of the compound with 5 ml. of saturated aqueous bromine in a porcelain dish, and evaporate to dryness on a water-bath. An orange residue, becoming red on cooling and violet-red on exposure to the vapours of concentrated ammonia, indicates the presence of this salt.

2. Boil a little of the compound with 2 ml. of aqueous sodium carbonate, cool and add 1 ml. of silver nitrate solution. A dark-grey or black precipitate is given by ammonium urate.

Aldehyde ammonias

Decompose by distilling 2 g. with dilute sulphuric acid. If the aldehyde be steam-volatile, it will be found in the distillate and appropriate derivatives (see p. 37) should be prepared for identification purposes. Non-volatile aldehydes may be extracted with ether or filtered off.

GROUP II—CLASS II

DERIVATIVES OF HYDRAZINE (SIMPLE OR SUBSTITUTED HYDRAZONES, HYDRAZIDES, OSAZONES AND SEMICARBAZONES) DERIVATIVES OF HYDROXYLAMINE (ALDOXIMES AND KETOXIMES)

Classification test.—Boil a small quantity of the original compound with concentrated hydrochloric acid or 30 per cent sulphuric acid for half a minute, cool, make alkaline with caustic soda, and add to 2 ml. of Fehling's solution (see p. 290). Warm, and if an orange or reddish precipitate of cuprous oxide is formed, a substance of this class is present. If the original intense blue of the Fehling's solution is considerably reduced, and a white precipitate

forms, the substance is probably uric acid (see Purines, pp. 153 and 154).

Ammoniacal silver nitrate is also reduced by these substances after hydrolysis.

Note.—Diphenyl-hydrazine will not reduce Fehling's solution but will reduce ammoniacal silver nitrate.

Treatment of substance.—If the given substance is insoluble in water but soluble in dilute hydrochloric acid, it is probably a free base. Prepare a benzoyl derivative (see p. 131) or reduce to an amine by boiling with tin and hydrochloric acid (see p. 163).

If the original substance is insoluble in dilute hydrochloric acid, hydrolyse it by refluxing 2 g. with 10 ml. of concentrated hydrochloric acid or 30 per cent sulphuric acid for 30 min. The aldehyde, ketone or acid (from hydrazides) should be separated from the solution by steam distillation, filtration or extraction with ether, classified and identified by the preparation of suitable derivatives (see p. 37 for aldehydes and ketones, and p. 52 for acids). The residual liquid should be made alkaline, and if an oil or solid separates it should either be ether extracted or filtered off and a suitable derivative of the base prepared. If ammonia is evolved on making alkaline and formaldehyde has already been identified as a hydrolysis product, the original substance is hexamethylene tetramine (hexamine), M.P. 280° C. (ethiodide, M.P. 151° C.). If no oil or precipitate is produced, the original substance is probably a simple aldoxime, ketoxime or semicarbazone, the hydroxylamine, hydrazine or semicarbazide formed by the hydrolysis being soluble in the alkaline solution.

Hydrazones

$$\begin{matrix}CH_3\\ \diagdown\\ \quad C{=}N{-}NRR'\\ \diagup\\ CH_3\end{matrix} + HCl + H_2O = \begin{matrix}CH_3\\ \diagdown\\ \quad C{=}O\\ \diagup\\ CH_3\end{matrix} + H_2N{\cdot}NRR'{\cdot}HCl.$$

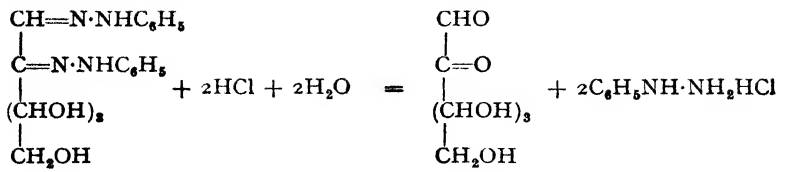
Semicarbazones

$$\begin{matrix}CH_3\\ \diagdown\\ \quad C{=}N{\cdot}NH{\cdot}CO{\cdot}NH_2\\ \diagup\\ H\end{matrix} + HCl + H_2O = \begin{matrix}CH_3\\ \diagdown\\ \quad C{=}O\\ \diagup\\ H\end{matrix} + H_2N{\cdot}NH{\cdot}CO{\cdot}NH_2{\cdot}HCl.$$

Hydrazides

$$R{\cdot}C(OH){=}N{\cdot}NHR + HCl + H_2O = R{\cdot}COOH + H_2N{\cdot}NHR{\cdot}HCl.$$

Osazones



Oximes

$C_6H_5{\cdot}CH{=}N{\cdot}OH + HCl + H_2O = C_6H_5{\cdot}CHO + H_2N{\cdot}OH{\cdot}HCl.$

TABLE XVIII.—HYDRAZINE DERIVATIVES

	B.P. °C.	Benzoyl deriv.	
Liquids			
unsym-Methylphenyl-hydrazine	227	153	Benzaldehyde → hydrazone, M.P. 106° C.
Phenylhydrazine	243	168	M.P. 19° C. Hydrochloride, M.P. 240° C. See derivs. of aldehydes, p. 37
m-Tolylhydrazine	145 20 mm.		Acetophenone → hydrazone, M.P. 81° C.
Solids	M.P.		
unsym-Diphenyl-hydrazine	34	192	Benzaldehyde → hydrazone, M.P. 122° C.
o-Tolylhydrazine	60	—	Acetophenone → hydrazone, M.P. 101° C.
p-Tolylhydrazine	66	146	Acetophenone → hydrazone, M.P. 125° C. Benzaldehyde → hydrazone, M.P. 125° C.
Benzalazine	93	—	Boiling conc. HCl → benzaldehyde
Semicarbazide	96	—	Hydrochloride, M.P. 173° C. See semicarbazones of aldehydes and ketones (p. 38)
α-Naphthylhydrazine	116	—	Benzaldehyde → hydrazone, M.P. 144° C.
β-Naphthylhydrazine	125	—	Benzaldehyde → hydrazone, M.P. 192° C.
Acetylphenyl-hydrazine	128		
Hydrazobenzene	130	138 (di)	Reduces warm Fehling's solution Easily oxidized to orange-red azobenzene
p-Nitrophenyl-hydrazine	157	—	Benzaldehyde → hydrazone, M.P. 190° C.
2 : 4-Dinitrophenyl-hydrazine	199	—	See derivs. of aldehydes (p. 37)

GROUP II—CLASS III

PRIMARY ALIPHATIC AMINES AND THEIR SALTS, AMIDES INCLUDING UREA, SUBSTITUTED UREAS AND THEIR SALTS, GUANIDINE, SOME SUBSTITUTED GUANIDINES AND THEIR SALTS, ALIPHATIC AMINO-ACIDS, SOME CARBOXYLIC ESTERS OF AMINO-ACIDS, AMIDE ESTERS, e.g. ALKYL CARBAMATES OR URETHANES

Classification test.—To 2 ml. of *cold* 75 per cent sulphuric acid add a cold concentrated solution of sodium nitrite drop by drop until the solution is blue. To the resulting cold solution add a little of the original compound dissolved or suspended in cold 75 per cent sulphuric acid. A *sustained and vigorous effervescence*, due to evolution of nitrogen, indicates the presence of a substance of this class. If a positive result be obtained then additional tests, as indicated below, should be applied for the various types of compounds appearing in this class.

Primary aliphatic amines

$$R{\cdot}NH_2 + HNO_2 = R{\cdot}OH + H_2O + N_2.$$

Amides

$$R{\cdot}CO{\cdot}NH_2 + HNO_2 = R{\cdot}COOH + H_2O + N_2.$$

Aliphatic amino-acids

$$H_2N{\cdot}R{\cdot}COOH + HNO_2 = OH{\cdot}R{\cdot}COOH + H_2O + N_2.$$

Carboxylic esters of amino-acids

$$H_2N{\cdot}R{\cdot}CH_2{\cdot}COOR' + HNO_2 = OH{\cdot}R{\cdot}CH_2{\cdot}COOR' + H_2O + N_2.$$

In some cases, diazo-compounds are formed by the action of nitrous acid, e.g. the esters of α-amino acids give diazo-esters.

$$R{\cdot}CH(NH_2)COOR' + HNO_2 = R{\cdot}CN_2{\cdot}COOR' + 2H_2O.$$

According to Angeli, the essential condition for the formation of diazo-compounds from aliphatic amines is the presence of the grouping:

$$R{:}\overset{|}{C}{\cdot}\overset{|}{C}H{\cdot}NH_2, \text{ where R = C, O, or N, e.g. } NH_2{\cdot}CH_2{\cdot}CN.$$

A. Primary aliphatic amines and their salts

The lower members of this class are fairly volatile basic liquids, having a fishy ammoniacal odour, and are most likely to be met with as one of their salts (only nitrates and carboxylic acid salts from C, H and O acids are included in the group under consideration).

General tests

1. 2 : 4-*Dinitrochlorobenzene test.*—Moisten a piece of filter paper with a saturated alcoholic solution of 2 : 4-dinitrochlorobenzene and add a drop of a solution of the base in water. An intense yellow colour is given by the amines. In the case of salts, warm gently with sodium hydroxide solution and allow the vapour evolved to come into contact with the paper.

Note.—Ammonia does not give this test.

2. *Rimini test.*—To a suspension of one drop of the suspected aliphatic primary amine in 5 ml. of water, add 1 ml. of acetone and one drop of a 1 per cent solution of sodium nitroprusside. A violet-red colour develops within 2 min.

Derivatives

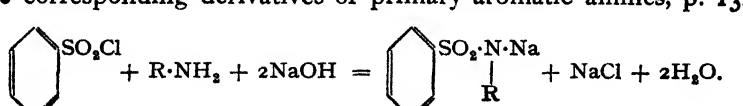
Acetyl derivative (substituted acetamide).—For the method of preparation see the corresponding derivative for phenols, p. 66.

$$R{\cdot}NH_2 + CH_3{\cdot}COOH = R{\cdot}NH{\cdot}COCH_3 + H_2O.$$

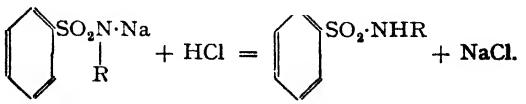
2. **Benzoyl derivative (substituted benzamide).**—For the method of preparation (Schotten-Baumann) see the benzoyl derivative of primary aromatic amines, p. 131.

$$R{\cdot}NH_2 + C_6H_5{\cdot}CO{\cdot}Cl + NaOH = R{\cdot}NH{\cdot}COC_6H_5 + NaCl + H_2O.$$

3. **Benzenesulphonamide and *p*-toluenesulphonamide (*p*-tosyl derivative).**—For method of preparation (Hinsberg) see corresponding derivatives of primary aromatic amines, p. 132.



The sodio-derivative is soluble in water and *mineral acid must be added to liberate the sulphonamide.*



4. Phenyl thiourea or iso-thiocyanate derivative.—This derivative is useful for the identification of water-soluble amines of low molecular weight, and may be prepared using an aqueous solution of the amine.

Mix equal amounts of the amine and phenyl *iso*-thiocyanate. If no reaction occurs, heat the mixture over a small flame for 2 min. Add 50 per cent alcohol and cool when the thiourea will be deposited. Recrystallize from alcohol.

$$R{\cdot}NH_2 + C_6H_5N : C : S = C_6H_5{\cdot}NH{\cdot}\overset{\displaystyle S}{\overset{\|}{C}}{\cdot}NHR.$$

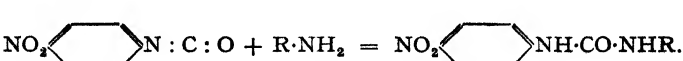
(4-diphenylyl and α- or β-naphthyl-*iso*-thiocyanates may also be used to give the corresponding thioureas.)

5. Substituted ureas

(*a*) **α–Naphthyl iso-cyanate derivative.**—Dissolve a little of the amine in a small quantity of petroleum ether (B.P. 100–120° C.) and add an equivalent amount of α-naphthyl *iso*-cyanate. Filter and recrystallize from petroleum ether or alcohol.

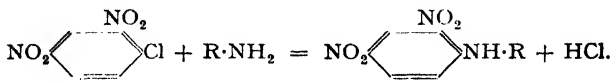
$$C_{10}H_7{\cdot}N : C : O + R{\cdot}NH_2 = C_{10}H_7NH{\cdot}CO{\cdot}NHR.$$

(*b*) ***p*-Nitrophenyl iso-cyanate derivative.**—Mix benzene solutions of the amine and *p*-nitrophenyl *iso*-cyanate (*p*-nitrophenyl carbimide). The substituted urea may be precipitated from the solution by the addition of petroleum ether. Recrystallize from ethyl alcohol.

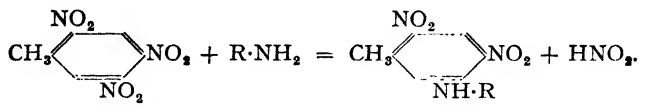


6. 2 : 4-Dinitrophenyl derivative.—Add a saturated alcoholic solution of 2 : 4-dinitrochlorobenzene to a few drops of the amine dissolved in alcohol. Allow to stand for 5 min. If no precipitate is formed during this time add a little anhydrous sodium

acetate to act as condensing agent. Filter and recrystallize from alcohol.



7. **Dinitro-alkyl-*m*-toluidide.**—Add 5 drops of the amine to 5 ml. of hot alcohol containing 0·2 g. of 2 : 4 : 5-trinitrotoluene. Redissolve the precipitate by boiling, then allow the solution to cool. Recrystallize from alcohol.



8. **Derivative with picric acid.**—See corresponding derivative of hydrocarbons (p. 91).

B. Amides

Included in this class are the amides of simple carboxylic acids, urea, some substituted ureas of the type $RR'N{\cdot}CO{\cdot}NH_2$ and their salts, guanidine, some substituted guanidines $NH : C\langle^{NRR'}_{NH_2}$ and their salts.

Urea itself is a weak mon-acid base, and may be met with as one of its salts, which in the present group may be the nitrate, oxalate or citrate, while guanidine and some of its derivatives are strong bases generally found as salts, e.g. carbonate, nitrate, acetate, &c.

Besides evolving nitrogen when acted upon by nitrous acid, these compounds give ammonia when boiled with sodium hydroxide.

Special tests

1. *The "biuret" test.*—Heat *gently* a small quantity of the original compound in a dry test-tube until it just melts and ammonia is evolved. After being maintained at this temperature for about 1 min. solidification occurs due to the formation of biuret (urea citrate darkens, and does not give the biuret test).

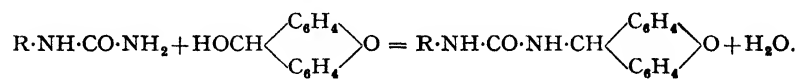
$$2NH_2{\cdot}CO{\cdot}NH_2 = NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_3.$$

Dissolve the residue in 1 ml. of dilute sodium hydroxide solution and add 1–2 drops of a very dilute solution of copper sulphate,

shaking the solution. If a pink, then violet, and finally deep blue colour is produced, urea, oxamide or malonamide is present.

Since the coloration is formed when sodium hydroxide and dilute copper sulphate act on a compound containing two —CO·NH— groups attached to the same carbon atom, or to the same nitrogen atom or to one another, the biuret test is given by oxamide and malonamide without preliminary heating.

2. *Xanthydrol test.*—Add one ml. of 5 per cent solution of xanthydrol in methyl alcohol to a very dilute solution of the original substance in 50 per cent acetic acid. Urea, its salts and mono-substituted compounds give an immediate precipitate which may be purified (see p. 114) and used as a derivative.



3. *Dilute potassium permanganate.*—This reagent is readily reduced by guanidine, its substituted compounds and salts.

Derivatives, &c.

1. **Hydrolysis.** (*a*) **Amides.**—This may be carried out by heating the substance under a reflux condenser with dilute caustic soda, concentrated hydrochloric acid or 50 per cent sulphuric acid. In the first case, the resulting solution after cooling should be acidified with dilute sulphuric acid, and the liberated acid isolated and identified as in the case of ester hydrolysis (see p. 69).

Hydrochloric acid is only convenient in the case of amides derived from non-volatile acids.

$$R{\cdot}CO{\cdot}NH_2 + NaOH = R{\cdot}COONa + NH_3$$
$$2R{\cdot}CO{\cdot}NH_2 + H_2SO_4 = 2R{\cdot}COOH + (NH_4)_2SO_4.$$

(*b*) **Substituted ureas and guanidines.**—These, when refluxed with sodium hydroxide, will give either volatile or liquid bases; hydrolysis with acid results in the formation of salts of these bases. In the latter case the solution should be made alkaline before separating the base and identifying it by the preparation of a suitable derivative (pp. 110 and 130).

$$\underset{\text{phenyl urea}}{C_6H_5{\cdot}NH{\cdot}CO{\cdot}NH_2} + 2HCl = C_6H_5NH_2{\cdot}HCl + NH_4Cl + CO_2$$

$$\underset{\text{methyl guanidine}}{(NH_2)_2C{=}N{\cdot}CH_3} + 3HCl + 2H_2O = CH_3NH_2{\cdot}HCl + CO_2 + 2NH_4Cl.$$

(*c*) For those amides which are difficult to hydrolyse, e.g. triphenyl acetamide, derivatives of benzamide with substituents in the 2 : 6 positions, &c., the nitrous acid reaction may be used.

$$R{\cdot}CO{\cdot}NH_2 + HNO_2 = R{\cdot}COOH + N_2 + H_2O.$$

To a cooled solution of the amide in 90 per cent sulphuric acid a concentrated solution of sodium nitrite is added below the surface of the acid. The mixture is stirred, and the temperature kept between 20° C. and 30° C. It is finally heated gently in a large flask until evolution of gas ceases and then poured into water. The precipitated acid is filtered off, dissolved in sodium carbonate and reprecipitated by the addition of excess dilute hydrochloric acid.

2. ***N*-Xanthyl amide.**—In the preparation of this derivative method (*a*) is preferable, but if the amide is not sufficiently soluble in glacial acetic acid method (*b*) should be adopted.

(*a*) Dissolve 0·5 g. of xanthydrol in 7 ml. of glacial acetic acid. Decant the clear solution if an oil separates. To this solution add 0·5 g. of the amide and allow to stand, or if a more rapid condensation is required, heat in a loosely corked tube in a water bath for not more than 40 min. If no product appears in the hot solution, cool to crystallize. The derivative can be recrystallized from 65 per cent dioxan and water, using a higher proportion of dioxan for the more insoluble products. Pyridine and water, or acetic acid and water are alternative solvents. Dry at 80° C. for 15 min.

(*b*) Dissolve 0·5 g. of xanthydrol in a mixture of 5 ml. ethyl alcohol, 2 ml. glacial acetic acid and 3 ml. water. If an oil separates, decant the supernatant liquid, and to the latter add 0·5 g. of the amide and heat to 85° C. in a corked tube in a water-bath. Continue as in method (*a*) above.

3. **Salts.**—Urea and its alkyl derivatives form well-defined and (in some cases) sparingly soluble salts. Of these the nitrate and oxalate can conveniently be used as derivatives.

To a saturated solution of the original substance in water, add concentrated nitric acid or a saturated aqueous solution of oxalic acid till a crystalline precipitate appears. Filter, wash the precipitate carefully with cold water, dry and determine its melting-point.

C. Aliphatic amino-acids

In addition to the evolution of nitrogen on treatment with nitrous acid, the following tests should be carried out if those for A and B have proved negative.

General tests

1. Dissolve about 0·5 g. of the original compound in water or alcohol and neutralize to phenolphthalein with sodium hydroxide. To the resulting faintly pink solution, add a few ml. of formalin previously neutralized to phenolphthalein. The immediate disappearance of the pink colour, due to the development of acidity, indicates a compound of this class.

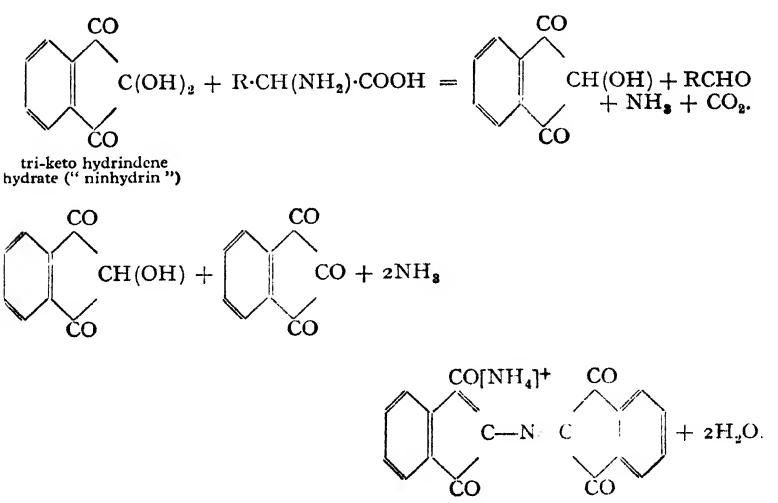
$$\underset{\text{"Zwitter ion"}}{\overset{+}{N}H_3\cdot CH_2\cdot \overset{-}{C}OO} + HCHO = H_2C{=}N\cdot CH_2\cdot \overset{-}{C}OO + H_2O + \overset{+}{H}$$

or possibly more correctly

$$\overset{+}{N}H_3\cdot CH_2\cdot \overset{-}{C}OO \rightleftharpoons NH_2\cdot CH_2\cdot COOH \xrightarrow[H\cdot CHO]{}$$

$$CH_2{=}N\cdot CH_2\cdot COOH \rightleftharpoons CH_2{=}N\cdot CH_2\cdot \overset{-}{C}OO + \overset{+}{H}.$$

2. If test 1 gives a positive result, apply the "*ninhydrin*" *test* for α-amino acids. This is carried out by heating an aqueous solution of the compound with a few drops of a 0·2 per cent aqueous solution of ninhydrin. A blue colour is given by an acid of this type.



Derivatives, &c.

1. **Acetyl derivative.**—Dissolve one gram of the amino-acid in 10 ml. of 20 per cent sodium hydroxide solution. Add about 2 ml. (0·5 ml. at a time) of acetic anhydride, shaking vigorously and keeping cool during the addition. Acidify with dilute mineral acid, maintaining a low temperature to prevent hydrolysis of the derivative. Filter and recrystallize from aqueous alcohol.

$$CH_2(NH_2)COONa + (CH_3CO)_2O + NaOH = CH_2(NH{\cdot}OC{\cdot}CH_3)COONa + CH_3COONa + H_2O$$

2. **Benzoyl derivative.**—As for Schotten-Baumann method for phenols (see p. 63) but using sodium carbonate instead of sodium hydroxide. The derivative will remain in solution as the sodium salt. Filter and precipitate the derivative together with benzoic acid by acidifying with concentrated hydrochloric acid. Filter, wash, dry, extract with cold benzene and recrystallize the residue from water.

3. ***p*-Toluene sulphonyl (*p*-tosyl) derivative.**—Dissolve about 1 g. of the original substance in 10 ml. of sodium hydroxide solution and add about 10 ml. of ether containing 1 g. of *p*-toluene sulphonyl chloride. The mixture should be shaken (preferably mechanically) for 3–4 hours. After separation of the two layers, acidify the aqueous layer with dilute hydrochloric acid to Congo red. Recrystallize any solid which separates from a small quantity of 50 per cent alcohol. If an oil is obtained, cool in ice and crystallize.

Note.—The sodium salts of the derivatives of phenylalanine and tyrosine are sparingly soluble in water. On acidifying the ether-water mixture, the sodium salt goes into solution in the water, the *p*-toluene sulphonyl derivative being recovered from the ether layer.

4 **α-Naphthyl (or phenyl) isocyanate derivative.**—Dissolve 0·5 g. of the original compound in about 30 ml. of N/5 potassium hydroxide solution and shake for a few minutes with 1 g. of the isocyanate. Allow the mixture to stand for about 30 min. and filter off any insoluble di-naphthyl urea formed by hydrolysis of the excess reagent. Acidify the filtrate and recrystallize

the precipitated derivative from alcohol, chloroform or carbon tetrachloride.

$$C_{10}H_7\cdot N{=}CO + NH_2\cdot R\cdot COOH + KOH = C_{10}H_7\cdot NH\cdot CO\cdot NH\cdot R\cdot COOK + H_2O.$$

Note.—α-Naphthyl isocyanate has the advantage over phenyl isocyanate in that it is more stable in presence of water.

5. **Addition compound with picric acid.**—See corresponding derivative for hydrocarbons (p. 91).

6. **Equivalent weight.**—Weigh out accurately about 0·5 g. of the substance, dissolve in water, and adjust the acidity until the solution is faintly pink to phenolphthalein. Add 10 ml. of 40 per cent solution of formaldehyde which has also been rendered *just alkaline* to phenolphthalein and titrate the solution with 0·1 N sodium hydroxide to a faint pink end-point. The equivalent weight of the acid is that weight which reacts with 1000 ml. of N sodium hydroxide. See p. 115 for the equation to the reaction.

D. Some carboxylic esters of aliphatic amino-acids and amide esters, e.g. alkyl carbamates or urethanes

If tests for substances of the type A, B or C have proved negative the following tests should be applied to the substance under investigation.

General tests

1. Warm a saturated solution of the compound in dioxan with alcoholic potassium hydroxide. Alkyl carbamates give crystalline potassium cyanate.

$$R\cdot O\cdot CO\cdot NH_2 + KOH = R\cdot OH + KOCN + H_2O.$$

The separated solid may be identified as potassium cyanate by adding it to a solution of β-naphthylamine in glacial acetic acid and warming the resulting solution until all the cyanate has dissolved, then pouring into a large volume of water. β-naphthyl urea melting at 213–214° C. is precipitated.

$$C_{10}H_7NH_2\cdot HCNO \longrightarrow C_{10}H_7\cdot NHCO\cdot NH_2.$$

2. If test 1 gives a positive result, heat about 1 g. of the original compound with 2 ml. of aniline under a reflux air condenser. Alkyl carbamates give ammonia, the corresponding alcohol and carbanilide, M.P. 238° C. The carbanilide separates as a solid.

Table XIX.—PRIMARY ALIPHATIC AMINES

	B.P. °C.	Acetyl deriv.	Benzoyl deriv.	Benzenesulphonyl deriv.	*p*-Toluenesulphonyl deriv.	Phenyl thiourea	*α*-Naphthyl urea	*p*-Nitrophenyl urea	2 : 4-Dinitrochlorobenzene deriv.	2 : 4 : 5-Trinitrotoluene deriv.	Picrate	*α*-Naphthyl thiourea	Miscellaneous
Liquids													
Methylamine	6	28	80	30	76	113	197	—	178	173	215	192	HCl, M.P. 225° C.
Ethylamine	19	—	69	58	63	106	200	158	113	126	168	121	
iso-Propylamine	33	—	100	98	51	101	143	—	94	—	150		
n-Propylamine	49	—	84	36	52	63	—	151	95	101	135	103	HCl, M.P. 157° C.
Allylamine	56	—	—	39	64	100	—	—	76	—	140		
sec-Butylamine	63	—	76	71	55	101	—	—	—	—	140		
iso-Butylamine	69	—	57	53	78	82	—	—	80	112	—	137	
n-Butylamine	77	—	42	—	—	65	—	146	58	96	151	109	HCl, M.P. 195° C.

iso-Amylamine	95	—	—	—	65	102	132	—	—	87	138	97	
n-Amylamine	104	—	—	—	—	69	—	—	81	99	—	103	
Ethylenediamine	116	172	249	168	160	102	—	—	302	280	233		
iso-Hexylamine	125	—	—	—	—	112	—	—	—	—	123	79	
n-Hexylamine	128	—	—	96	—	77	—	—	—	—	127	79	
Cyclohexylamine	134	104	148	89	87	148	—	170	156	138	158	142	
1 : 3-Diaminopropane	136	126	147	96	148								
n-Heptylamine	155	—	—	—	—	75	—	—	—	50	121		
Ethanolamine (2-Aminoethyl alcohol)	171	—	—	—	—	138	—	—	—	118	160		
Pentamethylenediamine (Cadaverine)	178	—	135	—	—	148							
Benzylamine	184	60	106	88	116	147	203	—	116	100	199	172	HCl, M.P. 248° C.
1-Phenylethylamine	185	—	120										
2-Phenylethylamine	197	114	116	66	64	135	—	—	154	129	167		
l-Menthylamine	205	145	156	—	—	135							
Solids	M.P.												
Tetramethylenediamine	27	—	177	—	—	168	—	—	—	—	250		
Hexamethylenediamine	42	—	155	154	—	124	—	—	—	—	220d		

Cool and add sufficient boiling dilute hydrochloric acid to dissolve the excess aniline. Filter, wash the solid with dilute hydrochloric acid and with water. Crystallize from alcohol.

$$R{\cdot}O{\cdot}CO{\cdot}NH_2 + 2C_6H_5NH_2 = R{\cdot}OH + NH_3 + CO(NHC_6H_5)_2.$$

3. If test 1 gives a negative result treat the substance as a carboxylic ester of an amino-acid (not α-amino acids). Reflux about 5 g. of the original compound with sodium hydroxide as for a carboxylic ester (see p. 67). If possible separate and identify the alcohol. Do not attempt to separate the amino-acid from the alkaline solution but prepare directly from it an appropriate derivative, e.g. the benzoyl derivative (see p. 116).

Table XX.—Simple Amides Including Ureas and Guanidines

A comprehensive list of the melting points of amides with their corresponding acids is to be found in Tables VII and VIII.

	B.P. °C.	Xanthydrol deriv.	Anilide	Miscellaneous
Liquids				
Formamide	195	184		
Solids	M.P.			
Guanidine	—	—	—	Nitrate, M.P. 214° C. Conc. H_2SO_4 and HNO_3 in the cold → nitroguanidine, M.P. 232° C.d.
Methylguanidine	—	—	—	Nitrate, M.P. 150° C.
as-Dimethylguanidine	—	—	—	Picrate, M.P. 224° C.
Propionamide	79	214	103	
Allylurea	80			
Acetamide	82	245	115	
β-Phenylpropionamide	82	189		
α-Phenylbutyramide	86	158		
n-Heptamide	94	154		
Methylurea	101	230		
n-Caproamide	101	160		
Dicyandiamidine	105	—	—	Picrate, M.P. 265° C. Ni salt, yellow.
Palmitamide	106	141		
n-Valeramide	106	167		
Stearamide	108	140		

TABLE XX—(*contd.*)

	M.P. °C.	Xanthydrol deriv.	Anilide	Miscellaneous
Solids				
n-Caprylamide	110	148		
n-Butyramide	115	186	90	
iso-Caproamide	120	160		
Cyanoacetamide	123	223		
Benzamide	128	224	160	
iso-Butyramide	128	211	105	
Urea	132	274	—	Conc. $HNO_3 : H_2O$ (1 : 1) → nitrate, M.P. 163° C. Saturated soln. of oxalic acid → oxalate, M.P. 161° C.d.
iso-Valeramide	137	183		
Salicylamide	139	—	—	Acetyl deriv., M.P. 138° C. Benzoyl deriv., M.P. 200° C.
o-Toluamide	140	200		
m-Tolylurea	142			
Furoamide	142	210		
Phenylurea	147	225		
Benzylurea	149			
Methylguanidine nitrate	150			
Nitrourea	150d			
α-Phenylacetamide	154	196	117	
Hydantoic acid	156d			
p-Toluamide	160	225		
Urea nitrate	163	274*	—	* As for urea
Malonamide	170	270	224	
Urea oxalate	161d	274†	—	† As for urea.
p-Phenetylurea (" Dulcin ")	173	—	—	Sweet taste
p-Tolylurea	181			
as-Diphenylurea	189	180		
as-Dimethylurea	182	225	—	Nitrate, M.P. 104° C. Picrate, M.P. 130° C.
o-Tolylurea	191	228		
Biuret	192d	260	210	
Guanidine carbonate	197			
p-Nitrobenzamide	201	232		
Dicyanodiamide	207			
Guanidine nitrate	214			
Acetylurea	218			
Phthalamide	219d	—	205	
Guanidine acetate	229			
Nitroguanidine	232d			
Succinamide	260d	275	156	
Oxamide	419			

TABLE XXI.—ALIPHATIC AMINO-ACIDS

	‡ Decomposition point °C.	Benzoyl deriv.	*p*-Toluenesulphonyl deriv.	Phenyl *iso*-cyanate deriv.	α-Naphthyl *iso*-cyanate deriv.	Picrate	*	
d- or *l*-Glutamic acid	200	—	—	174	—	—	3	
β-Alanine	198	138	117	—	236	—	1	Hydrochloride, M.P. 210° C.
d- or *l*-Lysine	224	145	—	184	—	—	2	
d- or *l*-Asparagine	226	—	—	164	199	180d		
dl-Glutamic acid	227	157	—	—	—	—	1	
dl-Serine	228	171	213	169	—	—	3	
Glycine	232d	187	147	163	191	190	3	$FeCl_3$ → red colour $CuSO_4$ → blue colour Acetyl deriv. 206° C.
dl-Threonine	235	148	—	—	—	—	3	
d-Arginine	238	—	—	—	—	206	2	
dl-Arginine	238	315	—	—	—	201	2	
d- or *l*-Threonine	253	148						
d- or *l*-Aspartic acid	270	180	140	162	115	—	1	Acetyl deriv. 185° C.
dl-β-Phenylalanine	273	187	135	182	—	—	3	

l-Histidine	277	—	204	—	—	86	2	
d- or *l*-*iso*-Leucine	279	117	132	120	—	—	3	
α-Amino-*iso*-butyric acid	280	198	—	—	198			
dl-Aspartic acid	280	165	—	—	—	—	1	
d-α-Amino-*n*-butyric acid	285	121	—	—	195	—	—	*p*-Nitrobenzyl ester, M.P. 223° C.
l-Tryptophane	289	—	176	166	158	—	3	
dl-*iso*-Leucine	292	118	140	—	—	—	3	
dl-Alanine	295	166	139	190	—	—	3	
d- or *l*-Alanine	297	151	133	168	198	—	3	
dl-Valine	298	132	—	163	204	—	3	Formyl deriv., M.P. 145° C.
dl-α-Amino-*n*-butyric acid	307	147	—	170	194			
d- or *l*-Valine	315	—	147	147	—	—	3	Formyl deriv., M.P. 156° C.
dl-Tyrosine	318	197	—	—	—	—	4	
d- or *l*-Phenylalanine	320	146	161	181	—	—	3	Formyl deriv., M.P. 167° C.
dl-Norleucine	327	—	124	—	—	—	3	Formyl deriv., M.P. 114° C.
d- or *l*-Leucine	—	107	122	115	—	—	3	
l-Tyrosine	—	210	114	104	205	—	4	
dl-Ornithine	—	267d	—	192	—	195		
d- or *l*-Ornithine	—	240d	—	190	—	204		
dl-Lysine	—	249	—	196	—	—	2	

The numbers in the column marked * refer to the following properties of the acids:

1. Form barium or calcium salts sparingly soluble in aqueous alcohol.
2. Form precipitates with phosphotungstic acid.
3. Can be extracted from neutral solution by butanol saturated with water.
4. Sparingly soluble in water.

‡ Decomposition points vary considerably with rate of heating.

TABLE XXII.—CARBAMATES (URETHANES)

	M.P. °C.	Xanthydrol deriv.
Ethyl carbamate	49	169
Methyl carbamate	52	193
n-Butyl carbamate	54	
iso-Butyl carbamate	55	148
n-Amyl carbamate	57	
n-Propyl carbamate	60	
iso-Amyl carbamate	64	145
n-Butyl oxamate	88	
iso-Propyl carbamate	92	
Ethyl oxamate (Oxamethane)	114	

GROUP II—CLASS IV

SECONDARY AMINES, PRIMARY AROMATIC AMINES, SOME TERTIARY AROMATIC AMINES

Classification test.—Dissolve or suspend 0·5 g. of the original compound in dilute or concentrated hydrochloric acid or glacial acetic acid, keeping the temperature below 25° C. *Cool the solution well* and add one drop of a cold 2 per cent solution of sodium nitrite. Shake the solution well and add it to starch/potassium iodide solution. If no blue colour develops immediately, then the original substance is reacting with the nitrous acid.

The following types of compounds will give no blue colour in the above test and the result of the reaction is as indicated, though this will only be apparent when the amount of nitrite used approximates to the theoretical requirement:

(*a*) Aliphatic and aromatic secondary amines—an oily precipitate or emulsion.

(*b*) Primary aromatic amines—some give yellow or orange solutions; *meta*-diamines give a brown or black colour, but *meta*-diamines with a substituent group *ortho* to both amino groups react normally to give *bis*-diazo compounds. N.B.—If the solutions are at all warm, a precipitate of yellow or orange diazo-amino compound may be formed.

(*c*) Tertiary aromatic amines with the *para*-position unoccupied —a brown precipitate of the *p*-nitroso compound (see p. 148 and Table XXXI).

(*d*) Tertiary aromatic amines with a hydroxyl group in the para-position—coloured oxidation products.

It should be noted that compounds of types other than those listed above will react with nitrous acid, but these have already been identified, or proved absent as a result of previous tests.

A. Secondary amines

Substances of this class will generally be soluble in dilute mineral acids, though the salts of very weak bases such as diphenylamine and its derivatives are extensively hydrolysed in solution.

The following general tests are only to be applied when the classification test with nitrous acid is positive:

General tests

1. To a cold solution or suspension of the original substance in dilute hydrochloric acid, add cold 2 per cent aqueous sodium nitrite drop by drop, shaking after each addition until there is a slight excess of nitrous acid present, as shown by the addition of a drop of the solution to starch/iodide solution. If a precipitate or emulsion of a nitrosamine is formed, a secondary amine is present.

$$RR'NH + HONO = RR'N{\cdot}NO + H_2O.$$

All secondary amines, whether aromatic, aliphatic or mixed aromatic-aliphatic, react in the above manner.

2. *Liebermann's nitroso reaction.*—The formation of a nitrosamine should always be confirmed by this test.

The liquid resulting from the above test 1 is placed in a separating funnel and a little urea added to destroy the excess of nitrous acid. The oily nitrosamine is taken up in ether, the ether layer separated and washed with aqueous alkali followed by water. (If the nitrosamine is required as a derivative the ethereal solution may be dried over anhydrous magnesium sulphate at this stage.) Evaporate off the ether and to a portion of the residual oil or solid add a drop of concentrated sulphuric acid. Nitrosodiphenylamine gives a blue colour. If no blue colour is formed, add to a second portion of the residue a small crystal of phenol, followed by a few drops of

concentrated sulphuric acid. A green or blue colour which turns purple on dilution and blue on making alkaline, indicates the presence of a nitrosamine.

Note.—A few secondary amines, e.g. piperidine, piperazine and diethylamine, do not readily give a nitrosamine. To include these, carry out the following test: Add a few drops of the original compound to dilute sodium nitroprusside solution followed by a few drops of dilute acetaldehyde. A deep blue or violet solution results in the case of a secondary amine which did not give a positive test with nitrous acid.

Derivatives

These are similar in type to those obtained from primary aromatic and aliphatic amines.

The best derivatives for *aliphatic* secondary amines are those obtained with α-naphthyl or *p*-nitrophenyl *iso*-cyanate, α-naphthyl *iso*-thiocyanate (p. 111), and the addition compound with picric acid (p. 112).

With other secondary amines the most useful are the acetyl (p. 130), benzoyl (p. 131), formyl (p. 133), *p*-nitrobenzoyl (p. 131) derivatives, benzene or *p*-toluene sulphonamides (p. 132), phenylthioureas (p. 111 for water soluble compounds), the substituted ureas (p. 111, using phenyl or α-naphthyl *iso*-cyanate), and addition compounds with picric acid (p. 112).

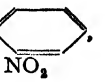
The most convenient method for preparing *acetyl derivatives* of lower *alkyl anilines* consists of distilling a mixture of equal volumes of amine and acetic anhydride, rejecting the distillate boiling below 200° C. The acetyl derivative will crystallize on cooling the residue or pouring it into water.

In the case of the *sulphonamides*, the product from secondary amines is insoluble in alkali, while that from primary amines is soluble. Tertiary amines do not react with the sulphonyl chlorides, and these differences are the basis of Hinsberg's method for the separation of primary, secondary and tertiary amines.

$$(C_6H_5)_2NH + C_6H_5SO_2Cl = (C_6H_5)_2N{\cdot}SO_2{\cdot}C_6H_5 + HCl.$$

Secondary amino-phenols.—Some indication of the presence of such compounds, e.g. *p*-methyl amino-phenol, is given in the preliminary test with sodium hydroxide as these substances, in alkaline solution, darken in air.

Alkyl nitranilines and their homologues.—Secondary aromatic amines containing a nitro-group in the nucleus,

e.g. ethyl *o*-nitraniline C_2H_5NH  ,

are coloured yellow, orange or red, their salts being colourless when unhydrolysed.

B. Primary aromatic amines and salts

The salts (from C, H and O acids only in this group) are generally soluble in water, while the free bases, on the whole, are soluble in dilute mineral acids of approximately 5N strength. Some amines are, however, soluble in acid only within a narrow concentration range. Thus, in the case of naphthylamines and nitranilines, at acid concentrations below the lower limit, their salts become hydrolysed, while at concentrations above the upper limit the salt of the amine, e.g. the hydrochloride, is precipitated.

General tests

These tests are only to be applied when the classification test with nitrous acid (p. 125) is positive.

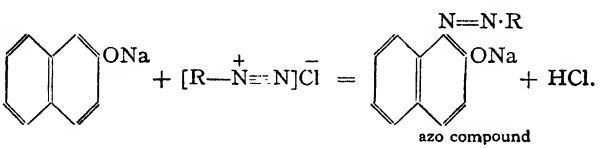
The changes which may occur in the solution in the course of the following test should be accurately observed and noted.

About 0·1 g. of the original compound dissolved or suspended in 2 ml. of 5N hydrochloric acid, is well cooled (preferably to 0° C.) and treated dropwise with a 2 per cent aqueous solution of sodium nitrite until a slight excess is present as shown by the starch/iodide test. If at this stage the solution develops a brown to black coloration, or a dark red, yellow or brown precipitate is formed, the given substance may be: (*a*) an *ortho-* or *meta*-diamine or salt of such compound (see p. 129 for additional tests for diamines); (*b*) a tertiary aromatic amine, a di-alkyl aniline or nuclear substituted di-alkyl aniline or salt in which the *para-* position is unoccupied. Confirm by cautiously adding cold dilute caustic soda to the solution. If the yellow or red hydrochloride of the *p*-nitroso compound is converted to the green or blue free nitroso base, a compound of type (*b*) is present. See tertiary amines (p. 147) for further tests and derivatives; (*c*) a tertiary aromatic amine with an —OH group in the para position. The coloured product formed is probably due to oxidation.

If the solution be clear, or only faintly coloured following the addition of the sodium nitrite solution, pour *into* an alkaline solution of β-naphthol. (Do not add the alkaline solution to the diazotized solution as a precipitate of α-nitroso β-naphthol is sometimes formed thus.) The formation of a bright red, orange-red or reddish blue coloration or precipitate of an azo-compound indicates that the original compound is a *primary aromatic amine*, i.e. has an $—NH_2$ group attached to a carbon atom of a ring. If the azo-compound is soluble, the presence of one or more hydroxyl groups in the amine is indicated.

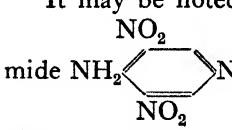
$$RNH_2{\cdot}HCl + HNO_2 = [R—\overset{+}{N}{\equiv}N]{\cdot}\overset{-}{Cl} + 2H_2O.$$

aryl diazonium chloride



azo compound

If a colour or precipitate forms, it is well to establish whether or not this is due to the formation of an azo dye by taking a portion of the diazotized solution and making it alkaline with caustic soda. If no identical colour or precipitate forms, then the original compound is a primary aromatic amine.

It may be noted that amines such as trinitro-aniline or picramide  containing a number of negative groups, e.g. nitro- or halogen in the nucleus, may not diazotize under the above conditions and special methods must be adopted. Dissolve the amine in glacial acetic acid and then treat with nitrosyl sulphuric acid (0·7 g. of sodium nitrite in 160 g. $H_2SO_4{\cdot}H_2O$) in the cold. An intense colour develops when a solution of β-naphthol in glacial acetic acid is added to the diazotized solution.

Anilides, R'NH·COR, may give a reaction similar to that given by primary aromatic amines with nitrous acid. Nitrosoamides R'N(NO)·COR are formed, which on adding to alkaline β-naphthol produce azo-compounds by reaction with the alkali.

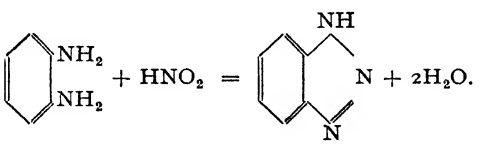
$$Ph{\cdot}N(NO)CO{\cdot}CH_3 + 2NaOH = Ph{\cdot}N{:}N{\cdot}ONa + CH_3{\cdot}COONa + H_2O.$$

Some indication of the presence of anilides will have been given in the preliminary tests with dilute or concentrated sulphuric acid,

when a volatile acid will have been evolved, and they will be treated as a separate class (see p. 160).

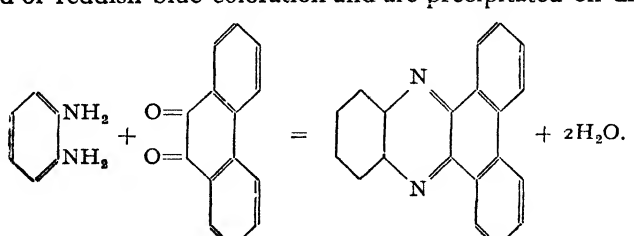
A definite distinction between primary aromatic amines and anilides may be made by bringing a crystal of the original substance into contact with a crystal of 2 : 4-dinitrochlorobenzene. An intense colour develops immediately in the case of a primary aromatic amine, while anilides produce no colour. Secondary amines give slowly a less pronounced colour.

Diamines.—As indicated above, *ortho-* or 1 : 2- and *meta-* or 1 : 3-diamines give yellow or brown colorations or precipitates in the nitrous acid test. The *ortho*-compounds give azimides, which may be yellow or even white in the pure state.



Meta-diamines give a more or less intense brown colour (reaction used in the determination of small quantities of nitrites) except in the case of 1 : 3-diamines having substituent groups in the nucleus *ortho-* to both amino groups. These give normal *bis*-diazo compounds with nitrous acid. *Para-* or 1 : 4-diamines diazotize normally to give a mixture of *mono-* and *bis*-diazo compounds.

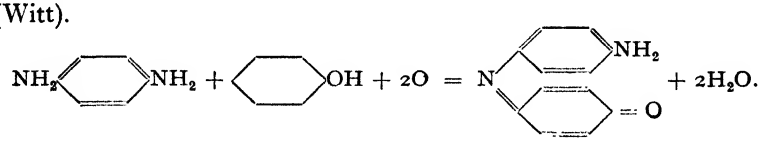
Special tests for diamines.—1. Dissolve 0·1 g. of the given compound in 1 ml. of alcohol and add an equivalent amount of phenanthraquinone dissolved in hot glacial acetic acid. A yellow precipitate of a phenazine separates out in the case of ortho-diamines. These phenazines, which have no definite melting-points, dissolve in concentrated sulphuric acid with formation of an intense brownish red, red or reddish blue coloration and are precipitated on dilution.



Other 1 : 2-diketones, e.g. benzil, react in similar fashion to phenanthraquinone. *Meta-* and *para*-diamines do not give this reaction.

2. Oxidize a small quantity of the original compound with potassium dichromate and sulphuric acid. On warming, the characteristic odour of a *para*-quinone is detectable in the case of a *para*- or 1 : 4-diamine.

3. Mix a little of the original compound with phenol and add an alkaline solution of hypochlorite. Formation of a violet colour due to an indophenol indicates the presence of a 1 : 4-diamine (Witt).



Aromatic amino-acids.—These are generally soluble in both acid and alkali and derivatives involving certain reactions of the amino group (Nos. 1–9, pp. 130–3) or the carboxyl group (No. 5, p. 53) may be prepared.

Nitro-amines and their salts.—Such compounds, containing one nitro group in the nucleus, are generally yellow, orange or red, while their unhydrolysed salts are colourless. It may be noted that the presence of nitro groups in the nucleus of aromatic amines retards acetylation and method 1 (*b*) (p. 131) should be used.

Proof of the presence of the nitro group can best be obtained by reduction of the acetyl derivative with zinc and boiling alcohol, filtering and diazotizing the resultant amine in the usual way (see p. 162).

Amino phenols and their salts.—These darken on gently warming with caustic soda solution. They reduce Tollens' reagent (see p. 36). In some cases addition of ferric chloride solution produces a violet or red coloration. Derivatives as for primary aromatic amines.

Derivatives

1. **Acetyl derivative or substituted acetamide.**—(*a*) This method is useful for aniline and its homologues as it prevents the formation of the diacetyl derivative.

Prepare a suspension of 1 g. or 1 ml. of the amine in 3 ml. of water (or aqueous acetic acid for amines of comparatively high molecular weight)* and add about 1 ml. of acetic anhydride drop by drop, shaking well after each addition. Heat is generally evolved

* For salts of amines use water and add also 1 g. of crystalline sodium acetate.

in the reaction, the suspension becoming pasty. Allow to stand for about 15 min. or warm *gently* to hydrolyse any excess acetic anhydride. Cool, filter and recrystallize from an alcohol/water mixture of such concentration that the amide will dissolve in the hot solution and separate on cooling.

(*b*) The following method is useful for those amines containing a nitro-group or halogen atom in the nucleus as these tend to retard acetylation at ordinary temperatures:

About 0·5 g. of the base is boiled for 2 min. with 1 ml. of acetic anhydride containing *one drop* of concentrated sulphuric acid. Water is added drop by drop, the mixture being cooled and shaken during the addition. Excess acetic anhydride is removed as in (*a*) and the derivative recrystallized as before.

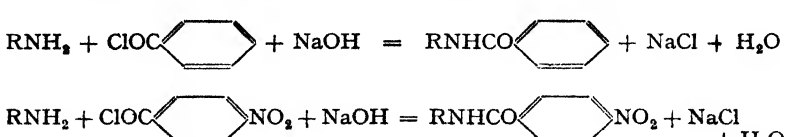
2. Benzoyl and *p*-nitro-benzoyl derivative, i.e. substituted benzamide and *p*-nitrobenzamide.

(*a*) *Schotten-Baumann reaction.*—Dissolve 0·5 g. or 0·5 ml. of the original compound in 2 ml. of acetone. Then add about 25 ml. of aqueous 10 per cent sodium hydroxide followed by 1 ml. of benzoyl chloride drop by drop, shaking vigorously in a corked tube or flask during the addition. Continue shaking for about 10 min. or until the odour of benzoyl chloride has disappeared. If necessary add sodium carbonate and continue shaking. Care must be taken that the solution is alkaline to litmus at this stage. Filter off the solid formed, wash with cold dilute hydrochloric acid and then with cold water. Recrystallize from alcohol.

(*b*) Add about 0·5 g. or 0·5 ml. of the amine to a solution of 0·5 ml. of benzoyl chloride in 10 ml. of *dry* benzene. Reflux for about 15 min. Cool, filter if necessary, and wash the benzene solution successively with 2 per cent sodium carbonate, 2 per cent hydrochloric acid and distilled water. Evaporate off the benzene and recrystallize the residue from aqueous alcohol.

For the preparation of the *p*-nitrobenzoyl derivative use 1 g. of *p*-nitrobenzoyl chloride in place of benzoyl chloride.

(*c*) The use of pyridine instead of sodium hydroxide for removal of the hydrochloric acid formed in the reaction is sometimes useful. For details see benzoyl derivative of phenols, p. 63.

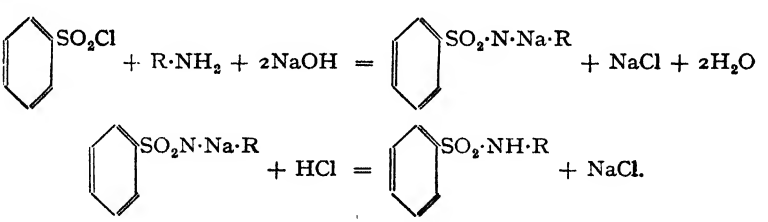


3. Benzene sulphonyl derivative (Hinsberg's method).

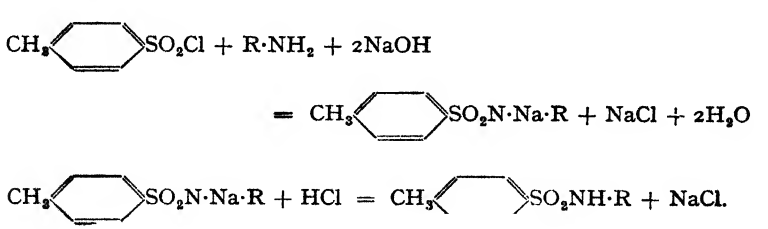
To 0·5 g. of the base in a test-tube add 10 ml. of 10 per cent sodium hydroxide and 0·5 g. of benzene sulphonyl chloride. Cork the tube and shake the mixture vigorously. Keep the liquid cool and test to make sure that the mixture remains alkaline. If necessary, add more caustic soda. Filter and acidify the filtrate with concentrated hydrochloric acid. If an oil separates, shake vigorously until it solidifies. Filter off the solid, wash well with cold water, and recrystallize from 95 per cent alcohol.

Note that the derivative of a primary amine is soluble in alkali as a sodium compound and is only precipitated on acidification, while in the case of a secondary amine, the derivative is insoluble (containing no acidic hydrogen atom) and is formed directly by the above procedure.

In some cases disulphonyl derivatives of primary amines may be formed, and these are insoluble in alkali. In order to hydrolyse them to the mono-sulphonyl derivative, they must be refluxed with an alcoholic solution of sodium ethoxide (0·8 g. of sodium in 20 ml. of absolute alcohol for every 1 g. of the original base). Dilute the solution. Distil off the alcohol and add excess acid.



4. *p*-Toluene sulphonyl (*p*-tosyl) derivative.—Use the above procedure with *p*-toluenesulphonyl chloride in place of benzenesulphonyl chloride and with the addition of a small amount of ether to the reaction mixture.



Note.—Methods 3 and 4 may be used for the separation of primary, secondary and tertiary amines, the derivatives of primary amines being soluble in alkali, those from secondary amines insoluble, while tertiary amines do not react with either reagent.

5. **Addition compound with picric acid, or 1 : 3 : 5-trinitrobenzene.**—Method as for hydrocarbons (see p. 91).

6. **Isothiocyanate derivative or phenyl thiourea.**—As for primary aliphatic amines (see p. 111). The reaction mixture should, however, be warmed.

7. **Phenyl or α-naphthyl iso-cyanate derivative.**—As for alcohols (see p. 79).

8. **Formyl derivative.**—Mix 0·5 g. of the amine with 5 ml. of 90 per cent formic acid and boil under a reflux for 10 min. Dilute with 10 ml. of cold water. If no solid separates, cool in a freezing mixture. Addition of sodium chloride also serves as an aid to separation. Filter, wash with cold water and recrystallize from alcohol, water or petrol-ether (B.P. 60°–80° C.).

$$ArNH_2 + H{\cdot}COOH = \underset{\displaystyle CHO}{\overset{\displaystyle |}{ArNH}} + H_2O.$$

9. **Benzaldehyde derivative.**—Dissolve 1 g. of the primary amine in 5 ml. of alcohol and add 1 g. (or 2 g. in the case of a diamine) of benzaldehyde. Warm under a reflux for 10 min. Cool, filter and recrystallize from alcohol or benzene.

$$ArNH_2 + C_6H_5CHO = ArN{=}CHC_6H_5 + H_2O.$$

Table XXIIIa.—SECONDARY AMINES

	B.P. °C.	Acetyl deriv.	Benzoyl deriv.	Benzene sulphonamide	*p*-Toluene sulphonamide	Nitrosamine	Formic acid deriv.	Picrate	Phenyl thiourea	*a*-Naphthyl urea	1:3:5-Trinitrobenzene deriv	Miscellaneous
Liquids												
Dimethylamine	7	—	42	47	79	—	—	158	135	159		
Diethylamine	55	—	—	42	60	—	—	155	34	128		
Di-*iso*-propylamine	86	—	—	—	—	—	—	140				
Pyrrolidine	89	—	—	—	123							
Piperidine	105	—	48	93	—	—	—	152				
Di-*n*-propylamine	110	—	—	51	—	—	—	75	69	93		
Diallylamine	111											
Morpholine	130	—	75	118	147	—	—	146	136			
Pyrrole	131	—	—	—	—	—	—	69				
Di-*iso*-butylamine	139	—	86	55	—	—	—	119	113	119		
Di-*n*-butylamine	160	—	—	—	—	—	—	60	86			
Di-*iso*-amylamine	187	—	—	—	—	—	—	—	72	95		
Methylaniline	192	102	63	79	95	—	—	147	87	—	82	HCl, M.P. 121° C.
Ethylbenzylamine	199											
Ethyl aniline	205	54	60	38	88	—	—	132	89	—	56	HCl, M.P. 176° C.
Di-*n*-amylamine	205	—	—	—	—	—	—	—	72			
Methyl-*m*-toluidine	206	66										
Methyl-*o*-toluidine	207	55	66	—	120	—	—	90				
Methyl-*p*-toluidine	208	83	53	—	—	53	—	131				
iso-Propylaniline	213	39										

Ethyl-*p*-toluidine	217	—	40	66	70							
Ethyl-*o*-toluidine	218	—	72	62	69							
Ethyl-*m*-toluidine	221	—	72									
n-Propylaniline	222	47	—	54	—	—	—	—	104			
Tetrahydroquinoline	250	—	75	67	—	—	—	—	—	—	100	
Methyl-α-naphthylamine	293	93	121	—	163							
Dibenzylamine	300	—	112	68	81	61	52					
Methyl-β-naphthylamine	309	51	84	107	—	88						
Ethyl-β-naphthylamine	315	49	—	—	—	56	—	—	—	—	106	
Ethyl-α-naphthylamine	325	68	—	—	—	—	—	—	—	—	154	
Solids	M.P.											
Diethanolamine	28	—	—	130	99	—	—	110				
Benzylaniline	37	58	107	119	140	58	48	—	103	—	92	HCl, M.P. 119° C.
Indole	52	—	68	—	—	—	52	—	—	—	187	
Diphenylamine	54	101	180	124	142	66	74	182	152	—	100	Tetrabromo, M.P. 183° C.
Phenyl-α-naphthylamine	62	115	152	—	—	—	—	—	—	—	130	
Methyl-*m*-nitroaniline	66	95	156	83	—	69						
Benzyl-β-naphthylamine	68	—	115	—	—	—	—	141	—	—	141	
p-Tolyl-α-naphthylamine	79	124	140	83								
Di-*p*-tolylamine	79	85	125									
Ethyl-*p*-nitroaniline	96	118	98	—	107	119						
p-Tolyl-β-naphthylamine	103	85	139								124	
Piperazine	104	134	191	282	—	158	—	280				
Phenyl-β-naphthylamine	108	93	148	—	—	93	—	—	—	—	116	
αβ-Dinaphthylamine	111	—	—	—	—	—	—	173				
αα-Dinaphthylamine	115	217	—	—	—	—	—	169	—	—	157	
p-Nitromethylaniline	152	153	111	120	—	101						
ββ-Dinaphthylamine	171	—	—	—	—	—	—	165	—	—	147	
Carbazole	243	69	98									

TABLE XXIII*b*.—SECONDARY AMINO-PHENOLS

	M.P. °C.	Acetyl deriv.	Benzoyl deriv
m-Hydroxyethylaniline	62		
p-Hydroxymethylaniline	85	240 (mono) 97 (di)	175
o-Hydroxymethylaniline	87	150	150

TABLE XXIV.—PRIMARY AROMATIC AMINES

	B.P. °C.	Acetyl deriv.	Benzoyl deriv.	Benzene sulphonamide	*p*-Toluene sulphonamide	Benzaldehyde deriv.	Formyl deriv.	Picrate	Phenyl *iso*-thiocyanate deriv.	Phenyl *iso*-cyanate deriv.	1 : 3 : 5-Trinitro-benzene deriv.	Miscellaneous
Liquids												
Aniline	184	112	163	110	103	54	47	165	154	238	123	Tribromo deriv., M.P. 118° C.
o-Toluidine	200	109	144	124	110	—	59	200	136	207	126	Dibromo deriv., M.P. 50° C.
m-Toluidine	203	66	125	83	114	—	—	195	91	173	—	HCl, M.P. 228° C.
4-*m*-Xylidine (4-Amino-1 : 3-dimethyl benzene)	212	130	192	130	—	—	114	209	—	242		

o-Cumidine (*o*-Amino-*iso*-propyl benzene)	214	72	—	—	—	—	—	160				
2-*p*-Xylidine (2-Amino-1 : 4-dimethyl benzene)	215	139	140	139	119	101	117	171	148			
2-*m*-Xylidine (2-Amino-1 : 3-dimethyl benzene)	216	177	170	—	—	—	165	180	204			
5-*m*-Xylidine (5-Amino-1 : 3-dimethyl benzene)	220	144	136	—	—	—	77	200	153			
3-*o*-Xylidine (3-Amino-1 : 2-dimethyl benzene)	221	136	189	—	—	—	—	221				
o-Anisidine (*o*-Methoxy-aniline)	225	85	60	89	127	—	83	—	135	144	98	
p-Cumidine (4-Amino-*iso*-propyl benzene)	225	103	162									
o-Phenetidine (*o*-Ethoxy-aniline)	229	79	104	102	164	—	62	—	137	169	—	HCl, M.P. 214° C.
Mesidine (2-Amino-1 : 3 : 5-trimethyl benzene)	229	216	206	137	—	43	176	190	193			
m-Phenetidine (*m*-Ethoxy-aniline)	248	97	103	—	157	—	52	158	138			
m-Anisidine	251	81	—	—	68	—	57	169				
p-Phenetidine	254	134	173	143	106	76	69	—	136	178	—	HCl, M.P. 234° C.
p-Aminodiethylaniline	262	104	172	—	—	—	—	—	—	—	79	
Ethyl anthranilate	267	61	98	92	—	—	—	—	—	—	71	
ar-Tetrahydro-α-naphthyl-amine	275	158	—	—	—	—	—	—	—	—	113	
Ethyl-*m*-aminobenzoate	294	—	114	—	—	—	—	—	—	—	84	
Solids	M.P.											
o-Aminoacetophenone	20	76	98	—	148	—	76	—	—	—	—	B.P., 252 °C. Phenylhydrazone, M.P. 108° C.

[*Contd over*

TABLE XXIV.—(*contd.*)

	M.P. °C.	Acetyl deriv.	Benzoyl deriv.	Benzene sulphonamide	*p*-Toluene sulphonamide	Benzaldehyde deriv.	Formyl deriv.	Picrate	Phenyl *iso*-thiocyanate deriv.	Phenyl *iso*-cyanate deriv.	1 : 3 : 5-Trinitro-benzene deriv.	Miscellaneous
Solids												
Isoduridine	24	211										
Methyl anthranilate	25	101	100	107	—	—	—	—	—	—	106	
ar-Tetrahydro-β-naphthyl-amine	38	107	167					204				
2 : 4′-Diaminodiphenyl	45	202	278									
p-Toluidine	45	145	158	120	117	35	53	169	141	213	—	HCl, M.P. 240° C.
4-*o*-Xylidine (4-Amino-1 : 2-dimethyl benzene)	49	99	—	118	154	—	52					
2-Aminodiphenyl (*o*-Xenyl-amine)	49	119	102	—	—	—	75					
α-Naphthylamine	50	160	161	171	157	73	139	161	157	222	214	HCl, M.P. 286° C.
4-Aminodiphenyl (*p*-Xenyl-amine)	53	175	233	—	255	149	175	—	211			
p-Aminodimethylaniline	53	131	228	—	—	98	108	186				
2-Aminopyridine	57	71	165	—	—	—	—	217				
p-Anisidine	57	127	154	96	114	69	81	—	157	—	82	
2 : 3-Diaminotoluene	61											
m-Phenylenediamine	63	191	240	194	172	104	155	184				
2 : 5-Diaminotoluene	64	220	307	147m	150m							
1 : 8-Diaminonaphthalene	67		312									

pseudo-Cumidine (5-Amino-1 : 2 : 4-trimethylbenzene)	68	162	167	137	—	—	121					
8-Aminoquinoline	70	103	98	—	155							
p-Aminodiphenylamine	75	158	203	—	—	108						
3-Aminoquinoline	84 or 94	167	—	—	—	—	—	210	—	—	—	Two forms
m-Aminoacetanilide	89	191	—	—	241							
Ethyl *p*-aminoacetanilide	89	110	148	—	—	—	—	—	—	—	85	
3 : 4-Diaminotoluene	89	210	264		140m							
p, *p'*-Diaminodiphenylmethane	94	224										
7-Aminoquinoline	94†	167	189	—	—	—	—	—	—	—	—	†Anhydrous
1 : 2-Diaminonaphthalene	95	234	291	—	—	—	—	—	—	—	204	
2 : 4-Diaminotoluene	99	220	224	192	192	175	176	170				
o-Phenylenediamine	102	185	301	185	201	106	170	208	—	—	—	Benzil-quinoxaline, M.P. 124° C.
p-Aminoacetophenone	106	167	205	128	203	96	103	—	—	—	137	
5-Aminoquinoline	110	178	—	—	204							
β-Naphthylamine	112	134	162	102	133	102	128	195	157	220	162	
6-Aminoquinoline	114†	138	169	—	193	—	—	—	—	—	—	†Anhydrous
1 : 4-Diaminonaphthalene	120	303	280	—	188m	—	—	—	—	—	218	
p-Aminobenzophenone	124	153	152									
p-Aminoazobenzene	125	145	211	—	—	130	162					
Benzidine	127	317	352	232	243	238						
2-Aminoquinoline	129	—	—	—	—	—	—	256d	—	—	186	
o-Tolidine	129	315	265	—	—	152	254	185	—	—	128	
o-Aminoacetanilide	132											
o-Dianisidine	135	243	236	—	—	—	264d	225	—	—	144	
p-Phenylenediamine	140	304	>300	247	266	140	206	202				
4-Aminoquinoline	154†	176	—	—	—	—	—	274	—	—	111	†Anhydrous
p-Aminoacetanilide	163	303	—	—	—	165						
2-Aminoanthraquinone	307	262	228	271	304							

TABLE XXV.—AROMATIC AMINO-ACIDS (SOLIDS)

	M.P. °C.	Acetyl deriv.	Benzoyl deriv.	Benzene sulphonamide	*p*-Toluene sulphonamide	Formic acid deriv.	Benzaldehyde deriv.	Phenyl urethane	α-Naphthyl urethane	1 : 3 : 5-Trinitrobenzene deriv
Anthranilic	144d	185	182	214	217	168	127	181	193	205d
m-Aminobenzoic	174d	250	248	—	—	225	119	270	—	201
p-Aminobenzoic	186d	252	278	—	223	268	193	300	151	248
p-Aminophenylacetic	200d	170	206							
3-Aminosalicylic	235	138	189	194	—	—	215d			
5-Aminosalicylic	283d	218	252							

TABLE XXVI.—NITRO-AMINES (SOLIDS)

	M.P. °C.	Acetyl deriv.	Benzoyl deriv.	Benzene sulphonamide	*p*-Toluene sulphonamide	Benzaldehyde deriv.	Formic acid deriv.	Picrate	Phenyl thiourea	1 : 3 : 5-Trinitrobenzene deriv.	Miscellaneous
o-Nitroaniline	71	93	93	104	115	—	122	73	142	91	
4-Methyl-2-nitroaniline	72	93	172	160	—	78	134				
4-Nitromesidine	75	191	169	163							
4-Amino-5-nitro-1 : 3-dimethylbenzene	76	173	185								
4-Amino-2-nitrotoluene	77	148	172	160	164	—	—	—	171		

2-Methyl-6-nitroaniline	91	157	167								
2-Methyl-3-nitroaniline	95	158									
2-Amino-3-nitrotoluene	97	158									
8-Nitro-1-naphthylamine	97	191	—	194							
2-Amino-4-nitrotoluene	107	151	183	172	—	116	186				
m-Nitroaniline	114	154	155	136	138	73	134	143	155	98	
4-Amino-3-nitrotoluene	116	96	148	102	146						
5-Nitro-1-naphthylamine	119	220	—	183	—	—	199				
4-Amino-6-nitro-1 : 3-dimethylbenzene	123	159	200	149							
1-Nitro-2-naphthylamine	126	124	168	156	159	—	—	—	—	116	
2-Amino-5-nitrotoluene	130	202	174	158	174	—	162				
3-Amino-6-nitrotoluene	135	102									
3-Nitro-1-naphthylamine	137	255	220	—	200	—	122	216			
2 : 6-Dinitroaniline	138	197									
2-Amino-5-nitro-1 : 4-dimethylbenzene	142	166	—	162							
2-Amino-5-nitronaphthalene	144	186	182								
1-Amino-2-nitronaphthalene	144	199	175								
p-Nitroaniline	147	216	199	139	191	115	194	100			
4-Amino-3 : 5-dinitrotoluene	166										
4-Amino-2 : 6-dinitrotoluene	169										
2 : 4-Dinitroaniline	180	120	220	—	219	133					
Picramide (2 : 4 : 6-Trinitroaniline)	188	230	196	211	—	—	—	—	—	—	Diazotized only in conc. H_2SO_4
Dinitromesidine	194	275									
1-Amino-4-nitronaphthalene	195	190	224	158	185						

Table XXVII.—Amino Phenols

	M.P. °C.	Acetyl deriv.	Benzoyl deriv.	Benzene sulphonyl deriv.	*p*-Toluene sulphonyl deriv.	Benzaldehyde deriv.	Formic acid deriv.	Picrate	Phenyl thiourea	Miscellaneous
2 : 4-Diaminophenol	79d	180 (tri)	231 (tri)	—	—	—	—	180d		
m-Aminophenol	122	101 (di) 148 (mono)	153 (di)	—	157	—	—	—	156	HCl, M.P. 237° C.
Picramic acid	168	201	220							
5-Amino-2-hydroxytoluene	173	103 (di) 179 (mono)	194 (di)	—	—	208				
o-Aminophenol	174	201 (mono)	182 (di)	141	139	89	129	—	146	HCl, M.P. 210° C.
p-Aminophenol	184d	150 (di) 168 (mono)	234 (di)	125	143	182	140	—	150	HCl, M.P. 306° C.
4-Amino-2-naphthol	185d	—	310							
5-Amino-2-naphthol	190	187	223	—	—	—	—	170		
5-Amino-1-naphthol	192	—	276							
7-Amino-2-naphthol	201	156	181							
8-Amino-2-naphthol	207	—	208							
3-Amino-2-naphthol	234	188								
2-Amino-1-naphthol	—	116	180							
4-Amino-1-naphthol	—	158	215	—	—	137	168			
1-Amino-2-naphthol	—	206	230	—	184	129	204	110		

GROUP II—CLASS V

NITRO-PARAFFINS

These compounds are neutral, although those having the general formula $RR'CH{\cdot}NO_2$ react with aqueous alkali to give sodium salts.

$$RR'CH{\cdot}NO_2 \rightleftharpoons RR'C : N\begin{matrix}O\\ \diagup\\ \diagdown\\ OH\end{matrix}.$$

(*aci*- or *iso*-nitro form)

In the case of aryl substituted nitro-paraffins the *iso*-nitro compound may be precipitated by adding an excess of dilute hydrochloric acid to an ice-cold solution of the sodium salt.

Classification test (Konovaloff's reaction).—Treat a little of the original compound with a few drops of a concentrated solution of potassium hydroxide (or alcoholic sodium ethoxide). Extract the resultant salt (if any) with a small quantity of water and cover the water extract with ether. Add ferric chloride, drop by drop, shaking during the addition. A precipitate of ferric hydroxide is first formed, further addition of ferric chloride producing a red or reddish brown colour in the ether layer if a primary or secondary nitro compound is present.

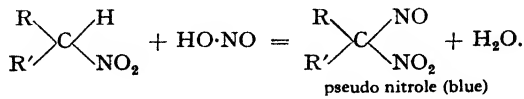
Additional test.—If the above reaction be positive, dissolve a little of the nitro compound in concentrated caustic potash solution containing a little potassium nitrite. Dilute slightly and add dilute sulphuric acid drop by drop. A primary nitro-paraffin $R{\cdot}CH_2NO_2$ gives a blood-red colour, which disappears when excess acid is present, reappearing on making alkaline. Secondary nitro-paraffins $RR'CH{\cdot}NO_2$ give a blue or blue-green coloration, soluble in chloroform.

The above test holds for primary nitro-paraffins up to nitrohexadecane, but all secondary nitro-paraffins do not give the test. The reaction depends on the formation of nitrolic acids which form red alkali salts, in the case of primary nitro-paraffins,

$$RCH_2{\cdot}NO_2 + HO{\cdot}NO = R{\cdot}C\begin{matrix}NO_2\\ \diagup\\ \diagdown\\ NOH\end{matrix} + H_2O,$$

nitrolic acid (red potassium salt)

and blue pseudo nitroles in the case of secondary nitro-compounds.



Tertiary nitro-compounds do not give this test.

Derivatives.—Reduce with tin and concentrated hydrochloric acid as for aromatic nitro compounds (see p. 163). Primary, secondary and tertiary nitro-compounds all yield primary aliphatic amines. These will be present in solution as hydrochlorides. Make the solution alkaline, extract and identify the amine.

TABLE XXVIII.—NITRO-PARAFFINS

	B.P. °C.	Benzoyl deriv. of amine	Miscellaneous
Liquids			
Nitromethane	101	80	
Nitroethane	113	71	
Nitroform	115		
2-Nitropropane	117		M.P. 15° C. Explodes on rapid heating
Tetranitromethane	126		
1-Nitropropane	131	84	
Nitrobutane	152		
Phenylnitromethane	226d	105	*iso*-Nitro compound, M.P. 84° C.
Solids	M.P.		
3 : 5-Dimethylphenyl-nitromethane	47	—	*iso*-Nitro compound, M.P. 53° C.
p-Nitrophenylnitro-methane	91	—	Oxidation → *p*-nitrobenzoic acid, M.P. 241° C. *iso*-Nitro compound, M.P. 91° C.

GROUP II—CLASS VI

NITROSO-COMPOUNDS

These compounds may be divided into two classes: (*a*) the *N-nitroso compounds*, known as nitrosamines, in which the nitroso group is attached to nitrogen as in $\begin{matrix} R \\ R' \end{matrix}\!\!>\!N\cdot NO$, R and R′ being alkyl or aryl radicals; (*b*) the *C-nitroso compounds* in which the nitroso group is attached to carbon, e.g. nitroso benzene C_6H_5NO.

The classification tests for both types should be carried out.

(a) N-nitroso compounds or nitrosamines

Classification test. Liebermann's test.—Treat a small amount of the original compound with about 2 ml. of concentrated sulphuric acid (diphenyl nitrosamine gives a deep blue solution) followed by a small crystal of phenol. Warm gently. If a green or blue colour develops, a compound of this type is present. Add water drop by drop, when the colour will change through violet to reddish violet and finally to red. On making alkaline a green or blue colour appears.

(b) C-nitroso compounds

Classification test.—An indication of the presence of these compounds will have been obtained in the preliminary tests, as they are often coloured green, or if white in the crystalline state, assume a green or blue colour when fused or vaporized.

Furthermore, freshly prepared solutions in solvents such as benzene, alcohol or ether are colourless but become blue on warming.

It may be noted that salts of these compounds, e.g. the hydrochloride of *p*-nitroso dimethyl aniline $(CH_3)_2N \cdot C_6H_4 \cdot NO$ (1 : 4), are yellow, and the above-mentioned colour reactions are only shown by the free base which is liberated from such salts by the addition of sodium hydroxide (see preliminary tests, p. 104).

Derivatives

(a) N-nitroso compounds. *Conversion to secondary amines.*—(*a*) With aliphatic nitrosamines, elimination of the nitroso group to give the parent secondary amine may be effected by boiling with concentrated hydrochloric acid. On making the resulting solution alkaline, the free base will be liberated and may be isolated by extraction with ether and converted to a suitable derivative. In certain cases the alkaline solution may be used for this purpose.

(*b*) In this method, an excess of a solution of cuprous chloride (35 g. cuprous chloride plus 200 ml. of concentrated hydrochloric acid) is added to the nitrosamine, when nitric oxide is evolved. The reaction mixture is gently warmed to complete the reaction. An excess of ammonia is then added, and the secondary amine isolated by extraction with ether or by steam distillation.

(b) C-nitroso compounds.—Reduction in acid solution with zinc, iron or stannous chloride yields an amine.

$$R \cdot NO + 4H = R \cdot NH_2 + H_2O.$$

TABLE XXIX.—N-NITROSO COMPOUNDS

	B.P. °C.	Miscellaneous
Liquids		
N-Nitroso methylaniline	227d	
N-Nitroso ethylaniline	236d	
Solids	M.P.	
N-Nitroso-methyl-*p*-toluidine	53	
N-Nitroso-ethyl-β-naphthylamine	56	
N-Nitroso-benzylaniline	58	
N-Nitroso-dibenzylamine	61	
N-Nitroso-diphenylamine	66	Trace with conc. H_2SO_4 → blue colour
N-Nitroso-*m*-nitromethylaniline	69	
N-Nitroso-triacetonamine	72	
N-Nitroso-methyl-β-naphthylamine	88	
N-Nitroso-phenyl-β-naphthylamine	93	
N-Nitroso-*p*-nitromethylaniline	101	
N-Nitroso-ethyl-*p*-nitroaniline	119	
N-Nitroso-piperazine	158	

TABLE XXX.—C-NITROSO COMPOUNDS (SOLIDS)

	M.P. °C.	Miscellaneous
p-Nitroso-di-*n*-propylaniline	42	
p-Nitroso-methyldiphenylamine	44	
p-Nitroso-benzylethylaniline	62	
p-Nitroso-methylethylaniline	66	
Nitrosobenzene	68	
p-Nitroso-diethylaniline	84	Oxid. with $KMnO_4$ → *p*-nitro-diethylaniline, M.P. 77° C.
p-Nitroso-dimethylaniline	85	Oxid. with $KMnO_4$ → *p*-nitro-dimethylaniline, M.P. 163° C.
p-Nitroso-dibenzylaniline	91	
α-Nitroso-β-naphthol	109	Dil. HNO_3 in cold → α-nitro-β-naphthol, M.P. 103° C. In AcOH—reddish-brown ppt. with cobalt salts
p-Nitroso-methylaniline	116	
p-Nitroso-phenol	125d	Acetyl deriv., M.P. 107° C.
o-Nitroso-nitrobenzene	126	
p-Nitroso-diphenylamine	145	
β-Nitroso-α-naphthol	152d	
p-Nitroso-*m*-cresol	153	
Nitroso-thymol	162	
p-Nitroso-*m*-hydroxydimethyl-aniline	169	
4-Nitroso-1-naphthol	201d	

GROUP II—CLASS VII

TERTIARY AMINES, HETEROCYCLIC BASES

This class includes the aliphatic and aromatic tertiary amines together with the heterocyclic bases, e.g. pyridine and quinoline. Such compounds are generally soluble in acid, being reprecipitated by adding excess alkali.

Those aromatic tertiary amines with the *para*-position unoccupied will have been indicated in the nitrous acid test for primary aromatic amines (see p. 125) when *p*-nitroso compounds are formed.

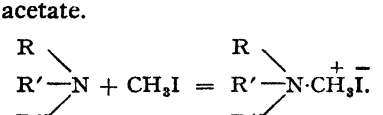
Classification test.—To 0·5 g. of the original compound add 0·5 g. of methyl iodide and allow to stand for 5 min. Heat for a further 5 min. in a water bath and then cool in ice, scratching the sides of the test-tube with a glass rod. If the mixture solidifies, then the substance is of this class. Confirm by dissolving the quaternary ammonium salt in water and shaking with a slight excess of silver oxide. Filter and test the filtrate with litmus. If strongly alkaline, due to the presence of a quaternary ammonium hydroxide, the original compound is a tertiary amine.

Additional tests.—1. Dissolve about 0·5 g. of the substance in 2 ml. of dry ether and saturate with *dry* hydrochloric acid gas. Tertiary amines give a precipitate of the hydrochloride which in some cases may be used as a derivative.

2. Dissolve the substance in dilute hydrochloric acid and add Nessler's solution. A white precipitate is given by most tertiary amines and heterocyclic bases, including alkaloids.

Derivatives

1. **Quaternary ammonium iodide.**—Prepared as in the classification test above, or by dissolving a small quantity of the amine in the minimum amount of *dry* ether, adding a slight excess of methyl iodide and allowing to stand for 15 min. The derivative should be recrystallized from dry alcohol/ether mixture, dry acetone or ethyl acetate.



2. Addition compound with picric acid or 1 : 3 : 5-trinitrobenzene.—See corresponding derivative for hydrocarbons (p. 91).

3. *p*-Nitroso derivative.—This derivative can only be prepared in the case of those tertiary aromatic amines having an unoccupied *para*-position.

Dissolve about 1 g. of the base in 1 : 1 hydrochloric acid. Cool (preferably in ice) and add, drop by drop, a concentrated solution of sodium nitrite, stirring during the addition, until free nitrous acid is present, as shown by the starch/iodide test. Filter off the coloured hydrochloride and wash with dilute hydrochloric acid. Suspend the salt in water and add an aqueous solution of sodium hydroxide till definitely alkaline. Extract with ether, wash the ethereal solution with water, dry over anhydrous sodium sulphate, and evaporate off the solvent. Determine the melting-point of the green base.

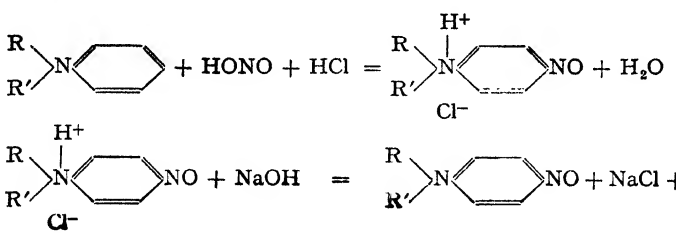


TABLE XXXI.—TERTIARY AMINES AND HETEROCYCLIC BASES

	B.P. °C.	Addition compounds			Miscellaneous
		Picrate	Methyl iodide	1 : 3 : 5-Trinitrobenzene	
Liquids					
Trimethylamine	3	216	230d		Hydrochloride, M.P. 277° C.
Triethylamine	89	173	—	—	Hydrochloride, M.P. 253° C.
Pyridine	116	167	117	—	Styphnic acid deriv., M.P. 185° C.
α-Picoline	129	169	230	—	Styphnic acid deriv., M.P. 180° C.
γ-Picoline	143	167	152		
2 : 6-Lutidine	143	161	238		
β-Picoline	144	150	92	—	Styphnic acid deriv., M.P. 153° C.
Tri-*n*-propylamine	153	116	208		
2 : 4-Lutidine	157	179	113		
2 : 5-Lutidine	160	169			
2 : 3-Lutidine	163	184	205		
3 : 4-Lutidine	164	163			
2 : 4 : 5-Trimethylpyridine	166	131			
3 : 5-Lutidine	170	229			
2 : 4 : 6-Trimethylpyridine	171	156			
2 : 3 : 6-Trimethylpyridine	177	143			
Dimethyl-*o*-toluidine	185	122	210	—	Hydrochloride, M.P. 156° C.
Dimethylaniline	193	162	228	109	*p*-Nitroso deriv., M.P. 85° C. HNO_3 in HOAc → dinitro deriv., M.P. 87° C.
Methylethylaniline	201	134	125	—	*p*-Nitroso deriv., M.P. 66° C. Hydrochloride, M.P. 114° C.
Diethyl-*o*-toluidine	206	180	224		
Dimethyl-*p*-toluidine	210	127	215	124	
Tri-*n*-butylamine	211	107	180		
Dimethyl-*m*-toluidine	212	—	177		

[*Contd. over*

TABLE XXXI—(*contd.*)

	B.P. °C.	Addition compounds			Miscellaneous
		Picrate	Methyl iodide	1 : 3 : 5-Trinitrobenzene	
Liquids					
Diethylaniline	218	142	102	42	*p*-Nitroso deriv., M.P. 84° C.
Diethyl-*p*-toluidine	229	—	184	—	Hydrochloride, M.P. 157° C.
Quinoline	238	203	72	—	Styphnic acid deriv., M.P. 207° C. Dichromate, M.P. 165° C.
Di-*n*-propylaniline	245	125	156	—	*p*-Nitroso deriv., M.P. 42° C.
Tri-*iso*-amylamine	245	125			
Quinaldine	247	191	195	—	Boiling with conc. HNO_3 → nitroquinaldinic acid, M.P. 219° C. Dichromate, M.P. 110° C.
8-Methylquinoline	250	200	193	—	Styphnic acid deriv., M.P. 218° C.
7-Methylquinoline	252	237	215		
5-Methylquinoline	255	213	105		
6-Methylquinoline	258	234	219	—	Styphnic acid deriv., M.P. 201° C.
Di-*n*-butylaniline	261	125			
4-Methylquinoline (Lepidine)	263	212	174		Styphnic acid deriv., M.P. 237° C.
Dimethyl-α-naphthylamine	272	145	—	106	
Diethyl-α-naphthylamine	290	—	—	95	
Methyldiphenylamine	296	—	—	—	*p*-Nitroso deriv., M.P. 44° C.
Benzylethylaniline	299	116	161	—	*p*-Nitroso deriv., M.P. 62° C.
Dimethyl-β-naphthylamine	305	200			
Benzylmethylaniline	306	127	164		
Diethyl-β-naphthylamine	316	—	—	116	
Solids	M.P.				
3-Methylquinoline	17	187	221		Styphnate M.P. 190° C.
iso-Quinoline	24	222	159		

TABLE XXXI—(*contd.*)

	M.P. °C.	Addition compounds			Miscellaneous
		Picrate	Methyl iodide	1 : 3 : 5-Trinitrobenzene	
Solids					
Tetramethyl-*p*-phenylenediamine	51	—	265	142	
2 : 6-Dimethylquinoline	60	187	237		Styphnate, M.P. 200° C.
m-Nitro-dimethylaniline	60	119	205		
Dibenzylaniline	70	131d	135	—	*p*-Nitroso deriv., M.P. 91° C.
p-Dimethylaminobenzaldehyde	73	—	—	91	Oxime, M.P. 148° C. Phenylhydrazone, M.P. 148° C.
8-Hydroxyquinoline	75	204	143	—	Styphnic acid deriv., M.P. 193° C.
m-Hydroxydimethylaniline	85	—	182	—	*p*-Nitroso deriv., M.P. 169° C.
β-Naphthoquinoline	91	259	205	112	
Tribenzylamine	91	190	184	—	Hydrochloride, M.P. 227° C.
Acridine	108	208	224	115	
Antipyrine	113	181	—	—	Nitroso deriv., M.P. 200° C. Nitration → *p*-nitro deriv., M.P. 273° C.
6-Aminoquinoline	114	—	199	—	Styphnic acid deriv., M.P. 239° C.
Triphenylamine	127	—	—	—	Fuming HNO_3 in HOAc → trinitro deriv., M.P. 280° C. Conc. H_2SO_4 and trace of HNO_3 → violet changing to blue
2-Aminoquinoline	129	256d	247	186	
6-Nitroquinoline	149		245		Styphnate, M.P. 190° C.
4-Aminoquinoline	154†	274	224	111	†Hydrate, M.P. 70° C.
p-Nitrodimethylaniline	163				
Tetramethyldiaminobenzophenone (Michler's ketone)	174	156	105	—	Oxime, M.P. 233° C. Phenylhydrazone, M.P. 174° C.
2-Hydroxyquinoline	199				

GROUP II—CLASS VIII

ALKYL NITRITES, ALKYL NITRATES

Care must be taken to avoid inhaling the vapour of the alkyl nitrites as they have a pronounced action on the heart. Nitrates should not be heated rapidly as they are liable to decompose explosively.

Classification test.—To 5 ml. of cold 50 per cent sulphuric acid add a trace of diphenylamine and shake (the presence of a trace of nitrous acid in the sulphuric acid may produce a pale blue colour at this stage), and add one drop of the original compound. The *immediate* appearance of a deep blue colour indicates that the compound is a *nitrite*. If a deep blue colour is not immediately obtained, warm gently for one minute. Appearance of a deep blue colour indicates that the given substance is a *nitrate*.

Confirmatory tests.—(*a*) Dissolve 0·2 g. of 2-phenylindole * in boiling alcohol and add about 0·2 g. of the original substance and cool. The formation of 3-*iso*-nitroso-2-phenylindole (M.P. 280° C. on recrystallization from amyl acetate) confirms the original as an alkyl nitrite.

(*b*) Both alkyl nitrites and nitrates, on boiling with sodium hydroxide and Devarda's alloy, evolve ammonia.

Derivatives, &c.

1. *Hydrolysis.*—Hydrolysis with aqueous caustic potash as for carboxylic esters (p. 67) gives the corresponding alcohol which should be isolated and identified.

$$R{\cdot}O{\cdot}NO + KOH = R{\cdot}OH + KNO_2$$
$$R{\cdot}O{\cdot}NO_2 + KOH = R{\cdot}OH + KNO_3.$$

In the case of the nitrates, however, partial oxidation of the alcohol by the potassium nitrate may occur.

2. *Equivalent weight.*—(For nitrates only.) This value may be determined as in the case of carboxylic esters (see p. 72).

* Prepared by Hoesch's synthesis from phenylhydrazine and acetophenone in presence of zinc chloride (see p. 292).

TABLE XXXII.—NITRATES AND NITRITES

Nitrates	B.P. °C.	Nitrites	B.P. °C.
Methyl nitrate	65	Ethyl nitrite	17
Ethyl nitrate	87	*n*-Propyl nitrite	44
n-Propyl nitrate	110	*iso*-Butyl nitrite	67
iso-Butyl nitrate	123	*n*-Butyl nitrite	75
n-Butyl nitrate	136	*iso*-Amyl nitrite	99
iso-Amyl nitrate	147	*n*-Amyl nitrite	104

GROUP II—CLASS IX

PURINES

Only uric acid, caffeine, theophylline, theobromine and xanthine are dealt with.

If, in the preliminary test with sodium hydroxide, ammonia was evolved on prolonged boiling, and also on heating with soda-lime, and since compounds (with the exception of purines, nitriles and imides) which are capable of yielding ammonia under these conditions have been eliminated, a purine may be present.

Classification test.—To a small quantity of the given compound in a porcelain dish, add either sufficient concentrated nitric acid to moisten it or 5 ml. of saturated bromine water, and evaporate to dryness on the water-bath. If an orange residue remains which becomes reddish on cooling, and turns violet-red on exposure to ammonia vapour, a member of the purine group is present.

The principal reactions of the five specified substances are given below.

Uric acid.—A white crystalline solid, sparingly soluble in water, insoluble in alcohol and in ether. The aqueous solution is slightly acid. Decomposes on heating.

On boiling with Fehling's solution a white precipitate of cuprous urate is first formed, while on prolonged boiling a precipitate of cuprous oxide appears.

To a cold solution in sodium carbonate add a few drops of silver nitrate solution. A dark grey or black precipitate of silver is formed.

A solution of potassium permanganate acidified with dilute sulphuric acid is reduced in the cold.

Add 1 ml. of a very dilute solution of uric acid in caustic potash

to a cold saturated solution of phosphotungstic acid. A blue colour which fades on standing is produced.

Caffeine (1 : 3 : 7-Trimethyl xanthine).—M.P. 234° C. subl. White silky needles. Soluble in water, alcohol or benzene.

If the aqueous solution is acid to phenolphthalein, a salt of caffeine (hydrolysed in solution) is probably present. The citrate, salicylate or benzoate are the most common, and tests for the acids may be applied to the original compound.

With Dragendorf's reagent—bismuth iodide in potassium iodide—a brown precipitate is formed.

Mercurous nitrate solution gives no precipitate (distinction from theophylline).

Mercuric chloride solution gives an immediate white crystalline precipitate. Phosphomolybdic acid gives a yellow precipitate.

Theophylline (1 : 3-Dimethyl xanthine).—M.P. 264° C. Readily soluble in warm water to yield a neutral solution.

Mercurous nitrate solution gives a white precipitate when added to an aqueous solution.

Aqueous bromine slowly gives a crystalline precipitate.

Dragendorf's solution (see Caffeine) gives a brownish black precipitate.

Theobromine (3 : 7-Dimethyl xanthine).—M.P. 290° C. subl. Sparingly soluble in water to give a neutral solution.

To a solution of the substance in dilute nitric acid add silver nitrate solution. A white crystalline precipitate is slowly formed.

Dragendorf's reagent (see Caffeine) gives a slight red-brown precipitate.

Xanthine.—M.P. 360° C. Insoluble in alcohol and ether.

To a saturated aqueous solution add ammonia and silver nitrate. A white precipitate is formed.

To alkaline hypochlorite solution in a porcelain dish add a small amount of the substance. A dark green colour is formed which changes to brown and finally disappears.

GROUP II—CLASS X

NITRILES (CYANIDES)

These compounds, R·C⋮N, are unsaturated and highly reactive. The lower alkyl cyanides have a pleasant odour and are generally miscible with water; the aryl cyanides have the odour of bitter almonds and are insoluble in water.

If the preliminary tests have been carefully carried out, the possible presence of such compounds will have been indicated by the slow evolution of ammonia when boiled with sodium hydroxide.

$$R\cdot C{\vdots}N + NaOH + H_2O = R\cdot COONa + NH_3.$$

Classification test.—Prepare a solution of free hydroxylamine by dissolving about 0·5 g. of hydroxylamine hydrochloride in warm methyl alcohol and adding a small piece of sodium. When this last is completely dissolved, filter off the precipitated sodium chloride. Add 0·5 g. of the given compound and warm for several minutes. Cool and make acid to Congo red paper with hydrochloric acid. Add one drop of ferric chloride solution. A brownish red colour indicates the presence of a nitrile.

$$R\cdot C{\vdots}N + NH_2OH = R\cdot C\begin{matrix}\diagup NH_2\\ \diagdown N\cdot OH\end{matrix}$$

(amide oxime)

Confirmatory test.—(*a*) To about 0·5 g. of the given substance add 5 ml. of 2N caustic soda and 5–10 drops of 100 volume hydrogen peroxide. Rapid liberation of ammonia in the cold (or on warming) confirms the presence of a nitrile.

(*b*) The following reaction relies on the reduction of nitriles to primary amines followed by the detection of the latter by the sensitive iso-cyanide reaction.

$$R\cdot C{\vdots}N + 4H = R\cdot CH_2NH_2$$
$$R\cdot CH_2NH_2 + 3NaOH + CHCl_3 = R\cdot CH_2\cdot N{:}C + 3NaCl + 3H_2O.$$

Dissolve *one drop* of the original compound in about 5 ml. of alcohol and add a small piece of sodium. When this has completely reacted, add a few drops of chloroform and warm the solution. The characteristic and unpleasant odour of carbylamine indicates that the substance is a nitrile.

Note.—If iso-cyanide is formed, it should be immediately destroyed by treatment with excess concentrated hydrochloric acid.

Derivatives

1. Amide.—The following method appears to be more satisfactory for aromatic nitriles with the exception of those with substituent groups in the *ortho* position. Alkyl cyanides do not give good yields.

Treat 0·5 g. of the nitrile with 10 ml. of 20 volume hydrogen peroxide and 2 ml. of caustic soda. Allow to stand in water heated to about 40° C. Periodically give the reaction mixture a vigorous shake, and when the reaction is complete (the time may vary from ¼ hour to several hours) filter off the amide and recrystallize from water.

$$R{\cdot}CN + H_2O = RCONH_2.$$

2. Acid.—(*a*) The complete hydrolysis of alkyl cyanides can generally be carried out by refluxing with aqueous or aqueous/alcoholic sodium hydroxide.

Reflux about 1 g. of the nitrile with a solution obtained by dissolving 2 g. of caustic soda in 3 ml. of water and 10 ml. of alcohol for one hour. Remove the alcohol by distillation, dissolve the residue in a small amount of water and acidify with 50 per cent sulphuric acid. Identify the acid after separation by distillation, filtration or ether extraction.

(*b*) In the case of aryl cyanides it is more convenient to reflux about 2 g. of the nitrile with 10 ml. of 70 per cent sulphuric, 20 per cent hydrochloric or 20 per cent phosphoric acid for one hour. Water is then added and the acid filtered off. It may be purified from any amide present by dissolving in a small quantity of concentrated sodium carbonate solution, filtering and adding a slight excess of acid to the filtrate. Filter off the pure acid.

$$R{\cdot}CN + NaOH + H_2O = R{\cdot}COONa + NH_3.$$

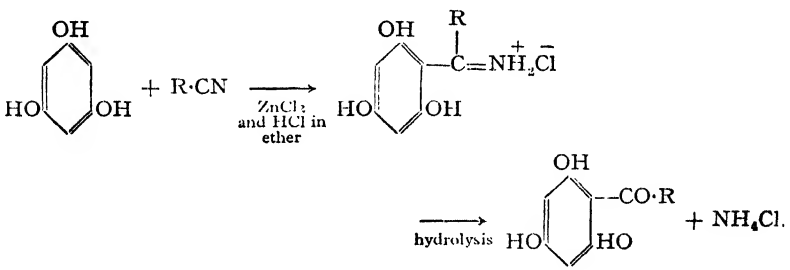
(*c*) Some aryl nitriles, especially those with substituent groups in the *ortho* position to the —CN group, are not easily hydrolysed to the acid. This may be effected by the following procedure, in which the nitrile is first hydrolysed to the amide by treatment with moderately concentrated sulphuric acid, and the amide converted to the acid by the action of nitrous acid.

Heat about 1 g. of the nitrile with about 25 ml. of 90 per cent sulphuric acid in an oil bath at 120°–130° C. for one hour. Cool, and add a slight excess of sodium nitrite dissolved in a small amount

of water, delivering it below the surface of the acid. Keep the temperature between 20° C. and 30° C. and stir after addition is complete. The mixture is then heated in a large flask until the evolution of nitrogen ceases, and then poured into water. Purify the acid as above.

$$R{\cdot}CO{\cdot}NH_2 + HO{\cdot}NO = R{\cdot}COOH + N_2 + H_2O.$$

3. **Phloracetophenone * derivative.**—Add 2 g. of powdered zinc chloride to 5 g. of phloroglucinol *, and 3 g. of nitrile in 25 ml. of *dry* ether. Dry hydrochloric acid gas is then passed through. After ½ an hour, the mixture sets to a thick paste. Set aside for several hours. Add 25 ml. of water and shake with ether, separate the two layers and boil the aqueous solution for ½ an hour. Cool, when the hydroxy-ketone will separate.



4. **Reduction to amine** followed by the preparation of a phenyl or α-naphthylthiourea.

Dissolve 1 g. of the nitrile in 20 ml. of *absolute* alcohol in a flask attached to a reflux condenser. Add small pieces of sodium (1·5 g.) through the condenser and maintain the temperature of the reaction mixture at 50°–60° C. Cool, cautiously acidify with concentrated hydrochloric acid and distil off the residual alcohol (approx. 20 ml.). Cool and add, with caution, a 50 per cent solution of caustic soda till the liquid is alkaline. Distil again almost to dryness, collecting the distillate by delivering it into about 3 ml. water. Shake this aqueous solution of the free amine vigorously with 1 ml. of phenyl or α-naphthyl isothiocyanate until solid separates. If necessary warm over a small flame for 2 min. and cool well. Recrystallize from alcohol.

For the melting-points of these derivatives see Tables XIX and XXIV.

* Pyrogallol may be substituted for phloroglucinol to yield the gallacetophenone derivative.

TABLE XXXIII.—NITRILES

	B.P. °C.	Acid	Amide	Miscellaneous
Liquids				
Acrylo-	78			
Aceto-	81	—	—	2 : 4 : 6-Trihydroxyphenyl ketone, M.P. 218° C.
Propio-	97	—	—	2 : 4 : 6-Trihydroxyphenyl ketone, M.P. 175° C.
iso-Butyro-	108			
n-Butyro-	118	—	—	2 : 4 : 6-Trihydroxyphenyl ketone, M.P. 181° C.
Allyl cyanide	118			
α-Hydroxy-*iso*-butyro-	120			
Methoxyaceto-	120			
iso-Valero-	130			
n-Valero-	141	—	—	2 : 4 : 6-Trihydroxyphenyl ketone, M.P. 149° C. (hydrate, M.P. 88° C.)
Furo-	146			
iso-Capro-	155	—	—	2 : 4 : 6-Trihydroxyphenyl ketone, M.P. 122° C. (hydrate, M.P. 104° C.)
n-Capro-	164	—	—	2 : 4 : 6-Trihydroxyphenyl ketone, M.P. 121° C. (hydrate, M.P. 96° C.)
Lacto-	182d			
Oenantho-	183			
Benzo-	191	122	128	Conc. HNO_3 and conc. H_2SO_4 → *m*-nitro deriv., M.P. 118° C.
Caprylo-	200			
o-Tolu-	205	102	142	Conc. HNO_3 and conc. H_2SO_4 → nitro deriv., M.P. 105° C.
Ethyl cyano-acetate	207			
m-Tolu-	212	110	97	
Malono-	219	133d	170	
β-Hydroxypropio-	221			
Phenylaceto- (Benzyl cyanide)	234	76	154	Conc. HNO_3 and conc. H_2SO_4 → *p*-nitro deriv., M.P. 116° C.
Cinnamo-	254	133	147	
Glutaro-	286			
Adipo-	295	152		
Solids	M.P.			
Mandelo-	21	133	—	B.P. 170° C.
p-Tolu-	29	178	158	B.P. 217° C.
α-Naphtho-	35	162	205	B.P. 299° C.

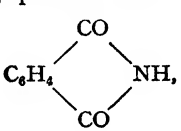
TABLE XXXIII—(*contd.*)

	M.P. °C.	Acid	Amide	Miscellaneous
Solids				
Anthranilo-	54			
Succino-	54			
Aniso-	61	184	162	
β-Naphtho-	66	186	192	
Cyanoacetic acid	66	—	—	Warm with benzaldehyde—α-cyanocinnamic acid, M.P. 180° C.
p-Hydroxybenzo-	113	213	162	
p-Nitrophenyl-aceto-	116	152	198	
m-Nitrobenzo-	118	140	142	
p-Nitrobenzo-	147	241	201	
Gallo-	233			

GROUP II—CLASS XI

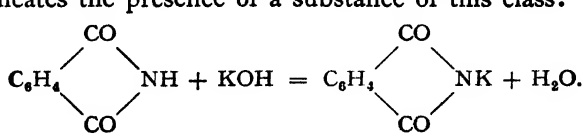
IMIDES

These compounds, e.g. phthalimide



have properties similar to those of amides, in that ammonia is evolved on boiling with sodium hydroxide.

Classification test.—To a *saturated* solution of the original compound in dioxan add a saturated solution of potassium hydroxide in alcohol. The formation of a precipitate of the potassium derivative indicates the presence of a substance of this class:



Derivatives.—1. Reflux about 1 g. of the given compound with 10 ml. of 30 per cent caustic soda, 50 per cent sulphuric acid or concentrated hydrochloric acid. In the case of alkaline hydrolysis, reaction is complete when evolution of ammonia ceases, and the

solution should then be acidified. The dibasic acid should be identified after isolation, by distillation, filtration or ether extraction.

2. **Xanthydrol derivative.**—Prepared as for simple amides (see p. 114).

TABLE XXXIV.—IMIDES

Solids	M.P. °C.	Acid	Xanthydrol deriv.
Succinimide	125	185	246
4-Nitrophthalimide	202	165	
3-Nitrophthalimide	218	218	
Phthalimide	233	195d	177

GROUP II—CLASS XII

SUBSTITUTED AMIDES

As indicated on p. 128 some compounds of this class with the structure R'NH·COR, more especially formyl and acetyl derivatives where R=H—, or CH_3—, will give a positive result in the test for primary amines. The preliminary tests with dilute or concentrated sulphuric acid will in these cases have indicated the presence of a derivative of a volatile acid such as formic or acetic, these acids being liberated by hydrolysis.

The following test should however be carried out.

Classification test.—Add to 0·5 g. of the substance 1 ml. of diethylene glycol followed by 0·5 ml. of syrupy phosphoric acid (S.G. 1·75), and 1 ml. of concentrated hydrochloric acid. Maintain the liquid just at the boil for 2 min. (the solution generally darkens somewhat). Allow to cool *in air*, add 5 ml. of dilute hydrochloric acid, boil and cool again. If a precipitate forms, filter. Treat the well-cooled solution or filtrate with 2 per cent sodium nitrite solution and note whether there is (i) an evolution of nitrogen, or (ii) the separation of an oil, indicating the presence of a primary aliphatic amino group or secondary amine respectively. If no perceptible reaction occurs, add the solution to a solution of β-naphthol in caustic soda. The formation of a coloured azo-compound, arising from a primary aromatic amine produced by hydrolysis of the original substance, indicates the presence of a substituted amide derived from a primary aromatic amine. Observations (i) and (ii) above will show the presence of a substituted

amide derived from a primary aliphatic amine or a secondary amine respectively. If, however, the original substance is definitely acid dissolving in sodium bicarbonate with effervescence, it is probably an acyl derivative of an amino-acid, e.g. hippuric acid or acetyl anthranilic acid. In this case hydrolysis will yield two acids, one of which is an amino-acid and consequently difficult to isolate. Determination of the equivalent weight of the original substance and preparation of a *p*-nitrobenzyl ester will lead to final identification.

Derivatives

1. **Hydrolysis.**—Reflux 1 g. of the substance with 20 ml. of 50 per cent sulphuric acid or concentrated hydrochloric acid (the time required varies from 30 min. to several hours according to the nature of the substituted amide). The mixture should be shaken periodically. Distil, filter off or extract with ether, to obtain the liberated acid. In the case of symmetrical di-substituted ureas, no acid will be obtained, an amine and carbon dioxide being the only products of hydrolysis. Make the residual liquid alkaline with sodium hydroxide and extract the base with ether. Identify both acid and base.

$$R'NH{\cdot}COR + H_2O = R'NH_2 + R{\cdot}COOH.$$

TABLE XXXV.—SUBSTITUTED AMIDES

The melting-points of many substituted amides will be found in Tables XIX, XXIII*a*, XXIV, XXVI and XXVII (formyl, acetyl and benzoyl derivatives of primary and secondary amines), Tables VII and VIII (anilides and toluidides of carboxylic acids), and Tables XXI and XXV (acetyl and benzoyl derivatives of amino-acids).

	M.P. °C.	
Acetoacetanilide	85	
Piperine	129	
l-Benzoyl alanine	144	
N-phenyl succinimide	156	
Acetyl methyl urea	179	
Hippuric acid (N-benzoyl glycine)	187	Amide, M.P. 183° C. Anilide, M.P. 208° C.
N-phenyl phthalimide	205	
sym-Di-*m*-tolyl urea	218	
sym-Diphenyl urea (carbanilide)	238	
sym-Di-*o*-tolyl urea	250	
sym-Di-*p*-tolyl urea	268	
sym-Di-α-naphthyl urea	298	

GROUP II—CLASS XIII

AROMATIC (TERTIARY) NITRO-COMPOUNDS, HYDRAZO COMPOUNDS, AZO-COMPOUNDS, AZOXY-COMPOUNDS

Nitro-compounds are frequently yellow or orange.
Hydrazo-compounds are colourless, but turn red in air.
Azo-compounds are invariably red or orange.
Azoxy-compounds are pale yellow.

Classification test.—Dissolve about 0·5 g. of the substance in alcohol and add a piece of tin about the size of a pin-head followed by 1 ml. of concentrated hydrochloric acid. Carry out a similar experiment without the addition of the original compound as a " blank ". Warm the solution to hasten the reduction. When all the tin has dissolved, dilute with aqueous alcohol and pass hydrogen sulphide into both solutions. If reduction of any of the above types of compound has taken place, the solution containing the original compound will give a yellow precipitate of stannic sulphide, while the " blank " will give a brownish black precipitate of stannous sulphide. Confirm reduction by filtering off the stannic sulphide, boiling off the hydrogen sulphide from the filtrate, cooling and diazotizing (p. 127). Add the diazotized solution to an alkaline solution of β-naphthol, when a coloured azo-dye should be produced.

$$R{\cdot}NO_2 + 6H + HCl = R{\cdot}NH_2{\cdot}HCl + 2H_2O$$

$$R{\cdot}NH{\cdot}NH{\cdot}R' + 2H + 2HCl = R{\cdot}NH_2{\cdot}HCl + R'NH_2{\cdot}HCl$$

$$R{\cdot}N : NR' + 4H + 2HCl = R{\cdot}NH_2{\cdot}HCl + R'NH_2{\cdot}HCl$$

$$R{\cdot}N : \underset{\underset{O}{\downarrow}}{N}{\cdot}R' + 6H + 2HCl = R{\cdot}NH_2{\cdot}HCl + R'{\cdot}NH_2{\cdot}HCl + H_2O.$$

Additional test.—Mix a small quantity of the original compound with 5 ml. of 50 per cent aqueous alcohol. Add 2 drops of calcium chloride and a pinch of zinc dust. Boil for $\frac{1}{2}$ minute. Filter into an ammoniacal solution of silver nitrate (Tollens' reagent, p. 36). Reduction (due to hydroxylamine derivative formed) to metallic silver occurs with the above-mentioned compounds.

Colour test for nitro-compounds.—Dissolve 0·1 g. of the com-

pound in 10 ml. of acetone and add 3 ml. of 5 per cent sodium hydroxide with shaking.

Mono-nitro-compounds				give no colour.
Di-	,,	,,	,,	a purplish blue.
Tri-	,,	,,	,,	a blood-red.

The presence of amino-, substituted amino- or hydroxyl groups in the nucleus interfere with the test, and acetylation of these groups will not remove the interference.

Nitro-aldehydes.—Give reactions for both the nitro- and the aldehydic group. Derivatives as for aldehydes, p. 37.

Nitro-acids.—Give reactions for both the nitro- and carboxyl groups. Reduction to the corresponding amino-acids is not recommended as a means of obtaining a derivative as isolation of such acids is difficult. See C, H and O acids for suitable derivatives, pp. 52 and 53.

Esters of these acids give a positive result in the ester test as for C, H and O compounds.

Nitro-phenols.—These give an intense yellow colour *immediately* when dissolved in alkali. All do not give a colour with ferric chloride, e.g. *o*-nitro-phenol.

Derivatives as for phenols (p. 62).

Nitro-alcohols.—Derivatives as for simple alcohols, p. 79.

Nitro-ethers.—See Table XLII for boiling- and melting-points.

Derivatives

1. **Reduction to amines.**—Suspend 1 g. of the substance in 10 ml. of concentrated hydrochloric acid and 2 ml. of alcohol. Add a few pieces of granulated tin and boil gently under a reflux condenser. When the solution becomes clear, decant from any undissolved tin and add 30 per cent caustic soda until the initial precipitate of tin hydroxide is completely dissolved. Extract the free amine with ether, dry over anhydrous sodium or magnesium sulphate and identify the amine by the preparation of a suitable derivative, e.g. benzoyl or acetyl (see pp. 130–1).

2. **Nitration to a poly-nitro-compound.**—See Hydrocarbons, p. 90.

3. **Oxidation of a side chain.**—See Hydrocarbons, p. 93.

4. **Molecular compounds with hydrocarbons, e.g.** using naphthalene (see p. 91).

TABLE XXXVI.—AROMATIC NITROHYDROCARBONS

	B.P. °C.	Benzoyl deriv. of amine	Miscellaneous
Liquids			
Nitrobenzene	209	163	Fuming HNO_3 + conc. H_2SO_4 → *m*-dinitrobenzene, M.P. 90° C.
o-Nitrotoluene	224	144	Conc. HNO_3 + conc. H_2SO_4 → 2 : 4-dinitrotoluene, M.P. 70° C.
o-Nitroethylbenzene	224	147	
2 : 6-Dimethylnitrobenzene	225	127	Fuming HNO_3 + conc. H_2SO_4 → 2 : 6-dimethyl-1 : 3 : 5-trinitrobenzene, M.P. 182° C. Oxid. → 2-nitro-*iso*-phthalic acid, M.P. 300° C.
m-Nitrotoluene	231	125	Oxid. → *m*-nitrobenzoic acid, M.P. 142° C.
2 : 5-Dimethylnitrobenzene	234	140	Fuming HNO_3 + conc. H_2SO_4 → 2 : 5-dimethyl-1 : 3 : 6-trinitrobenzene, M.P. 137° C.
2 : 4-Dimethylnitrobenzene	238	192	Warm conc. HNO_3 + conc. H_2SO_4 → 2 : 4-dimethyl-1 : 3 : 5-trinitrobenzene, M.P. 125° C. Oxid. with $KMnO_4$ → 4-nitro-*iso*-phthalic acid, M.P. 258° C.
p-Nitroethylbenzene	241	151	Fuming HNO_3 + conc. H_2SO_4 → 2 : 4 : 6-trinitroethylbenzene, M.P. 37° C.
2 : 3-Dimethylnitrobenzene	250		
2-Nitro-*p*-cymene	264	102	Conc. HNO_3 + conc. H_2SO_4 → 2 : 6-dinitrocymene, M.P. 54° C.
Solids	M.P.		
3 : 4-Dimethylnitrobenzene	29		
2-Nitrodiphenyl	37	102	
Nitromesitylene	44	204	Warm fuming HNO_3 → 2 : 4-dinitromesitylene, M.P. 86° C. Cold conc. HNO_3 + conc. H_2SO_4 → trinitromesitylene, M.P. 235° C.
2 : 5-Dinitrotoluene	50	—	Boiling dil. HNO_3 → 2 : 5-dinitrobenzoic acid, M.P. 181° C.
p-Nitrotoluene	54	158	Warm conc. HNO_3 + H_2SO_4 → 2 : 4-dinitrotoluene, M.P. 70° C.
2 : 6-Dinitro-*p*-cymene	54	—	2 : 3 : 6-Trinitro-*p*-cymene, M.P. 118° C.
3-Nitrodiphenyl	58		

TABLE XXXVI—(*contd.*)

	M.P. °C.	Benzoyl deriv. of amine	Miscellaneous
Solids			
1 : 2 : 4-Trinitrobenzene	58	—	Methylamine in alcohol → 2 : 4-dinitromethylaniline, M.P. 175° C.
2 : 6-Dinitrotoluene	60	—	Boiling dil. HNO_3 → 2 : 6-dinitrobenzoic acid, M.P. 202° C.
α-Nitronaphthalene	61	161	
2 : 4-Dinitrotoluene	70	224	Warm fuming $HNO_3 + H_2SO_4$ → 2 : 4 : 6-trinitrotoluene, M.P. 82° C.
5-Nitro-ψ-cumene	71	—	Trinitro-ψ-cumene, M.P. 185° C.
2:3-Dimethyl-1:4:5-trinitrobenzene	72		
3 : 5-Dimethylnitrobenzene	75	136	
3 : 4-Dimethyl-1 : 5-dinitrobenzene	76		
β-Nitronaphthalene	79	162	
2 : 4 : 6-Trinitrotoluene	82	—	Addition compound with naphthalene, M.P. 97° C. CrO_3 in conc. H_2SO_4 → 2 : 4 : 6-trinitrobenzoic acid, M.P. 220° C.
2 : 5-Dimethyl-1 : 3-dinitrobenzene	82		
2 : 4-Dinitromesitylene	86		
m-Dinitrobenzene	90	240	Alcoholic NH_4HS → *m*-nitroaniline, M.P. 114° C.
3 : 5-Dinitrotoluene	92	—	CrO_3 in conc. H_2SO_4 → 3 : 5-dinitrobenzoic acid, M.P. 202° C.
1 : 4-Dimethyl-2 : 3-dinitrobenzene	93		
2 : 4-Dimethyl-1 : 3-dinitrobenzene	93	—	Warm conc. HNO_3 + conc. H_2SO_4 → 2 : 4-dimethyl-1 : 3 : 5-trinitrobenzene, M.P. 125° C.
2 : 4 : 5-Trinitrotoluene	104		
2 : 4 : 6-Trinitrocumene	109		
4-Nitrodiphenyl	113	233	CrO_3 in HOAc → *p*-nitrobenzoic acid, M.P. 241° C.
1 : 2-Dimethyl-4 : 5-dinitrobenzene	115		
o-Dinitrobenzene	117	301	Alcoholic NH_4HS → *o*-nitroaniline, M.P. 71° C.

[*Contd. over*

TABLE XXXVI—(*contd.*)

	M.P. °C.	Benzoyl deriv. of amine	Miscellaneous
Solids			
1 : 3 : 5-Trinitrobenzene	122	—	See addition compounds with aryl amines, Table XXIV, p. 136.
1 : 4-Dimethyl-2 : 6-dinitrobenzene	123		
1:4-Dimethyl-2:3:5-trinitrobenzene	137		
1 : 8-Dinitronaphthalene	170	—	Boiling fuming HNO_3 + conc. H_2SO_4 → 1 : 3 : 8-trinitronaphthalene, M.P. 218° C.
p-Dinitrobenzene	172	300	Boiling 5 per cent NaOH → *p*-nitrophenol, M.P. 114° C. Naphthalene in HOAc → addition compound, M.P. 118° C.
1:3-Dimethyl-2:4:6-trinitrobenzene	182		
4 : 4′-Dinitrodiphenylmethane	183		
1 : 5-Dinitronaphthalene	214	—	Boiling with excess fuming HNO_3 and conc. H_2SO_4 → 1 : 4 : 5-trinitronaphthalene, M.P. 154° C.
4 : 4′-Dinitrodiphenyl	232	352	
Trinitromesitylene	235		

TABLE XXXVII.—AZO-COMPOUNDS

	M.P. °C.		M.P. °C.
2 : 2′-Azotoluene	55	*m*-Nitrobenzeneazoresorcinol	175
Azobenzene	68	β-Naphthaleneazo-β-naphthol	176
4-Phenylaminoazobenzene	82	4-Methylaminoazobenzene	180
Benzeneazo-*m*-cresol	108	2-Methoxybenzeneazo-β-naphthol	180
4-Dimethylaminoazobenzene	116	αα′-Azonaphthalene	190
2 : 4-Diaminoazobenzene	118	3-Nitrobenzeneazo-β-naphthol	193
4-Aminoazobenzene	126	*p*-Nitrobenzeneazoresorcinol (" Magneson ")	198
Benzeneazo-*o*-cresol	128	4-Nitro-4′-aminoazobenzene	204
o-Tolueneazo-β-naphthol	131	2-Nitrobenzeneazo-β-naphthol	209
Benzeneazo-β-naphthol	134	3-Nitro-4′-aminoazobenzene	212
p-Tolueneazo-β-naphthol	134	α-Naphthaleneazo-β-naphthol	229
4-Phenoxybenzeneazo-β-naphthol	139	4-Nitro-4′-dimethylaminoazobenzene	230
m-Tolueneazo-β-naphthol	140	4-Nitrobenzeneazo-β-naphthol	249
4 : 4′-Azotoluene	144		
4-Nitro-4′-phenylaminoazobenzene	151		
Benzeneazophenol	152		
Benzeneazoresorcinol	172		
4-Amino-αα′-azonaphthalene	173		

AZOXY-COMPOUNDS

	M.P. °C.
Azoxybenzene	36
o-Azoxytoluene	60
p-Azoxytoluene	75

HYDRAZO-COMPOUNDS

	M.P. °C.
Hydrazobenzene	130
p-Hydrazotoluene	129
o-Hydrazotoluene	165

TABLE XXXVIII.—NITRO-ALDEHYDES AND NITRO-KETONES

	M.P. °C.	Oxime	Semicarbazone	Phenylhydrazone	2 : 4-Dinitrophenylhydrazone	Miscellaneous
o-Nitrobenzaldehyde	44	102	256	153	247d	$KMnO_4$ → *o*-nitrobenzoic acid, M.P. 146° C.
m-Nitrobenzaldehyde	58	118	246	120	289d	$KMnO_4$ → *m*-nitrobenzoic acid, M.P. 140° C.
2 : 4-Dinitrobenzaldehyde	72	128	265d	228	258	
p-Nitroacetophenone	80	174	—	132		
m-Nitroacetophenone	81	132	257	135		
p-Nitrobenzaldehyde	106	129	220	155	320	$K_2Cr_2O_7$ + dil. H_2SO_4 → *p*-nitrobenzoic acid, M.P. 241° C.
m-Nitrocinnamaldehyde	116	—	—	160	292	
2 : 4 : 6-Trinitrobenzaldehyde	119	158	214	202	208	
2 : 6-Dinitrobenzaldehyde	123	115	217	159	233	
o-Nitrocinnamaldehyde	127	134 (anti) 140 (syn)	208	157	250	
p-Nitrocinnamaldehyde	141	179 (anti)	—	180	320	

TABLE XXXIX.—NITRO-CARBOXYLIC ACIDS AND ANHYDRIDES

	M.P. °C.	Equivalent weight	Amide	Anilide	*p*-Nitrobenzyl ester	*p*-Bromophenacyl ester	Miscellaneous
m-Nitrophenylacetic acid	120	181	110				
3-Nitrosalicylic acid (hydrated)	125	201	145				
m-Nitrobenzoic acid	140	167	142	154	141	132	*p*-Toluidide, M.P. 162° C.
o-Nitrophenylacetic acid	141	181	161				S.B.T. deriv., M.P. 162° C.
3-Nitrosalicylic acid (anhydrous)	144	183	145				
o-Nitrobenzoic acid	146	167	174	155	112	101	S.B.T. deriv., M.P. 159° C.
p-Nitrophenylacetic acid	152	181	198	—	—	207	
3-Nitrophthalic anhydride	162	96·5					See Table XII
4-Nitrophthalic acid	165	105·5	200d	192			
3 : 5-Dinitrosalicylic acid	173	288					
2 : 4-Dinitrobenzoic acid	183	212	203	—	142	158	
2 : 4-Dinitrophenylacetic acid	189	226		181			
m-Nitrocinnamic acid	199	193	196	—	174	178	
3 : 5-Dinitrobenzoic acid	202	212	183	234	157		S.B.T. deriv., M.P. 171° C.
3 : 5-Dinitro-2-methylbenzoic acid	206	226					
3-Nitrophthalic acid	218	105·5	201	234	190		
2 : 4 : 6-Trinitrobenzoic acid	220d	257	264d				
5-Nitrosalicylic acid	229	183	225	224			
o-Nitrocinnamic acid	240	193	185	—	132	141	
p-Nitrobenzoic acid	241	167	201	211	168	134	*p*-Toluidide, M.P. 203° C.
2-Nitroterephthalic acid	264	105·5					S.B.T. deriv., M.P. 186° C.
p-Nitrocinnamic acid	285	193	204	—	187	191	

TABLE XL.—ESTERS OF NITRO-ACIDS

	B.P. °C.	Equivalent weight
Liquids		
Methyl *o*-nitrobenzoate	275	181
Solids	M.P.	
Ethyl *o*-nitrobenzoate	30	195
Ethyl 2 : 4-dinitrobenzoate	41	240
Ethyl *o*-nitrocinnamate	42	221
Diethyl 3-nitrophthalate	45	133·5
Ethyl *m*-nitrobenzoate	47	195
Ethyl *p*-nitrobenzoate	57	195
Dimethyl 3-nitrophthalate	69	119·5
Methyl 2 : 4-dinitrobenzoate	70	226
Methyl *o*-nitrocinnamate	72	207
Methyl *m*-nitrobenzoate	78	181
Ethyl *m*-nitrocinnamate	78	221
Ethyl 3 : 5-dinitrobenzoate	92	240
Methyl *p*-nitrobenzoate	96	181
Ethyl 3 : 5-dinitrosalicylate	99	256
Methyl 3 : 5-dinitrobenzoate	107	226
Methyl 5-nitrosalicylate	117	215
Ethyl 5-nitrosalicylate	118	229
Ethyl 3-nitrosalicylate	118	229
Methyl *m*-nitrocinnamate	123	207
Methyl 3 : 5-dinitrosalicylate	127	242
Ethyl *p*-nitrocinnamate	136	221
Ethyl 2 : 4 : 6-trinitrobenzoate	155	285
Methyl 2 : 4 : 6-trinitrobenzoate	157	271
Methyl *p*-nitrocinnamate	161	207

Table XLI.—NITRO-PHENOLS

	M.P. °C.	Acetyl deriv.	Benzoyl deriv.	α-Naphthyl urethane	Phenyl urethane	*p*-Toluene sulphonyl deriv.	*p*-Nitro-benzyl ether	Bromo deriv.	Miscellaneous
o-Nitrophenol	45	40	59	113	126	83	130	117	
2 : 6-Dinitrothymol	55								
2-Nitroresorcinol	83								
2-Hydroxy-3 : 5-dinitro-toluene	86	95							
m-Nitrophenol	97	56	95	167	129	—	—	91	
1-Nitro-2-naphthol	103	61	142						
3-Hydroxy-2 : 4 : 6-trinitro-toluene	110								
p-Nitrophenol	114	82	142	151	148	97	187	142	
2 : 4-Dinitrophenol	114	72	132	—	—	121	209	118	
4-Nitro-2-naphthol	120	—	—	—	—	122			
Picric acid	122	76	—	—	—	—	—	—	Addition compound with naphthalene, M.P. 149° C.
2-Nitro-1-naphthol	127	118							
2 : 4-Dinitro-1-naphthol	138	—	174						
2 : 4-Dinitroresorcinol	148	—	—	—	—	126 (mono)			
5-Nitro-1-naphthol	171	114	109						

TABLE XLII.—NITRO-ETHERS

	B.P. °C.	Miscellaneous
Liquids		
o-Nitroanisole	265	Warm conc. HNO_3 + conc. H_2SO_4 → 2 : 4 : 6-trinitroanisole, M.P. 68° C.
o-Nitrophenetole	268	Cold conc. HNO_3 + conc. H_2SO_4 → 2 : 4-dinitrophenetole, M.P. 86° C.
Solids	M.P.	
m-Nitrophenetole	33	
m-Nitroanisole	38	
2-Nitro-3-methoxytoluene	51	
p-Nitroanisole	54	Fuming HNO_3 at o° C. → 2 : 4-dinitroanisole, M.P. 88° C.
p-Nitrophenetole	59	Cold conc. HNO_3 + conc. H_2SO_4 → 2 : 4-dinitrophenetole, M.P. 86° C.
2 : 4 : 6-Trinitroanisole	68	Boiling dil. NaOH → picric acid, M.P. 122° C.
2 : 4 : 6-Trinitrophenetole	78	
2 : 4-Dinitrophenetole	86	
2 : 4-Dinitroanisole	88	Warm conc. HNO_3 + conc. H_2SO_4 → 2 : 4 : 6-trinitroanisole, M.P. 68° C.
4 : 4′-Dinitrodiphenylether	143	

TABLE XLIII.—NITRO-ALCOHOLS

	M.P. °C.	Benzoate	Product of oxidation	
m-Nitrobenzyl alcohol	27	94	140	
o-Nitrobenzyl alcohol	74	101	144	
p-Nitrobenzyl alcohol	93	94	241	Acetate, M.P. 78° C.

GROUP II—CLASS XIV

ALKALOIDS

In certain cases the preliminary tests will have indicated the presence of compounds of this class. Direct information from the instructor or the circumstances calling for identification will usually show whether examination for alkaloids is necessary.

General properties.—Nearly all alkaloids are crystalline solids —a few, e.g. nicotine and coniine, are liquids, volatile in steam.

The majority of alkaloids are optically active, but the specific rotatory power of the free base may be different from that of its salts in the same solvent, and the two may even have opposite signs.

Most of the common alkaloids are insoluble or very sparingly soluble in water, alcohol being the best solvent. In aqueous solution they are often strongly alkaline.

In general, alkaloidal salts are more or less readily soluble in water and in alcohol, but as a rule not in ether or chloroform. Addition of a dilute solution of sodium hydroxide or sodium carbonate to an aqueous solution of such salts usually precipitates the free base. In a few cases, e.g. morphine, the alkaloid is soluble in excess of alkali.

Classification tests.—*All* the following tests must be carried out on the given substance, only the immediate formation of a precipitate being of significance. As a result its identity will be reduced to two or three possibilities, confirmatory tests being then applied, as indicated under the individual alkaloids, to achieve final identification.

Test 1.—To 2 ml. of a 1 per cent solution of the compound in N/10 hydrochloric acid (or a saturated solution if less soluble) add a few drops of *Mayer's reagent*—13·5 g. mercuric chloride and 50 g. potassium iodide in 940 ml. water.

Test 2.—To a solution of the compound prepared as in Test 1 above, add a few drops of a 5 per cent solution of *potassium ferrocyanide.*

Test 3.—To a solution of the compound prepared as in Test 1 above, add a few drops of a 5 per cent aqueous solution of *potassium chromate.*

TABLE XLIV.—ALKALOIDS

	B.P. °C.	1	2	3	4	5	Picrate	Styphnate	Common salts
Liquids									
Coniine	167	+			+	N.I.R.	75	—	Hydrochloride, M.P. 208° C.
Nicotine	247	+			+	I.R.	218	190	Salicylate; sulphate
Hyoscine	—	+			+	N.I.R.	188	—	Hydrobromide
Solids	M.P.								
Ephedrine	35–42					—	—	—	Hydrochloride, M.P. 217° C.; sulphate
Quinine	67 (hyd.) 172 (anhyd.)	+		+	+	I.R.	132	154	Hydrochlorides; hydrobromides; sulphate; citrate; benzoate; arsenate; acetyl salicylate, M.P. 157° C.; ethyl carbonate
Emetine	74		+	+	+	—	—	—	Hydrochloride
Cocaine	98	+		+	+	violet ppt.	155	187	Hydrochloride, M.P. 200–202° C.; sulphate; nitrate

Hyoscyamine	>107	+			+	N.I.R.	165	—	Hydrobromide, M.P. 152° C.; sulphate, M.P. >203° C.
Atropine	115	+			+	N.I.R.	175	180	Hydrochloride, M.P. 165° C.; hydrobromide, M.P. 162° C.; sulphate, M.P. 196° C.; salicylate
Papaverine	147	+	+	+	+	—	179d	—	Hydrochloride, M.P. 210–220° C.; sulphate
Codeine	155	+			+	I.R.	197	115	Hydrochloride, M.P. 264° C.; sulphate; phosphate
Quinidine	168 ca.	+	+	+	+	—	—	149	Sulphate; hydrochloride (anhydrous), M.P. 259° C.
Diamorphine (Heroin)	169	+		+	+	—	205	222	Hydrochloride, M.P. 233° C.
Brucine	177	+			+	I.R.	280	266	
Cinchonidine	210	+	+	+	+	I.R.	209	—	Sulphate, M.P. 207° C. ca.
Morphine	>230	+			+	white ppt.	228	189	Hydrochloride; sulphate; tartrate; acetate, M.P. 200° C. ca.
Cinchonine	255	+	+	+	+	I.R.	194	106	Hydrochloride (anhydrous), M.P. 218° C.
Strychnine	268	+	+	+	+	—	286	266	Hydrochloride; nitrate; sulphate, M.P. 200° C. ca.
Apomorphine	—	+	+	+	+	—	—	—	Hydrochloride

Test 4.—To a solution of the compound prepared as in Test 1 above, add a saturated solution of *picric acid*. A melting-point determination of the resulting picrate serves as a useful guide to identification.

Test 5.—To a neutral saturated solution of the original substance add a few drops of a solution of N/10 *potassium permanganate*.

In Table XLIV, col. 5, I.R. indicates immediate reduction, N.I.R., no immediate reduction. In cols. 1–4, + indicates immediate formation of a precipitate.

The styphnic acid derivative may be prepared in the same way as for hydrocarbons (see p. 92).

Coniine.—An almost colourless liquid becoming brown on exposure to air. Soluble in ether, alcohol or chloroform.

$$[\alpha]_D + 15{\cdot}7°.$$

Aurichloride.—Dissolve 0·05 g. of the alkaloid in 5 ml. of water and add one drop of dilute hydrochloric acid followed by a solution of gold chloride. The lemon-yellow oily precipitate, which rapidly crystallizes, is recrystallized from very dilute hydrochloric acid, M.P. 75° C.

Nicotine.—A hygroscopic, colourless or yellowish brown liquid, with the unpleasant odour of stale burnt tobacco. Soluble in water, alcohol or ether. Refractive index 1·530 at 15° C.

Hyoscine.—Usually a syrupy liquid. Gives the Vitali test (see Atropine). $[\alpha]_D$ of a 5 per cent aqueous solution of the anhydrous hydrobromide, prepared by drying the crystalline salt at 100° C. is −24°.

Aurichloride.—Prepared as for coniine, M.P. 198°–200° C.

Ephedrine.—$[\alpha]_D^{22°\,C.}$ in water +13·75°. If a solution of the base in chloroform be set aside overnight, crystals of the hydrochloride separate out, M.P. 217° C. If a neutral solution of the alkaloid be treated with two drops of a dilute solution of copper sulphate and 5 ml. of a 20 per cent solution of caustic soda, a violet colour is produced. On shaking the resulting solution with ether, the ether layer becomes red and the aqueous layer blue. If the base be heated with potassium ferricyanide and caustic soda, benzaldehyde is produced.

Nitrosamine (see p. 125), M.P. 92° C.

Dibenzoate (see p. 131), M.P. 131° C. $[\alpha]_D^{20°}$ of a 5 per cent solution of the hydrochloride in water is −33° to −36°.

Quinine.—A white flaky powder. Dilute solution in dilute

sulphuric or acetic acid shows a blue fluorescence which may be weakened or even destroyed by the addition of halides, ferrocyanide or thiosulphate.

Thalleioquin reaction.—To a faintly acid solution of quinine add dilute bromine water drop by drop *until a slight excess is present*, then add an excess of dilute ammonium hydroxide. An emerald-green coloration or precipitate is produced. Quinidine also gives this test.

Ferricyanide reaction.—Treat a faintly acid solution with dilute bromine water as in the thalleioquin reaction. Add one drop of a freshly prepared solution of potassium ferricyanide followed by dilute ammonia. A rose-red coloration is produced. Quinidine also gives this reaction.

To 1 ml. of a cold saturated solution of Rochelle salt add 1 ml. of a very dilute, faintly acid solution of the base or salt. Shake vigorously. A white crystalline precipitate is formed. Quinidine does not give this test.

With concentrated sulphuric acid quinine gives a pale green colour.

Emetine.—A colourless, amorphous powder readily soluble in ether or chloroform; almost insoluble in water. It rapidly becomes yellow on exposure to air. $[\alpha]_D$ in chloroform $-50°$. $[\alpha]_D$ of the hydrochloride in chloroform $+53°$.

Sprinkle some of the powder on to Fröhde's reagent (1 g. of ammonium molybdate in 100 ml. of concentrated sulphuric acid). A bright green colour is produced.

Cocaine.—Occurs as large colourless crystals or as a white crystalline powder. The test with potassium permanganate (Test 5 above), whereby cocaine gives a characteristic violet precipitate, and the following tests should be carried out on the hydrochloride. The alkaloid may be converted into the hydrochloride by dissolving in alcohol, neutralizing with N/2 hydrochloric acid to methyl red and evaporating to dryness.

Pisani's test.—Heat the hydrochloride with a few drops of concentrated sulphuric acid containing 2 per cent formamide. A wine-red colour is obtained which disappears to give a brownish grey precipitate.

Reichard's test.—To a solution of a cocaine salt containing at least 0·004 g. cocaine per ml. add a concentrated solution of sodium nitroprusside drop by drop. A precipitate consisting of reddish crystals is formed. This precipitate dissolves on warming and reappears on cooling.

Hyoscyamine.—Is very soluble in chloroform but only slightly soluble in ether. $[\alpha]_D$ of a 5 per cent solution in 50 per cent alcohol $-21°$. Gives Vitali's test as for atropine.

Aurichloride.—Prepared as for coniine, M.P. 165° C. The sulphate is a deliquescent crystalline solid very soluble in water. A 4 per cent aqueous solution of the sulphate gives $[\alpha]_D$ $-27{\cdot}8°$.

Atropine.—Occurs as colourless crystals or as a white crystalline powder. In alcoholic solution atropine is optically inactive.

Vitali's test.—Evaporate 0·01 g. to dryness on a water-bath with 5 drops of concentrated nitric acid, cool and moisten the residue with a freshly prepared solution of potassium hydroxide in methyl alcohol. A violet colour is produced. This colour is also given by hyoscine and hyoscyamine, while strychnine gives a similar colour.

Aurichloride.—Prepared as for coniine, M.P. 138° C. The picrate is only precipitated from concentrated solutions of the base in dilute acid. It may be recrystallized from acetone, M.P. 175° C.

Papaverine.—Fröhde's reagent (see Emetine) gives a deep blue colour.

Codeine.—A colourless crystalline compound soluble in excess ammonium hydroxide but insoluble in sodium or potassium hydroxide.

Dissolve 0·1 g. of the base or salt in 1 ml. of cold concentrated sulphuric acid and gently warm the resulting colourless solution with a trace of ferric chloride solution. A blue colour is produced; this changes to red and then yellow on the addition of a drop of dilute nitric acid.

Moisten a little codeine with formalin and add 5 drops of concentrated sulphuric acid. Shake. A violet-blue colour is produced immediately. Morphine and diamorphine give a violet-red solution changing to violet-blue.

Fröhde's reagent (see Emetine) gives an immediate green colour.

Quinidine.—Gives reactions similar to quinine except with Rochelle salt.

Diamorphine (diacetyl morphine, heroin).—Fröhde's reagent (see Emetine) gives a violet colour immediately (as for morphine).

Test with formalin and concentrated sulphuric acid (see Codeine).

Dissolve 0·1 g. in 1 ml. sulphuric acid by warming on a water-bath. Cool and dilute with 6 ml. of water. Add a 0·5 per cent

solution of potassium ferricyanide to which one drop of ferric chloride has been added. A deep blue colour is produced. Morphine gives this test even when the preliminary heating with sulphuric acid is omitted.

Diamorphine does not give the colour tests with potassium iodate and ferric chloride (see Morphine).

Brucine (dimethoxy strychnine).—Occurs as a white crystalline powder or colourless crystals. It contains four molecules of water of crystallization, the anhydrous form melting at 177° C.

Add one drop of nitric acid to a trace of the alkaloid. A blood-red colour is produced which becomes yellow on heating. Cool and treat with stannous chloride or sodium thiosulphate when a purple colour develops.

On warming with sodium in alcohol at 80° C. brucinic acid, M.P. 245° C., is formed.

Picrolonate (see p. 91), M.P. 256° C.

Cinchonidine.—A white crystalline compound.

Rochelle salt (see Quinine) gives a white crystalline compound, thus distinguishing it from cinchonine and quinidine. Cinchonidine, however, does not give the thalleioquin reaction for quinine.

The methiodide (see p. 147), formed at room temperature in alcoholic solutions after 24 hours, crystallizes out as colourless crystals, M.P. 248° C.

The sulphate shows a very slight blue fluorescence.

Morphine.—Forms white needle-shaped crystals.

Morphine being a phenol dissolves in sodium, potassium and calcium hydroxides but not in ammonium hydroxide. $[\alpha]_D$ in sodium hydroxide −70° ca.

Fröhde's reagent (see Emetine) gives immediate violet colour.

With nitric acid, morphine gives an orange-red colour.

A neutral solution of ferric chloride when added to a solution of the hydrochloride produces a greenish blue colour. Diamorphine and codeine give no colour.

The addition of 2 ml. of a 1 per cent solution of potassium iodate to an acid solution of morphine gives a brown colour due to liberated iodine. The addition of chloroform to the solution produces a violet layer. Diamorphine does not give this test.

To a solution of the alkaloid in N/10 hydrochloric acid add sodium nitrite followed by ammonia. A yellowish brown colour is formed.

Cinchonine.—Occurs as shining prisms or needles.

An M/40 solution in N/10 hydrochloric acid gives $[\alpha]_D$ +264°.

The methiodide (see p. 147), M.P. 254° C., only crystallizes with difficulty. On heating cinchonine hydrochloride in a dry test-tube purple vapours are evolved.

Strychnine.—Occurs as a white crystalline powder. $[\alpha]_D$ in alcoholic solution −133°.

Mandelin's reagent (one per cent ammonium vanadate in concentrated sulphuric acid) gives a deep violet-blue colour, changing to a deep purple on standing, and to a cherry-red on diluting with water.

Dissolve a crystal of the alkaloid in a drop of sulphuric acid on a plate and add a small crystal of potassium dichromate. A violet colour is produced.

Bromostrychnine, M.P. 222° C., is formed when the theoretical amount of bromine water is added to a dilute aqueous solution of the hydrochloride and then made alkaline with ammonium hydroxide.

Apomorphine.—On adding ammonium persulphate and sodium bicarbonate to an aqueous solution of the hydrochloride and shaking with chloroform the latter becomes red or violet.

Nitric acid gives a purple colour.

Solutions in sodium hydroxide rapidly become red and gradually blacken.

Add gold chloride to a dilute solution of the hydrochloride. A deep red-brown precipitate is produced.

CHAPTER V

Summary of Classification Tests, Derivatives, etc., for Compounds containing Carbon, Hydrogen, Sulphur, and possibly Oxygen and a Metal

Preliminary examination

1. Physical characteristics.
2. Ignition on a crucible lid.
3. Reaction to litmus.
4. Reaction with dilute sulphuric acid.
5. Soda-lime test.

Class	Classification Tests	Additional Tests	Derivatives, &c.
Bisulphite compounds of aldehydes and ketones	Dilute sulphuric acid	2 : 4-Dinitrophenylhydrazine *For sulphoxylates.* Indigo carmine test	Isolation of aldehyde or ketone followed by preparation of deriv.
Formaldehyde sulphoxylates (p. 185)			
Thioalcohols (mercaptans)	Mercuric chloride test		Mercury salt 2 : 4 - Dinitrophenyl thio-ether
Thiophenols (p. 185)			2 : 4 - Dinitrosulphone 3:5-Dinitrobenzoate Sulphone
Thio-ethers(sulphides) (p. 188)	Mercuric chloride test	Alkalinity of sulphonium hydroxide after treatment with ethyl iodide	Sulphone
Alkyl sulphuric acids and their salts	Barium chloride test	Results of preliminary tests	*For alkyl sulphuric acids (other than methyl and ethyl) and their salts*
Dialkyl sulphates (p. 190)			S-benzylthiuronium derivative *For dialkyl sulphates* Hydrolysis products β-Naphthyl ether
Alkyl esters of sulphonic acids (p. 191)	Sodium hydroxide and phenolphthalein test		Hydrolysis products and derivs. of these

Class	Classification Tests	Additional Tests	Derivatives, &c.
Sulphonic acids and their salts **Sulphinic acids and their salts** **Carboxylic derivatives of thiophene** (p. 192)	Soda-lime test	*For sulphonic and sulphinic acids and their salts* Evolution of sulphur dioxide after soda-lime test *For sulphonic acids and their salts* Test for phenol after soda-lime test *For carboxylic derivs. of thiophene* Isatin test for thiophene on distillate from soda-lime	*For sulphonic acids and their salts* Amide. Anilide S-benzyl thiuronium salt *For sulphonic acids* Aniline salts *For carboxylic derivs. of thiophene* As for C, H and O acids
Thio- and thiol-acids and their salts (p. 196)	Dilute mineral acid	Hydrolysis and tests for acetic, benzoic, glycollic, salicylic and lactic acids	*For thioacetic and thiobenzoic* Anilide *For thioglycollic and thiolactic* Benzaldehyde deriv. Dithioglycollic acid
Aryl esters of sulphonic acids (p. 198)	Ester test after nitration		Dinitro deriv.
Sulphones (p. 199)	Stability to oxidizing and reducing agents	Heating with excess carbon	*For aromatic sulphones* Nitro deriv.
Metallic xanthates and diethyl dithiocarbamates (p. 200)		Molybdate test Copper sulphate test	

GROUP III

COMPOUNDS CONTAINING CARBON, HYDROGEN, SULPHUR AND POSSIBLY OXYGEN AND/OR A METAL

Preliminary examination

1. *Physical properties*

Strong garlic-like odour	A thio-alcohol (mercaptan) or thiophenol.
A sharp sulphurous odour	Probably a thio-acid or thiol-acid.
A very powerful and unpleasant odour	A thio-ether or xanthate.
Odour of an aldehyde or ketone	Probably a bisulphite compound of an aldehyde or ketone.
If yellow	Probably the copper derivative of a xanthate.

2. *Effect of ignition on a crucible lid*

A non-combustible residue remains	A metallic salt of a thio- or thiol-acid, sulphonic acid, sulphinic acid, formaldehyde sulphoxylic acid or alkyl sulphuric acid. A bisulphite compound of an aldehyde or ketone, a xanthate or metallic diethyl di-thio carbamate.

3. *Reaction to litmus*

(*a*) Acid	Thio- and thiol-acids, sulphonic and sulphinic acids, alkyl sulphuric acids, carboxylic acid derivatives of sulphur compounds, e.g. thiophene.
(*b*) Alkaline	Sulphonium hydroxides.

4. *Action of warm dilute sulphuric acid*

Hydrogen sulphide evolved (lead acetate paper) and an organic acid or phenol formed	Thio-acid or thiophenol.
Precipitation of a metallic sulphide	Heavy metal salt of a thio-acid.
Garlic-like odour of a thioalcohol	Thioalcohol or metallic derivative of a thioalcohol.
Carbon disulphide and alcohol evolved	Xanthate.
Odour of an alcohol	Dialkyl sulphate, alkyl sulphuric acid or salt of such an acid.
Sulphur dioxide and odour of aldehyde or ketone	Bisulphite compound of aldehyde or ketone.
Sulphur dioxide and odour of alcohol	Alkyl sulphite.
Evolution of sulphur dioxide and formaldehyde, together with the precipitation of sulphur (requires acid stronger than 2N, approx. 3 parts of concentrated acid to 1 part water)	Formaldehyde sulphoxylate (sodium and zinc salts are the only common ones).

5. *Soda-lime test*

Odour of a hydrocarbon	Thio-acid or sulphinic acid.
Odour of alcohol	Aliphatic sulphonic acid or sulphonate, alkyl sulphuric acid.
Odour of phenol	Aromatic sulphonic acid or sulphonate.
Sublimate of metallic mercury	Mercury derivative of thioalcohol.

GROUP III—CLASS I

BISULPHITE COMPOUNDS OF ALDEHYDES AND KETONES. FORMALDEHYDE SULPHOXYLATES

The preliminary examination with dilute sulphuric acid will have indicated the probable presence of such compounds.

Classification tests.—(*a*) Add dilute sulphuric acid (1 ml. concentrated sulphuric acid : 3 ml. water) to some of the given compound and test for the evolution of sulphur dioxide with potassium dichromate paper. When all sulphur dioxide has been evolved, test for the presence of aldehyde or ketone in the residual liquid by means of 2 : 4-dinitrophenylhydrazine (see p. 36).

(*b*) In test (*a*) sulphoxylates produce sulphur in addition to sulphur dioxide and formaldehyde. On adding to a solution of indigo carmine acidified with dilute sulphuric acid, sulphoxylates discharge the colour.

Derivatives, etc.

Distil about 2 g. of the original compound with sodium carbonate solution. Collect the distillate and test for aldehyde or ketone (see p. 36). If the distillate contains no aldehyde or ketone, extract the alkaline liquid in the flask (after cooling) with ether. Separate and dry the ether layer. Distil off the ether and identify the residual carbonyl compound by the preparation of suitable derivatives (see p. 37).

Note.—Ketones with the carbonyl group attached to a benzene ring, e.g. acetophenone, do not form bisulphite compounds.

GROUP III—CLASS II

THIOALCOHOLS, THIOPHENOLS

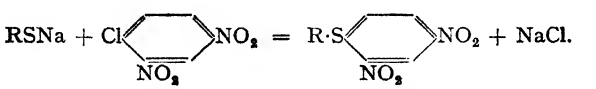
Classification test.—To the original compound add mercuric chloride solution. Formation of a colourless precipitate while an acid reaction develops in the solution indicates a thioalcohol or thiophenol.

$$RSH + HgCl_2 = R{\cdot}S{\cdot}HgCl + HCl.$$

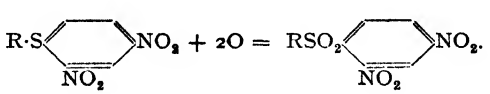
Derivatives

1. **Mercury salt.**—To a solution of the substance in 2 ml. of alcohol add an excess of a 10 per cent solution of mercuric cyanide. Filter off the precipitated mercury salt, recrystallize from alcohol and determine the melting-point

2. **2 : 4-Dinitrophenyl thio-ether.**—Mix a solution of 1 g. of the mercaptan in 30 ml. of alcohol with 0·4 g. of sodium hydroxide dissolved in 3 ml. of water and 2 g. of 2 : 4-dinitrochloro-benzene in 10 ml. of alcohol. Heat on a water-bath for 10 min. Filter while still hot. The thio-ether crystallizes out on cooling. Filter and recrystallize from alcohol.



3. **2 : 4-Dinitrosulphone.**—Add a 3 per cent aqueous solution of potassium permanganate (50 per cent excess over the theoretical) to a solution of 0·01 g. mol. of the 2 : 4-dinitrophenyl thio-ether (prepared as in Derivative 2 above) in glacial acetic acid. If the thio-ether tends to precipitate, add more acetic acid. Remove the excess permanganate by passing sulphur dioxide into the solution. Cooling in ice precipitates the sulphone which is recrystallized from absolute alcohol.



4. **3 : 5-Dinitrobenzoate.**—Mix about 1 ml. of the thioalcohol or thiophenol with about 0·5 g. of 3 : 5-dinitrobenzoyl chloride and 1 ml. of pyridine and boil gently for 5 min. Add about 10 ml. of water and cool in ice till the precipitate solidifies. Filter, wash with dilute hydrochloric acid to remove any pyridine, then with dilute sodium carbonate to remove free acid. Recrystallize from aqueous alcohol.

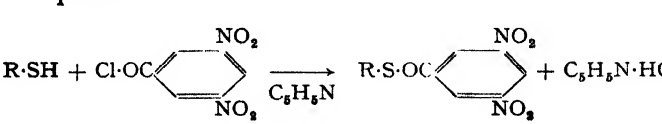


TABLE XLV.—THIOALCOHOLS AND THIOPHENOLS (MERCAPTANS)

	B.P. °C.	Mercury salt	2 : 4-Di-nitro phenyl thio-ether	2 : 4-Di-nitro sulphone	3 : 5-Di-nitro benzoate	Miscellaneous
Liquids						
Methyl mercaptan	6	175	128	190	—	
Ethyl	36	76	115	160	62	Lead salt, M.P. 150° C.
iso-Propyl	56	—	95	141		
n-Propyl	67	68	81	128	52	
iso-Butyl	88	95	76	106	64	
n-Butyl	97	86	66	92	49	Lead salt, M.P. 81° C.
iso-Amyl	117	100	59	95	43	
n-Amyl	126	—	80	83		
n-Hexyl	151	—	74	97		
Phenyl (Thiophenol)	169	—	121	161	149	Phenyl *iso*-cyanate deriv., M.P. 129° C.
n-Heptyl	176	—	82	101		
Benzyl	194	—	130	183	120	
o-Cresyl	194	—	101	155	—	M.P. 15° C.
α-Phenyl ethyl	199	—	90	134		
n-Octyl	199	—	78	98		
m-Cresyl	200	—	91	145		
α-Naphthyl	209	—	176	—	—	
n-Nonyl	220	—	86	92		
Undecyl	—	—	90	97		
Solids	M.P.					
p-Tolyl (*p*-Thiocresol)	43	—	103	190	—	B.P., 195° C.
Cetyl	50	—	91	105		
β-Naphthyl	81	—	145	—	—	
Diphenyl	111	—	146	170		
Allyl	—	—	72			
cyclo-Hexyl	—	—	148	172		
Decyl	—	—	85	93		
Dimethylene	—	—	248			
Furfuryl	—	—	130			
Lauryl	—	—	89	101		

GROUP III—CLASS III

THIO-ETHERS (SULPHIDES)

Classification tests.—(*a*) To the given compound add mercuric chloride solution. If a colourless precipitate forms, but no acidity develops in the solution, the substance is probably a thio-ether.

$$R_2S + HgCl_2 = R_2S{\cdot}HgCl_2.$$

In certain cases these addition compounds have definite melting-points, and may be used as an aid to final identification.

(*b*) Mix a small quantity of the compound with ethyl iodide and warm gently under a good reflux condenser. Cool. A crystalline sulphonium salt may separate. Filter, dissolve the solid in water and shake with silver oxide. Filter and test the filtrate for alkalinity. If strongly alkaline, the original compound was a dialkyl sulphide.

$$R_2S + R'I = R{>}\overset{+}{S}{<}^{R}_{R'}\,I^-$$

$$2\,R{>}\overset{+}{S}{<}^{R}_{R'}\,I^- + Ag_2O + H_2O = 2\,R{>}\overset{+}{S}{<}^{R}_{R'}\,OH^- + 2AgI.$$

sulphonium hydroxide (strongly alkaline)

Diaryl and aryl-alkyl sulphides do not yield sulphonium halides by the above method. They may, however, be converted to sulphonium salts by heating with dimethyl sulphate (*caution*—poisonous vapour) to 100° C.

Derivatives

Sulphone.—Method as for the oxidation of 2 : 4-dinitrothio-ethers to sulphones (see p. 186).

The intermediate oxidation product, the sulphoxide $R{>}\overset{+}{S}{<}^{R}_{R'}\,O^-$, may be obtained by controlled oxidation with 30 per cent hydrogen peroxide in acetic acid, but the process is too slow to be of much value in identification.

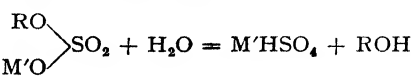
TABLE XLVI.—THIO-ETHERS (SULPHIDES)

	B.P. °C.	Sulphone	Addition compound with mercuric chloride	Miscellaneous
Liquids				
Methyl sulphide	37	109	150	
Ethyl sulphide	92	70	119	
n-Propyl sulphide	142	29		
iso-Butyl sulphide	172	17		
n-Butyl sulphide	182	43		
Methyl phenyl sulphide	188	88		
Ethyl phenyl sulphide	204	41		
iso-Amyl sulphide	215	31		
Phenyl sulphide	295	128	—	Bromine → 4 : 4′-Dibromo-deriv., M.P. 112° C.
Solids	M.P.			
Benzyl sulphide	49	150		
p-Tolyl sulphide	57	158		
Di-αα-naphthyl sulphide	110	187		
Di-ββ-naphthyl sulphide	151	177		

GROUP III—CLASS IV

ALKYL SULPHURIC ACIDS AND THEIR SALTS, DIALKYL SULPHATES

Classification test.—To an aqueous solution of the given compound add a solution of barium chloride. Filter if necessary. Acidify with dilute hydrochloric acid and boil. The gradual formation of a white precipitate of barium sulphate shows the presence of a compound of this class.



$$\begin{matrix} RO \\ M'O \end{matrix}\!\!>\!SO_2 + H_2O = M'HSO_4 + ROH.$$

If the preliminary examination has shown the formation of a non-combustible residue on ignition, examine the residue by the usual inorganic procedure for a basic radical. This will give the metallic constituent of a metallic salt of an alkyl sulphuric acid.

If the original substance is strongly acid it is an alkyl sulphuric acid. These are hygroscopic liquids and are rarely met with. Dialkyl sulphates are only faintly acid.

Derivatives, etc.

1. **S-benzyl thiuronium derivative.**—For alkyl sulphuric acids (other than methyl and ethyl) and their salts.

Method as for alcohols (see p. 79) subsequent to the formation of alkyl sulphuric acid from the alcohol.

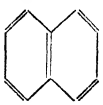
2. **Hydrolysis** of dialkyl sulphates.

Reflux about 5 g. of the original compound with dilute sulphuric acid. Distil off a few ml. from the acid solution and examine the distillate for an alcohol as in ester hydrolysis (see p. 68). If no alcohol distils over, extract the acid liquid with ether, wash the ether extract with dilute sodium carbonate solution followed by water. Dry, distil off the ether and identify the residual alcohol (see p. 79).

3. **β-Naphthyl ether.**—For dialkyl sulphates. In the preparation of this derivative use is made of the alkylating properties of these substances for the preparation of ethers.

Dissolve one gram of β-naphthol in 5 ml. of 2N sodium hydroxide and treat, in a stoppered bottle, with about 1 g. of the

dialkyl sulphate, the latter being added dropwise with vigorous shaking after each addition. Remove the stopper from time to time to release the pressure. Transfer the liquid to a small flask attached to a reflux condenser, add 5 ml. of caustic soda and heat on a water-bath to destroy any alkyl sulphate in excess. Cool. If a solid is now present, filter and recrystallize from alcohol. If an oil is formed, distil and collect the steam-volatile product from the condenser and recrystallize.



$+ R_2SO_4 + NaOH =$

$+ NaR{\cdot}SO_4 + H_2O.$

TABLE XLVII.—DIALKYL SULPHATES

	B.P. °C.	β-Naphthyl ether
Dimethyl sulphate	188	72
Diethyl sulphate	208	37

ALKYL SULPHURIC ACIDS

	M.W.	
Methyl sulphuric acid	112	Ammonium salt, M.P. 135° C.
Ethyl sulphuric acid	126	Ammonium salt, M.P. 99° C. (from alcohol)

M.P.s of S-benzyl thiuronium salts of other alkyl sulphuric acids will be found in Table XII (Alcohols).

GROUP III—CLASS V

ALKYL ESTERS OF SULPHONIC ACIDS

Classification test.—Carry out the ester test as for esters of carbon, hydrogen and oxygen acids (see p. 67). If fading occurs a compound of this class is present.

Derivatives, etc.

Hydrolysis.—Reflux about 5 g. of the substance with 10 per cent sodium hydroxide. Distil off and identify the alcohol (methyl, ethyl and butyl are the most probable ones). To the residual

liquid add dilute sulphuric acid until it is only just alkaline to phenolphthalein, concentrate by evaporation and prepare the S-benzylthiuronium derivative of the sulphonic acid. For melting-point of this derivative see Table XLIX (p. 194).

TABLE XLVIII.—ALKYL ESTERS OF SULPHONIC ACIDS

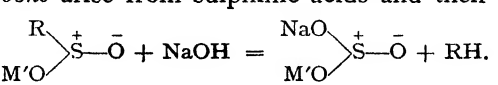
	B.P. °C.		M.P. °C.
Liquids		**Solids**	
Methyl benzene sulphonate	150/15 mm.	Methyl *p*-toluene sulphonate	28
Ethyl benzene-	156/15 mm.	Ethyl *p*-toluene sulphonate	33
n-Butyl *p*-toluene-	174/10 mm.		

GROUP III—CLASS VI

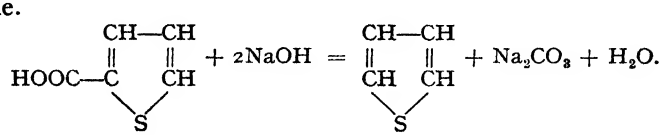
SULPHONIC ACIDS AND THEIR SALTS, SULPHINIC ACIDS AND THEIR SALTS, CARBOXYLIC DERIVATIVES OF THIOPHENE

Classification tests.—Mix about 1 g. of the given compound with an excess of dry soda-lime and distil from a hard-glass tube. Collect any distillate and test for (i) hydrocarbon (see p. 89); (ii) thiophene (see below); (iii) alcohol (see p. 77).

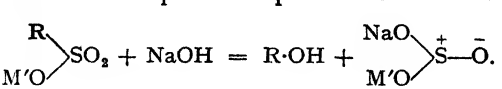
Hydrocarbons arise from sulphinic acids and their salts.



Thiophene is formed from carboxylic acid derivatives of thiophene.



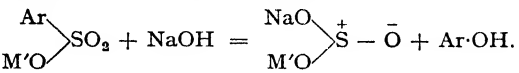
Alcohols arise from aliphatic sulphonic acids and their salts.



To test for thiophene, dissolve a crystal of isatin in concentrated sulphuric acid and add one drop of the distillate. Thiophene produces a strong blue colour.

Cool the residue in the distillation tube, remove it, dissolve in water and treat with dilute sulphuric acid till acid. Sulphur dioxide, as tested with potassium dichromate paper, will be evolved in the case of sulphonic and sulphinic acids and their salts. Extract the acid solution with ether and examine the residue for a phenol (see p. 61).

Phenols arise from aryl sulphonic acids, their salts and aryl esters.



Aryl esters of sulphonic acids are insoluble in water and neutral in reaction. For their final identification see p. 198.

Further, sulphinic acids and their salts are reduced to thio-alcohols by the action of tin and concentrated hydrochloric acid. Aryl sulphonic acids are not reduced.

Derivatives

1. **Amide.**—Mix about 1 g. of the original compound with a slight excess of phosphorus pentachloride and warm gently to form the sulphonyl chloride. From this stage proceed as in the preparation of amides from carboxylic acids (see p. 52).

In the case of free sulphonic acids, thionyl chloride can be used in place of phosphorus pentachloride.

$$\begin{cases} ArSO_2{\cdot}ONa + PCl_5 = ArSO_2Cl + POCl_3 + NaCl \\ ArSO_2OH + SOCl_2 = ArSO_2Cl + SO_2 + HCl \end{cases}$$
$$ArSO_2Cl + 2NH_3 = ArSO_2{\cdot}NH_2 + NH_4Cl.$$

2. **Anilide.**—Having prepared the sulphonyl chloride as in Derivative 1 above, proceed as in the preparation of benzene sulphonyl derivatives of amines (see p. 132).

3. **S-benzylthiuronium salts.**—If not already in that form, prepare a concentrated solution of the neutral sodium or potassium salt in water, and add this rapidly and with stirring to a slight excess of a 15 per cent solution of S-benzylthiuronium chloride in water. Cool, filter off the crystalline precipitate and recrystallize from 50 per cent alcohol.

4. **Aniline salt.**—For sulphonic acids. Dissolve 0·5 g. of the acid in the minimum amount of boiling absolute alcohol or dioxan. Add a few drops of aniline and cool in ice. Filter off the solid derivative and wash with absolute alcohol to purify.

TABLE XLIX.—SULPHONIC ACIDS

Since so few of the sulphonic acids have definite melting-points or boiling-points they are arranged below in alphabetical order.

	M.P. °C.	Amide	Anilide	S-benzyl thiuronium salt	Miscellaneous
Anthraquinone-2-	—	261	193	211	
Benzene *o*-di-	—	254	241	206	
Benzene *m*-di-	—	229	144	214	
Benzene *p*-di-	—	288			
Benzene-	66	153	110	148	
1-Butane-	—	45	—	—	B.P. 147° C./0·5 mm.
d-Camphor-10-	193	132	121	210	$[\alpha]_D$ 21°
ψ-Cumene-5-	—	175	—	—	Dihydrate, M.P. 112° C.
Cymene-3-	—	151	—	—	M.P. 131° C. after drying
Diphenyl-*pp'*-di-	72	300	—	171	
Ethane-	—	58	58	115	
p-Ethylbenzene-	—	108			
Mesitylene-	—	141	—	—	Dihydrate, M.P. 77° C.
Methane-	—	90	99	—	B.P. 167° C./10 mm.
Naphthalene-1 : 5-di-	245	310	249	257	
Naphthalene-1 : 4-di-	—	273	179		
Naphthalene-1 : 6-di-	125	298	—	235	
Naphthalene-2 : 6-di-	—	—	—	256	
Napthhalene-2 : 7-di-	—	242	—	205d	
Naphthalene-1-	90	150	152	137	Dihydrate, M.P. 88° C.
Naphthalene-2-	91	217	132	191	Hydrate, M.P. 124° C.
Naphthalene 1 : 3 : 5-tri-	—	—	—	250d	
1-Naphthol-3 : 6-di-	—	—	—	217	
1-Naphthol-4 : 8-di-	—	—	—	205	
2-Naphthol-3 : 6-di-	—	—	—	233	
2-Naphthol-6 : 8-di-	—	—	—	228	
1-Naphthol-2-	—	—	—	170	
1-Naphthol-4-	—	—	—	103	
2-Naphthol-6-	—	—	—	217	
2-Naphthol-8-	—	—	—	218	
Phenol *p*-	—	—	—	169	Warm with bromine water → tribromophenol, M.P. 95° C.
Salicyl- (Sulphosalicylic acid)	—	—	—	204	

TABLE XLIX—(*contd.*)

	M.P. °C.	Amide	Anilide	S-benzyl thiuronium salt	Miscellaneous
o-Sulphobenzoic acid	134	—	194	206	Hydrate, M.P. 70° C.
m-Sulphobenzoic acid	141	170	—	163	Hydrate, M.P. 96° C.
p-Sulphobenzoic acid	259	230	253	213	Hydrate, M.P. 94° C.
Toluene *o*-	57	153	136	170	
Toluene *m*-	—	108	96		
Toluene *p*-	92	137	103	182	Monohydrate, M.P. 107° C.
Toluene-2 : 4-di-	—	186	189		
Toluene-ω-	—	—	104		
Thymol-	116	—	—	212	
o-Xylene-	64	144	—	208	
m-Xylene-	—	137	110	146	Dihydrate, M.P. 60° C.
p-Xylene-	48	148	—	184	Dihydrate, M.P. 86°

TABLE L.—SULPHINIC ACIDS

	M.P. °C.
Toluene *o*-sulphinic	80
Benzene sulphinic	83
Toluene *p*-sulphinic	86

TABLE LI.—CARBOXYLIC ACID DERIVATIVES OF THIOPHENE

	M.P. °C.	Amide	Anilide	Miscellaneous
α-Thiophenic acid (Thiophene-2-carboxylic acid)	127	180	140	
β-Thiophenic acid	138	178		
Thiophene-2 : 4-dicarboxylic acid	280d	—	—	Dimethyl ester, M.P. 121° C.
Thiophene-2 : 5-dicarboxylic acid	>350	—	—	Dimethyl ester, M.P. 151° C.

GROUP III—CLASS VII

THIO-ACIDS (AND THIOL-ACIDS)

True thio-acids contain the grouping $\begin{matrix} & O \\ & \| \\ -C- & -SH \end{matrix}$, while thiol-acids contain the grouping $\begin{matrix} R-CH- \\ | \\ SH \end{matrix}$ and are derived from hydroxy acids. Thioacetic, thiobenzoic, thioglycollic and thiolactic acids are the only common ones.

If the preliminary tests have indicated the probable presence of a member of this class (or salt), add to 0·2 g. of the given substance a slight excess of aqueous caustic soda and boil. Filter if necessary. Add about 0·5 ml. of 20 vol. hydrogen peroxide and boil to oxidize sulphide. Neutralize the solution carefully, and test for (*a*) acetic acid, (*b*) benzoic acid, (*c*) salicylic acid, (*d*) glycollic acid, (*e*) lactic acid as follows:

For acetic, benzoic and salicylic acids, add neutral ferric chloride solution. Acetic acid gives a red colour and a reddish precipitate on boiling; benzoic acid gives a buff precipitate; salicylic acid a violet coloration.

For glycollic and lactic acids, warm one drop of the neutralized solution with 2 ml. of concentrated sulphuric acid for 2 min. Cool and add 2 drops of 5 per cent solution of guaiacol in alcohol. Lactic acid gives a red colour; glycollic acid a violet colour in presence of 1 ml. of glacial acetic acid.

Derivatives

1. **For thioacetic and thiobenzoic acids.**—Mix 1 g. of the acid with an equal weight of aniline and warm gently till hydrogen sulphide is freely evolved. Cool, pour into water and wash the precipitate with cold dilute hydrochloric acid and then with dilute sodium carbonate. Recrystallize the anilide from water or alcohol.

$$R{\cdot}CO{\cdot}SH + C_6H_5NH_2 = R{\cdot}CO{\cdot}NHC_6H_5 + H_2S.$$

2. **For thioglycollic and thiolactic acids.**—Mix 1·7 g. of the thiol acid with 1 g. of benzaldehyde. Allow to stand till solidi-

fication occurs. Wash with petrol-ether (B.P. 40–60° C.) and recrystallize from aqueous acetone.

$$2CH_3(SH)\cdot COOH + C_6H_5\cdot CHO = C_6H_5\cdot CH(S\cdot CH_2\cdot COOH)_2$$

$$2CH_3\cdot CH(SH)\cdot COOH + C_6H_5\cdot CHO = C_6H_5\cdot CH(S\cdot CH(CH_3)\cdot COOH)_2 .$$

3. **For thioglycollic acid.**—Take 0·5–1·0 g. of the acid, dissolve in water, just acidify with dilute hydrochloric acid and add iodine till oxidation is complete (test with starch). Discharge the colour with 5 per cent sodium bisulphite solution, filter if necessary, and adjust to the starch-iodine end point with N iodine. Add about half the volume of concentrated hydrochloric acid and extract with ether. Wash the ether extract twice with 10 ml. portions of water. Filter and evaporate off the ether on a water-bath. Recrystallize from benzene/ethyl acetate 9 : 1, cooling and scratching the inside of the tube. M.P. 100° C. raised to 107–108° C. by several recrystallizations. The equivalent weight of this acid is 91·2.

TABLE LII.—THIO- AND THIOL-ACIDS

	B.P. °C.	Amide	Anilide	Miscellaneous
Liquids				
Thioacetic acid	93	108	112	
Thioglycollic acid	123/29 mm.	52	111	Benzaldehyde deriv., M.P. 124° C.
dl-Thiolactic acid	99/14 mm.			
Solids		M.P.		
Thiobenzoic acid	ca. 24	116	164	
Thiosalicylic acid	165	—	—	Acetyl deriv., M.P. 125° C.

GROUP III—CLASS VIII

ARYL ESTERS OF SULPHONIC ACIDS

Classification test.—Dissolve some of the given compound in cold concentrated sulphuric acid and slowly add a few drops of concentrated nitric acid keeping the solution cool during the addition. Pour into cold water and filter off the solid formed. Wash well and dry. Carry out the ester test (see p. 67) on the dinitro-derivative. If fading now occurs the original compound was an aryl ester of a sulphonic acid.

Derivative

Dinitro-compound.—Prepared as in the above classification test. Recrystallize from aqueous alcohol.

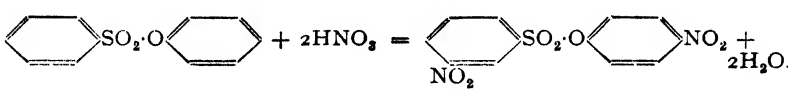


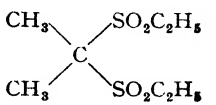
TABLE LIII.—ARYL ESTERS OF SULPHONIC ACIDS

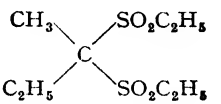
	M.P. °C.	Miscellaneous derivatives
Phenyl benzene sulphonate	35	Conc. HNO_3 and conc. H_2SO_4 → dinitro-deriv., M.P. 132 °C.
o-Cresyl benzene-	39	
p-Cresyl benzene-	43	
m-Cresyl benzene-	45	
m-Cresyl *p*-toluene-	51	
o-Cresyl *p*-toluene-	55	
Benzyl *p*-toluene-	58	
p-Cresyl *p*-toluene-	70	
Thymyl *p*-toluene-	71	
Resorcinyl *p*-toluene-	80	
α-Naphthyl *p*-toluene-	83	
Eugenyl *p*-toluene-	85	
Guaiacyl *p*-toluene-	85	
Phenyl *p*-toluene-	96	Conc. HNO_3 and H_2SO_4 → dinitro-deriv., M.P. 115° C.
β-Naphthyl *p*-toluene-	125	
Hydroquinone *p*-toluene-	159	

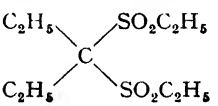
GROUP III—CLASS IX

SULPHONES

If no classification has yet been effected the compound may be a sulphone. The commonest of these are:

sulphonal 

trional 

tetronal 

All sulphones are colourless crystalline compounds showing marked resistance to oxidizing and reducing agents, and distilling unchanged from soda-lime.

Heating with excess of carbon reduces them to thioalcohols,

TABLE LIV.—SULPHONES

	M.P. °C.	Miscellaneous
iso-Butyl-	17	B.P. 265° C.
n-Propyl-	29	
Ethylphenyl-	41	
n-Butyl-	43	
Ethyl-	70	
Trional	76	
Tetronal	85	
Methylphenyl-	88	
Methyl-	109	
Phenyl sulphone	128	Conc. HNO_3 and conc. H_2SO_4 → dinitro-deriv., M.P. 201° C.
Sulphonal	127	
Benzyl-	150	
p-Tolyl-	158	
β-Naphthyl-	177	
α-Naphthyl-	187	

while treatment with metallic sodium in boiling toluene converts them to sulphinates and hydrocarbons.

$$2C_6H_5{\cdot}SO_2C_6H_5 + 2Na = 2C_6H_5{\cdot}SO_2Na + C_6H_5{\cdot}C_6H_5.$$

In the case of aromatic sulphones the presence of the sulphinate may be confirmed by applying Smiles' test.

Evaporate off the toluene, dissolve the residue in cold concentrated sulphuric acid and add one drop of anisole or phenetole. The development of a blue colour which is discharged on the addition of excess phenetole is due to a sulphinic acid.

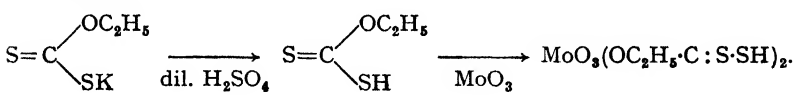
Note.—Some sulphones will also give the Smiles' test.

GROUP III—CLASS X

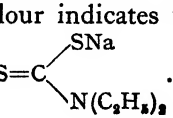
XANTHATES AND DI-ALKYL DITHIOCARBAMATES

If the given compound be a colourless crystalline solid with a characteristic unpleasant odour, the substance may be potassium ethyl xanthate, or sodium di-ethyl dithiocarbamate.

(*a*) Add a dilute aqueous solution of it to a very dilute solution of ammonium molybdate acidified with dilute sulphuric acid. A plum-coloured precipitate, soluble in ether, shows the presence of potassium ethyl xanthate.



(*b*) To a *very dilute* solution of copper sulphate acidified with sulphuric acid add an aqueous solution of the original substance. A yellow precipitate soluble in carbon tetrachloride to give a strongly yellow solution indicates the presence of a xanthate.

(*c*) To a very dilute ammoniacal solution of copper sulphate, add an aqueous solution of the original substance. Formation of a golden-brown colour indicates the presence of sodium di-ethyl di-thio carbamate, 

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CHAPTER VI

Summary of Classification Tests, Derivatives, etc., for Compounds containing Carbon, Hydrogen, Halogen, and possibly Oxygen and a Metal

Preliminary examination

1. Physical characteristics.
2. Ignition on a crucible lid.
3. Solubility in water and reaction to litmus.
4. Action of concentrated sulphuric acid.
5. Action of cold and hot 30 per cent sodium hydroxide solution.
6. Determination of the " mobility " of the halogen atoms.
7. Quantitative determination of halogen by (*a*) Stepanow's method (Bacon's modification), or (*b*) Reduction with Raney nickel.

Class	Classification Tests	Additional Tests	Derivatives, &c.
Aliphatic and aromatic halogen-substituted hydrocarbons (p. 207).	" Ferrox paper " test	Refer to results of preliminary examination, Test 6 *For chloroform, bromoform and iodoform* Sodium hydroxide and resorcinol test	*For simple aliphatic halides* Alkyl *iso*-thiourea picrate α-Naphthalide Alkyl mercuric halide β-Naphthyl ether Picrate of β-naphthyl ether *For aromatic halogen-substituted hydrocarbons* Nitro derivative Product of oxidation Picrate Sulphonamide
Carboxylic acid halides **Alkyl chloroformates** **Aliphatic α-halogen-substituted ethers** (p. 216).	Evolution of halogen hydracid on treatment with water	*For alkyl chloroformates* Evolution of carbon dioxide and halogen hydracid with water *For aliphatic α-halogen substituted ethers* 2 : 4-Dinitrophenylhydrazine test after hydrolysis	*For acid halides* Amide Anilide *p*-Toluidide *For alkyl chloroformates* Alkyl carbamate Carbanilate *For α-halogen substituted ethers* Derivatives of aldehyde formed by hydrolysis

Other aromatic halogen compounds (p. 219).			
A. Nuclear halogen-substituted aldehydes and ketones	2 : 4-Dinitrophenylhydrazine test	Schiff's reagent Tollens' reagent Dimedone	As for corresponding compounds containing carbon, hydrogen and oxygen only
B. Nuclear halogen-substituted acids and phenols	Sodium hydroxide and phenolphthalein test	*For phenols* Ferric chloride test Diazotized *p*-nitraniline test	
C. Esters of nuclear halogen-substituted acids	Alcoholic potash and phenolphthalein		
D. Nuclear halogen-substituted alcohols	Metallic potassium test	Hexanitrato ceric acid test	
E. Nuclear halogen-substituted ethers	By elimination of other types	Cold concentrated sulphuric acid test	
Other aliphatic halogen-substituted compounds (p. 226).			
A. Aliphatic halogen-substituted aldehydes and ketones	2 : 4-Dinitrophenylhydrazine test	Schiff's reagent Tollens' reagent Dimedone	As for aldehydes and ketones containing carbon, hydrogen and oxygen
B. Hydrates and alcoholates of halogen-substituted aldehydes	Concentrated sulphuric acid followed by 2 : 4-dinitrophenylhydrazine test		
C. Aliphatic halogen-substituted acids	Sodium bicarbonate test	Sodium hydroxide and phenolphthalein test Quantitative determination of halogen	As for simple carboxylic acids
D. Halogen-substituted alcohols	Hexanitrato ceric acid test	Acetyl chloride test	As for simple alcohols
E. Halogen-substituted esters	Concentrated ammonia	Hydrolysis and identification of alcohol formed	Amide

GROUP IV

COMPOUNDS CONTAINING CARBON, HYDROGEN, HALOGEN AND POSSIBLY OXYGEN AND A METAL

Preliminary examination

1. *Physical properties.*

Lachrymatory	Some halogen-substituted ketones; benzyl halides and their homologues; some aroyl halides; chloroformates; esters of some bromo- and iodo-substituted fatty acids, e.g. methyl and ethyl bromoacetates.
Camphor-like odour	Hexachloroethane; chlorobutol; α-chlorocamphor.
Deliquescent	Some halogen-substituted acetic acids.
Yellow	Possibly an iodo compound, e.g. iodoform.
	Some halogen-substituted hydrocarbons have characteristic odours, e.g. chloroform, iodoform, trichlorethylene, *p*-dibromobenzene.

2. *Ignition on a crucible lid.*

A residue remains	Probably a metallic salt of a halogen-containing acid or a halogenated phenol.

3. *Solubility in water and reaction to litmus.*

A vigorous reaction with the evolution of a halogen hydracid (test with silver nitrate and nitric acid on the end of a glass rod)	An aliphatic acid chloride; an aliphatic α-halogen-substituted ether.
Evolution of halogen hydracid on warming	Aromatic acid halides.
Evolution of halogen hydracid and carbon dioxide (test with slightly ammoniacal lime water on the end of a glass rod)	Chloroformates.
Soluble	A substance of comparatively low molecular weight containing a carboxyl, aldehydic or hydroxyl group.

Solution or mixture with water shows an acid reaction	Aliphatic or aromatic halogen-substituted acid; an easily hydrolysed halogen-substituted ester; an acid chloride; aliphatic α-halogen-substituted ether; chloroformate (chlorocarbonate); halogenated phenol.
Solution or mixture with water shows a neutral reaction	Probably a halogen-substituted alcohol, aldehyde, hydrocarbon, ester, aromatic ether or nuclear-substituted ketone.

4. *Action with concentrated sulphuric acid.*

Insoluble	Simple alkyl halides; unsaturated aromatic halogenated hydrocarbons may dissolve in the *hot* acid, but as the proportion of halogen increases the solubility of such compounds decreases.

5. *Action of cold and hot 30 per cent sodium hydroxide solution.*

Soluble in cold though insoluble in water	Probably a halogen-substituted acid, phenol or easily hydrolysed ester. *Note.*—The acidity of a simple phenol is increased by the introduction of one or more halogen atoms into the nucleus, and the halogen-substituted compound may even be soluble in a solution of sodium bicarbonate.
Odour of chloroform	Chloral; chloral hydrate; trichloracetic acid or one of its salts.
Odour of an alcohol	Alkyl halide; ester of a halogen-substituted carboxylic acid and a lower aliphatic alcohol.
Odour of an aldehyde (if aldehyde not affected by alkali)	A compound containing the —$CHCl_2$ group.
Solution turns yellow or brown on warming	A halogenated aliphatic aldehyde or phenol.

6. *The following tests must always be applied to determine whether or not the halogen is "mobile", i.e. easily removed from the compound.*

Dissolve about 0·2 g. of the substance in 1 ml. of alcohol and add about 1 ml. of silver nitrate solution. Note if any precipitate is formed in the cold, and if not, heat slowly till boiling. Test the solubility in dilute nitric acid of any precipitate formed, as sparingly soluble silver salts of organic acids may be formed. These, however, are soluble in dilute nitric acid.

<table>
<tr><td>Precipitate of silver halide

Rapidly produced from
Acid halides, R·COX
α-Halogen alkyl ethers, Al·O·CH₂Cl.</td><td colspan="2">No precipitate of silver halide
Reflux about 0·5 g. of the compound with 5 per cent alcoholic potash (or 2 per cent alcoholic pyridine, quinoline or dimethyl aniline) for 15 min. Cool, acidify with dilute nitric acid, filter if necessary and add silver nitrate solution.</td></tr>
<tr><td>Produced slowly or only on warming from
Aliphatic iodo compounds; lower aliphatic bromides; chloroformates, Cl·CO·OR. Aliphatic α-halogen-substituted compounds only give a precipitate on prolonged boiling.</td><td>Precipitate (neglect a slight turbidity)
Aliphatic halogen compounds including those ring compounds with a halogen in the side chain.</td><td>No precipitate
Compounds containing a halogen atom attached to a carbon atom forming part of aromatic nucleus</td></tr>
</table>

Note that halogen may be present in more than one form, as in *p*-bromo-benzyl chloride.

Determination of halogen

The determination of the percentage halogen in the compound is, when only one halogen is present, a simple and useful aid to identification. If more than one halogen is present the final stage, i.e. titration of the alkali halide, is more difficult, but may be carried out with the aid of adsorption indicators. For details of this titration a textbook of Inorganic Quantitative Analysis should be consulted.

1. **Stepanow's method, modified by Bacon.**—Weigh out 0·2–0·25 g. (= x) of halogen compound and introduce into a 300–400 ml. flask. Add a suitable volume of 98 per cent alcohol,* viz. $156x$ ml., $68x$ ml. or $44x$ ml., according as chlorine, bromine or iodine respectively is present in the original substance. Attach a reflux condenser to the flask and heat the solution to boiling. Remember that lower aliphatic halides are very volatile and require a very efficient condenser. Add gradually, over a period of 30 min., small pieces of clean metallic sodium, the total weight of which should be $19·5x$ g. if chlorine is present, $8·5x$ g. if bromine, and $5·5x$ g. if iodine is present. When all the sodium has been added, reflux for one hour. Allow to cool and add distilled water to the extent of twice the volume of the original alcohol. Remove the

* Higher alcohols or an ethanolamine dioxan mixture give better results.

alcohol by distilling off about one-third of the total volume. Cool the residual liquid, acidify with dilute nitric acid and add a definite volume of 0·1 N silver nitrate. Filter off the precipitated silver halide, wash the precipitate with dilute nitric acid, combining the washings with the first filtrate. Titrate the excess silver nitrate with 0·1 N thiocyanate solution, using iron alum solution as indicator (Volhard). Hence calculate the percentage of halogen in the original compound.

Alternatively dry and weigh the precipitated silver halide.

2. Reduction with nickel-aluminium alloy (Raney nickel) and aqueous alkali.

(*a*) *For alkali soluble compounds.*—Dissolve 0·3 g. of the compound in 10 ml. of 5 per cent sodium hydroxide in a tall-form beaker. Add 3 g. of Raney Ni/Al alloy in 3 or 4 portions extending over 10 min. (*Care.*) Heat on a steam-bath for 15 min. and then maintain at 90–95° C. for about one hour. Decant the clear colourless solution from the nickel which has settled out, into a 200 ml. graduated flask. Wash the nickel three times by decantation with hot water, adding the washings to the flask, then cool and make up to volume. Take 100 ml. or other aliquot part, acidify with 10 per cent nitric acid to congo-red paper and determine the halogen by any standard procedure.

(*b*) *For alkali insoluble compounds.*—Weigh out accurately about 0·3 g. of the compound and transfer to an Erlenmeyer flask fitted with a reflux condenser. Add 10 ml. of 95 per cent alcohol and 3·5 g. of Raney Ni/Al alloy. Cool in an ice-bath and add 75 ml. of cooled 10 per cent caustic soda solution. Heat over a low flame until the alloy has reacted completely (1½–2 hours). Any foaming which occurs may be moderated by the addition of a few drops of octyl alcohol. From this point proceed as in (*a*) above.

GROUP IV—CLASS I

ALIPHATIC AND AROMATIC HALOGEN-SUBSTITUTED HYDROCARBONS

Classification test.—If the original substance be a liquid, dry about 1 ml. over anhydrous magnesium or sodium sulphate. Decant off into a *dry* tube, and add a small square of "ferrox" paper (see p. 290). If the liquid does not become red, showing

absence of oxygen in the compound, it is probably a substance of this class.

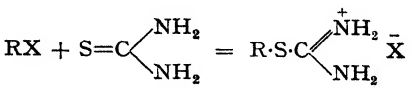
If the given compound be a solid, dissolve in perfectly dry benzene, toluene or other hydrocarbon and apply the "ferrox" paper text.

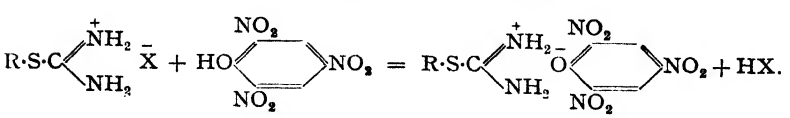
The preliminary tests with silver nitrate under varying conditions will have indicated whether the halogen atom is "mobile", i.e. attached to an aliphatic chain, or is attached to a carbon atom forming part of an aromatic nucleus. If the halogen is "mobile" and the original compound is insoluble in cold concentrated sulphuric acid, the presence of a simple alkyl halide should be suspected.

Test for chloroform, bromoform and iodoform.—Dissolve a few crystals of resorcinol in 2 ml. of aqueous sodium hydroxide, add a very small quantity of the original compound and boil. A red solution, turning violet-red on shaking, indicates the presence of one of these substances.

Derivatives

1. Alkyl-iso-thiourea picrate (for simple aliphatic halides). Dissolve one gram of the alkyl halide and 1 g. of thiourea in 10 ml. of alcohol and boil under a reflux condenser for 5 min. or longer, depending on the nature of the halide. Add 1 g. of picric acid to the solution and reflux again until a clear solution is obtained. Cool, and if no crystallization occurs, add a little water to precipitate the picrate. Filter, and recrystallize from alcohol.





2. α-Naphthalide or Anilide (for simple aliphatic halides). In a dry test tube provided with a cork carrying a calcium chloride tube place 0·4 g. of magnesium turnings. Add a small crystal of iodine and warm *gently* until the iodine has completely reacted. Cool the tube and add a solution of about 2 g. of *dry* alkyl halide in 4–5 ml. of *dry* ether. In some cases the reaction

will start immediately and become vigorous, when the tube should be cooled. Gradual addition of the solution of alkyl halide is advisable in such cases. If the reaction does not start spontaneously, heat the tube gently in warm water (30–35° C.). After reaction has commenced, control the temperature so that the ether continues in gentle ebullition until the alkyl halide has completely reacted. Cool, add 10 ml. of *dry* ether and decant through glass wool. To the solution add, drop by drop, a solution of 2 g. of α-naphthyl isocyanate in 5 ml. ether. The reaction mixture is then poured into 20 ml. of ice-water containing 1 ml. concentrated hydrochloric acid, and the whole thoroughly agitated. Separate the ether layer, dry over anhydrous magnesium sulphate and evaporate off the ether. Recrystallize the residual α-naphthalide from methyl alcohol, ether or petroleum-ether.

Substitution of phenyl isocyanate for α-naphthyl isocyanate yields the anilide

$$R{\cdot}MgX + C_{10}H_7{\cdot}N{=}C{=}O = C_{10}H_7{\cdot}N{=}\overset{\displaystyle R}{\overset{|}{C}}{-}OMgX$$

$$C_{10}H_7{\cdot}N{=}\overset{\displaystyle R}{\overset{|}{C}}{-}OMgX + HCl = C_{10}H_7{\cdot}NH{\cdot}COR + MgXCl.$$

3. **Alkyl mercuric halide** (for simple aliphatic halides).

Prepare the Grignard reagent as in (2) above, and allow the ethereal solution after its passage through glass wool to flow into an aqueous solution of 4–5 g. of mercuric chloride or bromide, depending on the halogen present in the original alkyl halide. Shake vigorously, and warm on a steam-bath for a few minutes. Evaporate the mixture to dryness. Boil the residue with 20 ml. of 95 per cent alcohol and filter. Dilute the filtrate with 10 ml. of water and cool in ice. Collect the derivative and recrystallize from 60 per cent alcohol.

$$R{\cdot}MgX + HgX_2 = R{\cdot}HgX + MgX_2.$$

4. **β-Naphthyl ether** (for simple aliphatic halides).

Reflux for about 15 min. one gram of the original compound, 2 g. of β-naphthol, 1 g. of potassium hydroxide and 10 ml. of alcohol. Add 20 ml. of water and about 2 g. of caustic potash, cool and shake. If a solid separates, filter, wash with cold water and recrystallize from alcohol.

If no solid separates, add a further 20 ml. of water and distil.

If a solid collects in the condenser, remove it, wash with cold water and dry. If, however, an oil distils over, extract with ether, distil off the ether and prepare a picrate of the residual liquid (see Derivative 5 below).

$$C_{10}H_7{\cdot}OK + RX = C_{10}H_7{\cdot}OR + KX.$$

5. **Picrate of β-naphthyl ether.**—Dissolve the ether prepared as in (4) above, in the minimum quantity of alcohol, and to the cold solution add a cold saturated solution of picric acid in alcohol. Allow to stand, filter, wash the derivative carefully with alcohol and dry.

6. **For aromatic halogen-substituted hydrocarbons (nuclear halogen).**

(i) *Nitro compounds* as for hydrocarbons (see p. 90).
(ii) *Oxidation* of a side chain as for hydrocarbons (see p. 93).
(iii) *Picrate* as for hydrocarbons (see p. 91).
(iv) *Sulphonamide* as for hydrocarbons (see p. 92).

TABLE LV.—ALKYL HALIDES

	B.P. °C.			Alkyl mercuric halide			Alkyl *iso*-thiourea picrate	α-Naphthalide	β-Naphthyl ether	Picrate of β-naphthyl ether	Anilide	Miscellaneous
	Chloride	Bromide	Iodide	Chloride	Bromide	Iodide						
Methyl	−24	5	43	—	160	145	224	161	72	118	114	
Ethyl	12	38	72	192	193	182	188	126	37	104	104	
iso-Propyl	36	60	89	—	93	—	196	—	—	92	103	
n-Propyl	46	71	102	147	138	112	177*	121	39	75	96	* Not from chloride
tert-Butyl	51	72	98	—	—	—	—	147	—	—	130	
sec-Butyl	67	90	119	—	39	—	166	129	—	—	107	
iso-Butyl	68	91	120	—	55	72	167	126	—	—	109	
n-Butyl	77	100	130	127	129	117	177	109	—	—	63	
tert-Amyl	86	108	128	—	—	—	—	138	—	—	91	
iso-Amyl	100	118	148	86	80	122	173	111	—	—	110	
n-Amyl	107	129	156	110	122	110	154	112	—	—	92	
n-Hexyl	134	157	180	125	118	110	157	106	—	—	65	
cyclo-Hexyl	142	165	—	—	153	—	—	188	—	—	146	
n-Heptyl	160	174	204	119	118	103	142	95	—	—	55	
Benzyl	179	198	24 (M.P.)	—	119	—	188	166	99	—	117	Oxid. with $KMnO_4$ → benzoic acid, M.P. 122° C.
n-Octyl	184	204	—	—	109	—	134	91	—	—	57	
β-Phenylethyl	190	218	—	—	169	—	139	—	—	—	97	
α-Phenylethyl	195	205	—	—	—	—	167	—	—	—	133	
Cetyl	289d	15 (M.P.)	102				137					

TABLE LVI.—HALOGEN DERIVATIVES OF ALIPHATIC HYDROCARBONS

	B.P. °C.	n_D	
Liquids			
Vinyl bromide	16	—	Anilide, M.P. 104° C. Polymerizes to rubber-like mass
2-Chloropropene	30		
1-Chloropropene	36	—	Anilide (crotonanilide), M.P. 114° C.
Methylene dichloride	42	1·4237	β-Naphthyl ether, M.P. 133°C.
Allyl chloride	46	—	Anilide (crotonanilide), M.P. 114° C.
2-Bromopropene	48		
Dichloroethylene (*cis*)	48	1·4490	
Vinyl iodide	56	—	Anilide, M.P. 104° C.
Chloroprene	59		
1-Bromopropene	60	—	Anilide (crotonanilide), M.P. 114° C.
Dichloroethylene (*trans*)	60	1·4518	
Ethylidene dichloride	60	1·4166	Di-β-naphthyl ether, M.P. 200° C.
Chloroform	61	1·4467	*iso*-Nitrile reaction
2 : 2-Dichloropropane	70	1·4093	
Allyl bromide	71	—	Anilide (crotonanilide), M.P. 114° C.
1 : 1 : 1-Trichloroethane	74	1·4349	
Carbon tetrachloride	78	1·4607	Slow *iso*-nitrile reaction
1-Bromo-1-chloroethane	83		
Ethylene dichloride	84	1·4443	
Trichloroethylene	88	1·4782	
2-Bromo-Δ^2-butene	94		
Methylene dibromide	98	—	β-Naphthyl ether, M.P. 133°C.
Propylene dichloride	98	1·4388	
Allyl iodide	103	—	Anilide (crotonanilide), M.P. 114° C.
1-Bromo-2-chloroethane	107		
Ethylidene dibromide	112	1·5128	Di-β-naphthalide, M.P. 200°C.
1 : 1 : 2-Trichloroethane	114	1·4711	
Tetrachloroethylene	121	1·5055	
Trimethylene chloride	125	—	Di-β-naphthyl ether, M.P. 148° C.
1 : 3-Dichloropropane	125		
Ethylene dibromide	131	1·5379	M.P. 10° C.
2 : 3-Dibromopropene	140		
Propylene dibromide	142	1·5203	
sym-Tetrachloroethane	147	1·4942	
iso-Butylene bromide	149	1·509	

TABLE LVI—(*contd.*)

	B.P. °C.	n_D	
Liquids			
Bromoform	151	1·589	M.P. 8° C.
1 : 2 : 3-Trichloropropane (Trichlorohydrin)	155		
2 : 3-Dibromobutane	159		
Pentachloroethane	161	1·504	
Tribromoethylene	163		
1 : 2-Dibromobutane	165		
Trimethylene dibromide	165	1·523	Di-β-naphthyl ether, M.P. 148° C.
1 : 3-Dibromobutane	174	1·507	
Methylene di-iodide	181	1·7425 (15° C.)	β-Naphthylether, M.P. 133°C. Addition compound with quinoline, M.P. 132° C.
1 : 4-Dibromopentane	197		
1 : 4-Dibromobutane	198		
β-Chlorostyrene	199	—	Anilide, M.P. 115° C.
sym-Tetrabromoethane	200d	1·638	
Benzal chloride	212	1·5515	Boil with Na_2CO_3 → benzaldehyde
o-Chlorobenzyl chloride	214		
1 : 2 : 3-Tribromopropane	219	1·584	
Benzotrichloride	220	1·5573	Boil with Na_2CO_3→sodium benzoate
Pentamethylene bromide	221		
β-Bromostyrene	221	—	Anilide, M.P. 115° C. Alkyl mercuric halide, M.P. 91° C.
Solids	M.P.		
p-Chlorobenzyl chloride	29	—	Boil with $NaCO_3$ sodium salt of *p*-chlorobenzoic acid, M.P. 242° C.
Heptachloropropane	29		
o-Bromobenzyl bromide	30	—	Boil with Na_2CO_3 → sodium salt of *o*-bromobenzoic acid, M.P. 150° C.
o-Xylylene dichloride	—	—	M.P. 55° C.
p-Bromobenzyl bromide	63		
Styrene dibromide	73		
m-Xylylene dibromide	76		
Ethylene di-iodide	82		
Carbon tetrabromide	92		
o-Xylylene dibromide	95		
p-Xylylene dichloride	100		
Iodoform	119	—	Quinoline addition compound (in dry ether) M.P. 65° C.

[*Contd. over*

TABLE LVI—(*contd.*)

	M.P. °C.	n_D	
Solids			
Butadiene tetrabromide	117	—	Isomeric form, M.P. 39° C.
p-Xylylene dibromide	145		
α-Benzene hexachloride	157		
sym-Tetramethyldichloroethane	160		
sym-Tetramethyldibromoethane	169		
Hexachloroethane	187	—	Camphor-like odour
β-Benzenehexachloride	310		
Carbon tetraiodide	—	—	Dark red crystals. On heating → iodine

TABLE LVII.—HALOGEN-SUBSTITUTED HYDROCARBONS (AROMATIC)

	B.P. °C.	Nitro-deriv.			Oxidation product	Miscellaneous
		M.P. °C.	Method of nitration	Position of nitro-groups		
Liquids						
Fluorobenzene	85	27	—	4		
o-Fluorotoluene	114					
m-Fluorotoluene	115					
p-Fluorotoluene	117	—	—	—	186	
m-Fluorochlorobenzene	125					
Chlorobenzene	132	52	a	2, 4	—	Sulphonamide, M.P. 143° C.
o-Fluorochlorobenzene	136					
p-Fluorobromobenzene	155					
Bromobenzene	157	75	a	2, 4	—	Sulphonamide, M.P. 160° C.
o-Chlorotoluene	159	64	a	3, 5	140	
m-Chlorotoluene	162	91	a	4, 6	158	
p-Chlorotoluene	162	38	a	2	242	
m-Dichlorobenzene	172	103	c	4, 6		
o-Dichlorobenzene	179	110	c	4, 5		
o-Bromotoluene	181	82	a	3, 5	147	
p-Chloroethylbenzene	182	—	—	—	242	

TABLE LVII—(*contd.*)

	B.P. °C.	Nitro-deriv. M.P. °C.	Nitro-deriv. Method of Nitration	Nitro-deriv. Position of nitro-groups	Oxidation product	Miscellaneous
Liquids						
m-Bromotoluene	183	103	a	4, 6	155	
p-Fluoroiodobenzene	183					
Iodobenzene	188	171	a	4		
2 : 4-Dichlorotoluene	195	104	—	3, 5	160	
m-Iodotoluene	204	—	—	—	186	
o-Iodotoluene	211	103	*	6	162	* Cold fuming HNO_3
1 : 2 : 4-Trichlorobenzene	213	56	—	5		
m-Dibromobenzene	219	61	a	2, 4	—	Sulphonamide, M.P. 190° C.
o-Dibromobenzene	224	114	a	4, 5	—	Sulphonamide, M.P. 175° C.
2-Bromomesitylene	225					
2-Bromocymene	234	97	†	—	—	† Cold fuming HNO_3
3 : 4-Dibromotoluene	241	—	—	—	233	
α-Chloronaphthalene	263	180	c	4, 5	—	Picric acid deriv., M.P. 137° C. Styphnate, M.P. 128° C.
α-Bromonaphthalene	279	85	a	4	—	Picric acid deriv., M.P. 134° C. Styphnate, M.P. 118° C. 1 : 3 : 5-Trinitrobenzene deriv., M.P. 137° C.
Solids	M.P.					
p-Bromotoluene	28	47	a	2	251	
2-Chlorodiphenyl	34	—	—	—	140	
p-Iodotoluene	35	—	—	—	265	
1 : 2 : 4-Tribromobenzene	44					
1 : 2 : 3-Trichlorobenzene	52	56	—	4		
p-Dichlorobenzene	53	54	a	2		
β-Iodonaphthalene	55					
p-Chloroiodobenzene	56					
β-Chloronaphthalene	56	175	a	1, 8	—	Picric acid deriv., M.P. 81° C.
β-Bromonaphthalene	59	—	—	—	—	Picric acid deriv., M.P. 79° C.

[*Contd. over*

TABLE LVII—(*contd.*)

	M.P. °C.	Nitro-deriv.			Oxidation product	Miscellaneous
		M.P. °C.	Method of nitration	Position of nitro-groups		
Solids						
1 : 3 : 5-Trichlorobenzene	63	68	—	2		
p-Chlorobromobenzene	65	72	—	2		
1 : 2-Dibromonaphthalene	67	—	—	—	196	
p-Chlorodiphenyl	77					
1 : 4-Dibromonaphthalene	82	—	—	—	135	
1 : 2 : 3-Tribromobenzene	87					
p-Dibromobenzene	89	84	a	2, 5		
p-Bromodiphenyl	89					
p-Bromoiodobenzene	91					
p-Iododiphenyl	113					
1 : 3 : 5-Tribromobenzene	120					
p-Diiodobenzene	129					
1 : 2 : 4 : 5-Tetrachlorobenzene	138					
1 : 2 : 4 : 5-Tetrabromobenzene	180	168	—	3		
Naphthalene tetrachloride	182					
9 : 10-Dichloroanthracene	211					
9 : 10-Dibromoanthracene	222					
Hexachlorobenzene	228	—	—	—	—	Fuming HNO_3 → chloranil, M.P. 290° C.
Hexabromobenzene	306					

GROUP IV—CLASS II

CARBOXYLIC ACID HALIDES, ALKYL CHLOROFORMATES, ALIPHATIC α-HALOGEN-SUBSTITUTED ETHERS

Substances belonging to the above classes are generally lachrymatory liquids with a sharp odour, although the higher members of the acyl halide series are crystalline solids. The lower members react violently with water forming a halogen hydracid and a carboxylic acid.

Classification tests.—(*a*) To 0·5 g. of the given substance add about 2 ml. of water drop by drop (*care*). Warm gently and test any vapours evolved for halogen hydracid by holding in them a drop of silver nitrate and nitric acid in the end of a glass tube. Formation of a turbidity in the drop, due to silver halide, indicates the presence of a member of this class.

(*b*) If test (*a*) gives a positive result, test the evolved gases for carbon dioxide by holding in them a drop of ammoniacal lime-water in the end of a glass tube. A milkiness in the drop indicates the presence of an alkyl chloroformate.

(*c*) If test (*b*) be negative, test with 2 : 4-dinitrophenylhydrazine (see p. 36) for the presence of an aldehyde in the residual liquid. A yellow precipitate indicates that the original compound is an aliphatic α-halogen-substituted ether.

If tests (*b*) and (*c*) are both negative while (*a*) is positive, a carboxylic acid halide is present.

$$R{\cdot}COCl + H_2O = R{\cdot}COOH + HCl$$
$$Cl{\cdot}COOR + H_2O = R{\cdot}OH + HCl + CO_2$$
$$R{\cdot}O{\cdot}CH_2Cl + H_2O = CH_2O + R{\cdot}OH + HCl.$$

Derivatives

1. **Amide** (for acid halides).

Add *slowly* 1 g. of the halide to 5 ml. of concentrated ammonia. Cork the tube and shake well. Cool, filter, and recrystallize from aqueous alcohol. For acyl halides of low molecular weight, the reaction should be carried out in the presence of a relatively large volume of ether. Separate the ether layer, distil off the ether and recrystallize the residual amide.

$$R{\cdot}COCl + 2NH_3 = R{\cdot}CONH_2 + NH_4Cl.$$

2. **Anilide** (for acid halides).

Dissolve about 3 g. of aniline in 10 ml. ether and add about 1 g. of the acid halide. Shake, filter off the aniline hydrochloride and wash the ethereal solution well with dilute hydrochloric acid to remove excess aniline. Dry over anhydrous sodium sulphate, distil off the ether and recrystallize the residue from aqueous alcohol.

$$R{\cdot}COCl + 2C_6H_5NH_2 = R{\cdot}CO{\cdot}NHC_6H_5 + C_6H_5NH_2{\cdot}HCl.$$

3. ***p*-Toluidide** (for acid halides).

As in Derivative 2 above, substituting *p*-toluidine for aniline.

4. Alkyl carbamate (urethane) (for alkyl chloroformates).

Add the chloroformate *slowly* to cold concentrated ammonia covered with a layer of ether. The urethane formed is soluble in ether. Separate the ether layer, dry and distil off the ether. Recrystallize the residual solid from alcohol.

$$Cl{\cdot}COOR + 2NH_3 = NH_2{\cdot}COOR + NH_4Cl.$$

5. Carbanilate (for alkyl chloroformates).

Method as for anilide from acid halide (see Derivative 2 above).

$$Cl{\cdot}COOR + 2C_6H_5NH_2 = C_6H_5NH{\cdot}COOR + C_6H_5NH_2{\cdot}HCl.$$

TABLE LVIII.—CARBOXYLIC ACID HALIDES

	B.P. °C.	Amide	Anilide	*p*-Toluidide	Acid
Liquids					
Acetyl chloride	55	82	112	147	
Oxalyl chloride	64	419d	245		
Propionyl chloride	80	79	105	124	
Acetyl bromide	81	82	112	147	
iso-Butyryl chloride	92	128	105	104	
n-Butyryl chloride	100	114	96	72	
Chloroacetyl chloride	105	120	137	162	
Dichloroacetyl chloride	107	98	125	153	
iso-Valeryl chloride	115	135	109	107	
Trichloroacetyl chloride	115	141	94		
n-Valeryl chloride	127	106	63	74	
Chloroacetyl bromide	127	120	137	162	
Bromoacetyl chloride	127	91	131	91	
Bromoacetyl bromide	149	91	131	91	
α-Bromopropionyl bromide	153	123	99	125	
n-Caproyl chloride	153	100	92	73	
Succinyl chloride	190d	260d	226	255	
n-Heptoyl chloride	193	96	71	80	
Benzoyl chloride	197	128	164	158	122
Phenylacetyl chloride	210	154	117	136	78
Benzoyl bromide	218	128	164	158	122
p-Chlorobenzoyl chloride	222	179	194	—	239
m-Chlorobenzoyl chloride	225	134	124	—	155
o-Chlorobenzoyl chloride	238	139	118	—	140
o-Methoxybenzoyl chloride	254	128	62	—	100
Phthalyl chloride (*sym*)	276	220	250	201	195d
Solids	M.P.				
Palmityl chloride	12	106	90	98	62
Stearyl chloride	22	108	94	102	69
Anisoyl chloride	26	162	168	186	184
o-Iodobenzoyl chloride	29	184	142	—	162
Cinnamoyl chloride	36	147	151	168	133

TABLE LIX.—ALKYL CHLOROFORMATES (CHLOROCARBONATES)

	B.P. °C	Alkyl carbamate (urethane)	Carbanilate	Miscellaneous
Methyl	71	52	47	Sharp odour
Ethyl	93	49	52	Sharp odour
iso-Propyl	105	92	90	Sharp odour
n-Propyl	115	60	58	
iso-Butyl	130	64	80	
n-Butyl	145	54		
iso-Amyl	154	64	55	

TABLE LX.—ALIPHATIC α-HALOGEN-SUBSTITUTED ETHERS

	B.P. °C.	Products with cold water
Chloromethyl ether	59	Methyl alcohol, formaldehyde
Chloromethyl ethyl ether	80	Ethyl alcohol, formaldehyde
α-Chloroethyl ether	98	Ethyl alcohol, acetaldehyde
αα′-Dichloromethyl ether	105	Formaldehyde
αα′-Dichloroethyl ether	116	Acetaldehyde
αβ-Dichloroethyl ether	140	Ethyl alcohol, chloroacetaldehyde hydrate
αα′-Dibromomethyl ether	150	Formaldehyde

GROUP IV—CLASS III

OTHER AROMATIC HALOGEN COMPOUNDS

If the preliminary test with alcoholic potash indicates that the halogen is attached to an aromatic nucleus and the compound is not a halogen-substituted hydrocarbon, classification tests as for carbon, hydrogen and oxygen compounds should be carried out in the following order:

A. Nuclear halogen-substituted aldehydes and ketones

Classification tests.—2 : 4-Dinitrophenylhydrazine test (see p. 36).
Schiff's reagent (see p. 36).
Tollens' reagent (see p. 36).
Dimedone derivative (see p. 39).

Derivatives as for aldehydes and ketones containing carbon, hydrogen and oxygen (see pp. 37–9).

B. Nuclear halogen-substituted acids and phenols

These two classes have been grouped together, as the presence of the halogen in the nucleus increases the acid character of the phenolic —OH group. Thus the highly halogenated phenols, e.g. tribromophenol, are strongly acidic and *their equivalent weight may be found by titrating a known weight with standard alkali using phenolphthalein as an indicator.*

All three of the following tests should therefore be applied:

(i) Dissolve 0·1 g. of the compound in water or neutral alcohol, add phenolphthalein followed by N/10 caustic soda drop by drop. A sharp end-point indicates a halogen-substituted acid or highly halogenated phenol.

(ii) Add *dilute* ferric chloride to an aqueous or alcoholic solution (neutralized to phenolphthalein) of the compound. A violet-blue or green colour which may be transient or permanent indicates a phenol. The absence of any definite colour does not necessarily mean the absence of a phenol, while the formation of a precipitate (if Test (i) above be positive) would indicate the presence of an acid.

(iii) Test for phenol with diazotized *p*-nitraniline (see p. 62). The absence of a red colour does not indicate that the given compound is not a phenol, because if both *ortho-* and *para*-positions in the ring are occupied by substituents, coupling cannot take place.

Derivatives of acids and phenols. Methods as for simple carboxylic acids (see pp. 52-4) and phenols (see pp. 62-6).

C. Esters derived from nuclear halogen-substituted acids

Classification test as for the corresponding carbon, hydrogen, oxygen compounds using alcoholic potash and phenolphthalein (see p. 67).

Derivatives, etc.—The hydrolysis and subsequent isolation of the alcohol or phenol and the acid, also the determination of the equivalent weight, may be carried out in the same way as for carbon, hydrogen, oxygen esters (see pp. 67, 72).

D. Nuclear halogen-substituted ethers

If the above tests for compounds A, B and C give no positive result, the given compound is probably of this type.

If so, it will be soluble in cold concentrated sulphuric acid and be reprecipitated on dilution with water.

Derivatives.—As for the corresponding carbon, hydrogen, oxygen compounds (see p. 86).

TABLE LXI.—NUCLEAR HALOGEN-SUBSTITUTED ALDEHYDES

	B.P. °C.	Oxime	Semi-carbazone	Phenyl-hydrazone	Oxidation product	2 : 4 Dinitro-phenyl hydrazone	Miscellaneous
Liquids							
o-Chlorobenzaldehyde	208	75	225	86	140	207	Dimedone deriv., M.P. 205° C.
m-Chlorobenzaldehyde	208	70	228	134	155	255	
m-Bromobenzaldehyde	236	72	205	141	155	257	
Solids	M.P.						
o-Iodobenzaldehyde	37	108	206	79	162	215	
p-Chlorobenzaldehyde	47	106	230	127	239	265	
m-Iodobenzaldehyde	57	63	226	155	187	258	
3 : 5-Dichlorobenzaldehyde	65	112	—	106			
p-Bromobenzaldehyde	67	157 (syn) 111 (anti)	228	113	251	257	
2 : 4-Dichlorobenzaldehyde	71	136	—	—	160		
2 : 6-Dichlorobenzaldehyde	71	149	—	—	139		
p-Iodobenzaldehyde	77	—	225	121	270	258	

TABLE LXII.—NUCLEAR HALOGEN-SUBSTITUTED KETONES

	B.P. °C.	Oxime	Semi-carbazone	Phenyl-hydrazone	2 : 4-Dinitro phenylhydrazone	Miscellaneous
Liquids						
p-Chloroacetophenone	232	95	—	114	231	
Solids	M.P.					
p-Chloropropiophenone	36	62	175			
p-Bromoacetophenone	51	128	—	126	230	
αα′-Bromocamphor	64	—	—	—	—	Oxid. with $KMnO_4$ → camphoric acid, M.P. 187° C.
2:4′-Dichlorobenzophenone	66					
p-Chlorobenzophenone	77	—	—	106	184	
p-Iodoacetophenone	85					
3:4′-Dichlorobenzophenone	105	153				
4:4′-Dichlorobenzophenone	147	135				
Chloranil	298					

TABLE LXIII.—NUCLEAR HALOGEN-SUBSTITUTED ACIDS

	M.P. °C.	Equivalent weight	Amide	Anilide	*p*-Nitro benzyl ester	*p*-Bromo phenacyl ester
2 : 6-Dichlorobenzoic	139	191				
o-Chlorobenzoic	140	157	139	118	106	106
o-Chlorophenoxyacetic	146	187		121	105	
o-Bromobenzoic	148	201	155	141	110	102
2 : 5-Dichlorobenzoic	153	191	155			
m-Bromobenzoic	155	201	155	146	105	126
m-Chlorobenzoic	155	157	134	124	107	116
p-Chlorophenoxyacetic	158	187		125	110	
2 : 4-Dichlorobenzoic	160	191				
o-Iodobenzoic	162	248	184	142	111	110
2 : 3-Dichlorobenzoic	164	192				
p-Fluorobenzoic	186	140	154			
m-Iodobenzoic	187	248	186	—	121	128
2 : 3 : 5-Triiodobenzoic	222	500				
3 : 5-Diiodo-2-hydroxybenzoic	230	390				
p-Chlorobenzoic	239	157	179	194	129	126
Tetrachlorophthalic	250	152	—	--	184	
p-Bromobenzoic	251	201	189	197	140	134
Tetrabromophthalic	266	241				
p-Iodobenzoic	270	248	217	210	141	147
3 : 5-Diiodo-4-hydroxybenzoic	278	390				
Tetraiodophthalic	327	335				

Table LXIV.—HALOGEN-SUBSTITUTED PHENOLS

	B.P. °C.	Acetyl deriv.	Benzoyl deriv.	Aryl oxy-acetic acid	*p*-Nitro benzoyl deriv.	Phenyl *iso*-cyanate deriv.	*p*-Toluene sulphonyl chloride deriv.	*p*-Nitro benzyl ether	Bromo deriv.	α-Naphthyl *iso*-cyanate deriv.	Miscellaneous
Liquids											
o-Chlorophenol	175	—	—	144	—	120	74	100	—	120	Picric acid deriv., M.P. 81° C.
o-Bromophenol	195	—	—	142	—	—	78	110	95	129	
Solids	M.P.										
m-Chlorophenol	32	—	71	109	—	—	—	—	—	158	B.P. 214° C.
m-Bromophenol	32	—	86	108	—	—	53				
2 : 4-Dibromophenol	36	36	97	153	184	—	—	—	95	—	Equiv. wt. 252
p-Chlorophenol	39	—	86	156	—	149	71	101	—	166	
m-Iodophenol	40	38	73	115		138					
2 : 4-Dichlorophenol	43	—	97	140	—	—	125	—	68	—	Equiv. wt. 163
o-Iodophenol	43	—	34	135		122	80				
2 : 6-Dibromophenol	56	—	—	—	—	—	—	—	—	—	Equiv. wt. 252
2-Hydroxy-3 : 5-dibromotoluene	57	—	—	—	—	—	—	—	—	—	Equiv. wt. 266
p-Chlorothymol	59										
p-Bromophenol	63	21	102	157	—	144	94	114	95	169	

[*Contd. over*

TABLE LXIV—(*contd.*)

	M.P. °C.	Acetyl deriv.	Benzoyl deriv.	Aryl oxy-acetic acid	*p*-Nitro benzoyl deriv.	Phenyl *iso*-cyanate deriv.	*p*-Toluene sulphonyl chloride deriv.	*p*-Nitro benzyl ether	Bromo deriv.	*α*-Naphthyl *iso*-cyanate deriv.	Miscellaneous
Solids											
2 : 4 : 5-Trichlorophenol	63	—	93	157	—	—	—	—	—	—	Equiv. wt. 197
2-Chloro-5-hydroxytoluene	64	—	86	—	—	139	—	—	70	154	
2 : 4 : 6-Trichlorophenol	67	—	70	182	106	—	—	—	—	188	Equiv. wt. 197
4-Chloro-6-phenylphenol	71										
p-Iodophenol	94	32	119	156	—	148					
2 : 4 : 6-Tribromophenol	95	82	81	200	—	168	—	164	120	153	Equiv. wt. 331
2 : 4-Dichloro-1-naphthol	106	—	75	—	—	—	—	—	—	—	Equiv. wt. 213
Chlorohydroquinone	106	72	130								
1 : 3-Dihydroxy-4-chlorobenzene (Chlororesorcinol)	107	48	66								
2 : 4-Dibromo-1-naphthol	109	—	—	—	—	—	—	—	—	—	Equiv. wt. 302
Bromohydroquinone	110	72	—	—	—	—	—	—	186		
2 : 4 : 6-Triiodophenol	158	—	—	224d	—	—	—	—	—	—	Equiv. wt. 472
Tetrabromo-*o*-cresol	210	154	—	—	—	—	—	—	—	—	Equiv. wt. 424
Tetrachlorohydroquinone	236	—	—	—	—	—	—	—	—	—	Equiv. wt. 236

TABLE LXV.—HALOGEN-SUBSTITUTED ESTERS—AROMATIC

	B.P. °C.	Equiv. Wt.	Miscellaneous
Liquids			
Methyl *o*-chlorobenzoate	234	171	
Ethyl *p*-chlorobenzoate	238	185	
Ethyl *o*-chlorobenzoate	243	185	
Methyl *o*-bromobenzoate	244	255	
Ethyl *m*-chlorobenzoate	245	185	
Ethyl *o*-bromobenzoate	254	229	
Ethyl *m*-bromobenzoate	259	229	
Ethyl *p*-bromobenzoate	262/737 mm.	229	
Solids	M.P.		
Methyl *m*-chlorobenzoate	21	171	B.P. 231° C.
Methyl *m*-bromobenzoate	29	215	
Methyl *p*-chlorobenzoate	43	171	
Methyl *m*-iodobenzoate	50	262	
Diethyl tetrachlorophthalate	60	180	
Methyl *p*-bromobenzoate	77	215	
Dimethyl tetrachlorophthalate	92	166	
Methyl *p*-iodobenzoate	114	262	

TABLE LXVI.—HALOGEN-SUBSTITUTED AROMATIC ETHERS

	B.P. °C.	Nitro deriv.	Nitrating agent
Liquids			
p-Fluoroanisole	157		
o-Chloroanisole	195	95	Fuming HNO_3
p-Chloroanisole	200	98	Fuming HNO_3
o-Chlorophenetole	208	82	Fuming HNO_3
o-Bromoanisole	218	106	Fuming HNO_3 and glacial acetic acid
p-Bromoanisole	223	88	Fuming HNO_3 and glacial acetic acid in the cold
o-Bromophenetole	224	98	
p-Bromophenetole	229	47	
o-Iodoanisole	240	95	
o-Iodophenetole	245	96	
Solids	M.P.		
p-Chlorophenetole	21	54	Conc. HNO_3
p-Iodophenetole	27	96	
β-Bromoethyl phenyl ether	32		
2 : 4 : 6-Trichlorophenetole	43	100 (di)	Long warming with a mixture of conc. HNO_3 and conc. H_2SO_4
2 : 4 : 6-Trichloroanisole	60	95 (di)	
2 : 4 : 6-Tribromophenetole	72	79	
2 : 4 : 6-Tribromoanisole	87		

GROUP IV—CLASS IV

OTHER ALIPHATIC HALOGEN-SUBSTITUTED COMPOUNDS

The compounds included in this class contain a halogen-substituted alkyl group.

A. Halogen-substituted aldehydes and ketones

Such compounds have a pungent odour while the ketones may be strongly lachrymatory.

Classification tests.—Apply the four following tests as for the corresponding carbon, hydrogen and oxygen compounds:

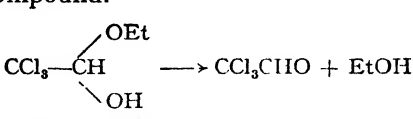
2 : 4-Dinitrophenylhydrazine reagent (see p. 36).
Schiff's reagent (see p. 36).
Tollens' reagent (see p. 36).
Dimedone derivative (see p. 39).

Derivatives as for the corresponding carbon, hydrogen, oxygen compounds (see pp. 37–9).

B. Hydrates and alcoholates of halogen-substituted aldehydes

Classification test.—Warm a small quantity of the given substance with concentrated sulphuric acid, cool, and apply the 2 : 4-dinitrophenylhydrazine test (see p. 36).

Confirmatory test.—To about 0·5 g. of the substance add a few ml. of 2N sodium hydroxide and boil for 1 min. Cool, make just acid to phenolphthalein with hydrochloric acid, add 1 ml. of mercuric chloride and boil. A white precipitate of mercurous chloride shows the presence of formate arising from the hydrolysis of the above type of compound.



chloral alcoholate

$$CCl_3CHO + NaOH \rightarrow CHCl_3 + HCOONa.$$

C. Halogen-substituted acids

Classification tests.—1. Such acids, even if insoluble in water, will be soluble in sodium bicarbonate solution, carbon dioxide being evolved.

2. In the classification test for simple carboxylic acids (see p. 50) with caustic soda and phenolphthalein, a sharp end-point is generally obtained, although the red colour may fade slowly, especially with acids containing bromine and iodine. This fading, due to hydrolysis causing the replacement of the halogen atom by a hydroxyl group, sometimes makes the determination of equivalent weight unsuitable for identification purposes.

Determination of the percentage of halogen present in the compound is a better method, and may be carried out either by refluxing an accurately weighed amount of the acid with 2N alcoholic potash, cooling, acidifying with nitric acid and determining the halogen by Volhard's method or by any of the methods indicated on pp. 206–7.

Derivatives.—As for the corresponding simple carboxylic acids (see pp. 52–4).

D. Halogen-substituted alcohols

Classification tests.—Apply the ceric ammonium nitrate test as for the simple alcohols (see p. 77).

If this test be positive, confirm the result by the following test:

Take one drop of the given substance in a dry test-tube and add *one drop* of acetyl chloride. If the substance be an alcohol, a vigorous reaction will ensue, especially if the alcohol be water soluble.

Derivatives.—As for the corresponding simple alcohols (see pp. 79–81).

E. Halogen-substituted esters

Classification tests.—The ordinary test for esters (see p. 67) is not applicable, as owing to hydrolysis and the formation of the potassium salt of a halogen hydracid all aliphatic halogen-containing substances will give a positive result.

Esters, however, react readily with concentrated ammonia to give sparingly soluble amides.

Shake about one gram of the ester with 5 ml. of concentrated ammonia in a corked test-tube. Cool well, and allow to stand for 5 min. The amide usually crystallizes out, and after separation may be recrystallized from dilute alcohol and used as a derivative of the acid from which the ester is derived.

Hydrolysis of the ester (see p. 67) and isolation of the alcohol will only serve for the identification of the alcoholic portion of the ester molecule.

Note.—Esters of trichloroacetic acid yield chloroform on *prolonged* boiling with alkali.

TABLE LXVII.—HALOGEN-SUBSTITUTED ALDEHYDES AND KETONES—ALIPHATIC

	B.P. °C.	Miscellaneous
Liquids		
Chloral	98	Water → chloral hydrate, M.P. 57° C. Semicarbazide → addition compound, M.P. 90° C.
Chloroacetone	118	Semicarbazone, M.P. 150° C.*
αα-Dichloroacetone	120	
Bromal	174	Water → bromal hydrate, M.P. 53° C. Acetic anhydride → diacetate, M.P. 76° C.
Solids	M.P.	
αγ-Dichloroacetone	45	
ω-Bromoacetophenone (Phenacyl bromide)	50	β-Naphthyl ether, M.P. 105° C. Cold fuming HNO_3 → nitro-deriv., M.P. 96° C.
ω-Chloroacetophenone (Phenacyl chloride)	59	Derivatives as for ω-bromoacetophenone
α-Bromocamphor	76	$KMnO_4$ → camphoric acid, M.P. 187° C.

TABLE LXVIII.—HYDRATES AND ALCOHOLATES OF HALOGEN-SUBSTITUTED ALDEHYDES

	B.P. °C.	Miscellaneous
Liquids		
Chloroacetal	157	
Bromoacetal	170d	
Solids	M.P.	
Bromal alcoholate	44	Bromal on distillation
Bromal hydrate	53	Bromal on distillation
Chloral alcoholate	56	
Chloral hydrate	57	
Butylchloral hydrate	78	

* Unstable. Decomposed by boiling water or alcohol.

TABLE LXIX.—HALOGEN-SUBSTITUTED ACIDS—ALIPHATIC

	B.P. °C.	Equivalent weight	Amide	Anilide	*p*-Toluidide	*p*-Nitro benzyl ester	*p*-Bromo phenacyl ester	Miscellaneous
Liquids								
α-Chloropropionic	186	108	80	92	124			
Dichloroacetic	189	129	98	125	153	—	99	
α-Bromo-*n*-butyric	217d	167	—	98	92			
α-Bromo-*n*-caproic	240	195						
Solids	M.P.							
β-Bromo-*iso*-butyric	22	167						
α-Bromopropionic	24	153	123	99	125	—	—	B.P. 205° C.
β-Chloropropionic	42	108						
α-Bromo-*iso*-valeric	44	181	133	116	124	—	—	B.P. 230° C.
Dibromoacetic	48	218	156	—	—	—	—	B.P. 234° C.
α-Bromo-*iso*-butyric	49	167	148	83	93	—	—	B.P. 200° C.
Bromoacetic	50	139	91	131	91	89	—	B.P. 208° C.
Trichloroacetic	57	163	141	94	. .	80	—	
β-Bromopropionic	62	153						
Chloroacetic	63	94	120	137	—	—	105	B.P. 185° C.
αβ-Dibromopropionic	64	232	130					
β-Iodopropionic	82	200	101					
Iodoacetic	83	186	95	143				
αβ-Dibromobutyric	87	246						
Trichlorolactic	124	193	145	164				
αβ-Dibromosuccinic	167	138	—	—	—	168		

TABLE LXX.—HALOGEN-SUBSTITUTED ALCOHOLS—ALIPHATIC

	B.P. °C.	α-Naphthyl *iso*-cyanate deriv.	Phenyl *iso*-cyanate deriv.	Miscellaneous
Liquids				
1-Chloro-2-propanol	127			
2-Chloroethanol (Ethylene chlorohydrin)	129	101	51	
2-Chloro-1-propanol	134			
2-Bromoethanol (Ethylene bromohydrin)	150	86	76	
Trimethylene chlorohydrin	161d	76		
1 : 3-Dichloro-2-propanol (Glycerol αα′-dichlorohydrin)	176	115	73	
Trimethylene bromohydrin	176d	74		
2 : 3-Dichloro-1-propanol (Glycerol αβ-dichlorohydrin)	182	93	73	
3-Chloro-1 : 2-propanediol (Glycerol α-monochlorohydrin)	215d			
2 : 3-Dibromo-1-propanol (Glycerol αβ-dibromohydrin)	219		77	
1 : 3-Dibromo-2-propanol (Glycerol αα′-dibromohydrin)	219d	—	84	
Solids	M.P.			
Trichloroethyl alcohol	19			
Trichlorobutyl alcohol (Chloretone)	96*	—	—	* Anhydrous; hydrated 80–81° C. Gives iodoform reaction

TABLE LXXI—HALOGEN-SUBSTITUTED ESTERS—ALIPHATIC

	B.P. °C.	Amide	
Chloromethyl acetate	111		
Bromomethyl acetate	130		
Methyl chloroacetate	130	119	
Methyl dichloroacetate	143		
Methyl bromoacetate	144	91	Sharp odour
Ethyl chloroacetate	145	119	
β-Chloroethyl acetate	145		
Ethyl α-chloropropionate	146	80	
Benzyl chloroacetate	147		
Methyl trichloroacetate	152		
Methyl β-chloropropionate	156		
Ethyl dichloroacetate	158	98	
Ethyl bromoacetate	159	—	Sharp odour Addition product with quinoline, M.P. 180° C.
Ethyl β-chloropropionate	162		
Ethyl α-bromopropionate	162		
β-Bromoethyl acetate	163		
Ethyl trichloroacetate	167	141	
Methyl iodoacetate	170	—	Very sharp odour
n-Butyl chloroacetate	175	119	
Ethyl iodoacetate	179	—	Very sharp odour
Ethyl β-bromopropionate	179		
Methyl iodopropionate	188		
Ethyl iodopropionate	200		
Ethyl bromomalonate	235		
Solids	M.P.		
Ethyl trichlorolactate	62	—	B.P. 162° C.

TABLE LXXII.—ALIPHATIC HALOGEN-SUBSTITUTED ETHERS —OTHER THAN α

	B.P. °C.
β-Chloroethyl ether	107
Epichlorohydrin	117
β-Bromoethyl ether	127
ββ′-Dichloroethyl ether	178
γγ′-Dichloropropyl ether	215

CHAPTER VII

Summary of Classification Tests, Derivatives, etc., for Compounds containing Carbon, Hydrogen, Nitrogen, Sulphur, and possibly Oxygen and/or a Metal

Preliminary examination

1. Physical properties.
2. Ignition on a crucible lid.
3. Solubility and reaction to litmus of water-soluble compounds.
4. Action of cold and hot sodium hydroxide.
5. Soda-lime test.

Class	Classification Tests	Additional Tests	Derivatives, &c.
Sulphates of organic bases (p. 234)	Hydrochloric acid and barium chloride	As for organic bases in C, H, N(O) group of compounds	As for organic bases in C, H, N(O) group of compounds
Ammonium salts of sulphonic, amino-sulphonic, nitro-sulphonic acids (p. 235)	Zinc or magnesium oxide test	Zinc/alkali test for nitrogen after removal of ammonia	As for sulphonic, amino-sulphonic and nitro-sulphonic acids
Thiourea, thioamides, mono- and di-substituted thioureas (p. 236)	Alcoholic yellow mercuric oxide	*For thiourea* Ferric chloride test after fusion *For thioamides* Hydrolysis with alcoholic potash	*For thiourea* S-benzylthiuronium chloride *For simple thioamides* Amide Xanthydrol deriv. *For mono-substituted thioureas* Addition compound with methyl iodide *For di-substituted thioureas* Di-substituted ureas

Class	Classification Tests	Additional Tests	Derivatives, &c.
Isothiocyanates (p. 239)	Dry yellow mercuric oxide	Reduction with zinc and hydrochloric acid	Substituted phenyl thioureas Mono-substituted thioureas Thiourethanes
Salts and esters of thiocyanic acid (p. 240)	Ferric chloride test	Reduction with zinc and hydrochloric acid	*For aryl thiocyanate* S-benzylthiuronium salt of sulphonic acid
Simple sulphonamides (p. 241)	Preliminary tests and absence of urea sulphate, thiourea and mono-substituted thioureas	Fusion with sodium hydroxide	Benzoyl deriv. Dimethyl deriv.
Amino-sulphonic acids and their salts (p. 244)	Diazotization and coupling with alkaline β-naphthol	*For sulphanilic and naphthionic acids* Oxidation to quinone	S - benzylthiuronium salt Equivalent weight
Nitro-sulphonic acids and their salts (p. 245)	Test for the presence of a nitro-group with tin and hydrochloric acid		Equivalent weight Amide. Anilide S - benzylthiuronium salt
Substituted sulphonamides (p. 246)	Hydrolysis with hydrochloric acid and phosphoric acid in diethylene glycol and test for primary and secondary amine		Methyl deriv.

GROUP V

COMPOUNDS CONTAINING CARBON, HYDROGEN, NITROGEN, SULPHUR, AND POSSIBLY OXYGEN AND/OR A METAL

Preliminary examination

1. *Physical properties.*

If yellow	Probably a nitrosulphonic acid.
An odour of leeks	Esters of thiocyanic acid.
An odour of mustard	Esters of isothiocyanic acid (mustard oils).

2. *Effect of ignition on a crucible lid.*

A non-combustible residue of metal oxide or carbonate remains	Salts of thiocyanic, aminosulphonic and nitrosulphonic acids; metallic derivatives of saccharin.

3. *Solubility in water and reaction to litmus.*

Soluble in the cold giving an acid solution	Sulphates of nitrogen bases; nitrosulphonic acids; some aminosulphonic acids.
Soluble with a neutral reaction	Thiocarbamide.
Sparingly soluble with an acid reaction	Many amino-sulphonic acids; some nitrosulphonic acids.
Sparingly soluble with a neutral reaction	Many substituted thioureas.
Insoluble	Alkyl thiocyanates and isothiocyanates; some aromatic aminosulphonic acids; some simple and substituted sulphonamides.

4. *Action of cold and hot sodium hydroxide.*

Ammonia evolved in the cold (litmus paper test)	Ammonium salt of sulphonic, sulphinic, aminosulphonic, nitrosulphonic acid; ammonium thiocyanate.
Ammonia liberated slowly on boiling	Urea sulphate, thiourea and monosubstituted thioureas, simple sulphonamides.
Precipitate or oily emulsion and an odour of an organic base in the cold or on warming	Sulphate of primary aromatic amine, secondary aromatic amine or substituted hydrazine.
A base liberated on prolonged boiling	Substituted thiourea.

5. *Soda-lime test* (see p. 21)

Ammonia evolved	Urea sulphate, thiourea, mono-substituted thioureas, simple sulphonamides, ammonium salt of an organic sulphur acid.
Odour of an organic base	Sulphate of an aliphatic or aromatic amine, sulphanilic acid, some substituted thioureas.
Odour of a nitrophenol	Nitrosulphonic acid.

GROUP V—CLASS I

SULPHATES OF ORGANIC BASES, ETC.

Some indication of the probable presence of such compounds will have been obtained in the preliminary examination with sodium hydroxide and soda-lime.

Classification test.—Dissolve the given compound in water, add dilute hydrochloric acid and barium chloride solution. A white precipitate of barium sulphate indicates the presence of the sulphate of a nitrogen base.

Examine the compound for:

(*a*) Reducing bases with Fehling's solution, &c. (see p. 106).

(*b*) Primary aliphatic amines, urea and substituted ureas, guanidine and guanidines with nitrous acid in 75 per cent sulphuric acid (see p. 109).

(*c*) Aliphatic and aromatic secondary amines with nitrous acid (see p. 124).

(*d*) Primary aromatic amines by diazotizing and coupling with β-naphthol (see p. 124).

(*e*) Alkaloids (see p. 173).

Preparation of derivatives of the base may generally be carried out directly using the original compound. If, however, a sample of the free base (not urea, &c.) is required, treat the given substance with an excess of warm sodium hydroxide* and extract the free base with ether. Separate the ether layer and dry over anhydrous sodium sulphate. Evaporate off the ether.

GROUP V—CLASS II

AMMONIUM SALTS OF SULPHONIC ACIDS, AMINO-SULPHONIC ACIDS AND NITRO-SULPHONIC ACIDS

Classification test.—If, in the preliminary test, ammonia was evolved on heating with soda-lime, test for the presence of an ammonium salt with zinc or magnesium oxide as for compounds containing carbon, hydrogen, nitrogen and oxygen (see p. 105).

If an ammonium salt is proved present, boil the original compound with sodium hydroxide till all ammonia is evolved, neutralize with dilute sulphuric acid and evaporate to dryness. Test the residue for the presence of *nitrogen* by the zinc/carbonate fusion (see p. 16).

If nitrogen is absent, the given compound is the ammonium salt of a sulphonic acid. Eliminate the ammonia as above, and identify the sodium salt formed as in Group III, Class VI (see p. 193).

If nitrogen is present, the original compound is the ammonium salt of an amino- or a nitro-sulphonic acid. Examine it as in the case of these acids (see pp. 244–5).

* For sulphates of amino-phenols use cold sodium bicarbonate solution.

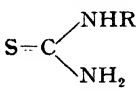
GROUP V—CLASS III

THIOUREA, THIOAMIDES, MONO- AND DI-SUBSTITUTED THIOUREAS

Classification test.—Add some of the given compound to an alcoholic suspension of yellow mercuric oxide. If no reaction occurs in the cold, warm gently. Formation of black mercuric sulphide indicates the presence of a substance of the above type. Esters of isothiocyanic acid produce no more than a slight darkening.

If the above test is positive, continue as follows:

(*a*) Heat a small quantity of the compound just to the fusion temperature. Cool, dissolve in water and add ferric chloride solution. Formation of a blood-red colour indicates the presence of thiourea or a monosubstituted thiourea.

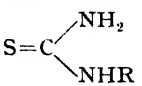


$$\rightleftharpoons R.NH_3^+ CNS^-$$

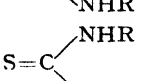
(R = H, Alk. or Ar.)

(*b*) If test (*a*) above is positive, heat a small quantity of the substance with soda-lime. An organic base (2 : 4-dinitrochlorobenzene test) is evolved from a mono-substituted thiourea.

Heat the given compound with alcoholic potash under a reflux condenser. Cool, boil a portion in a test-tube and test any vapours evolved with 2 : 4-dinitrochlorobenzene test paper. An intense yellow colour shows the presence of a primary aliphatic amine arising from an alkyl mono- or di-substituted thiourea.



$$+ 4KOH = K_2S + NH_3 + K_2CO_3 + H_2O + RNH_2$$



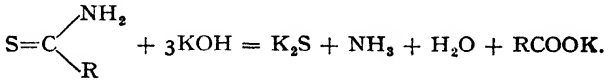
$$+ 4KOH = K_2S + K_2CO_3 + H_2O + 2RNH_2.$$

Acidify a second portion with dilute hydrochloric acid and boil off the hydrogen sulphide. After cooling well, test for the presence of a primary aromatic amine with sodium nitrite and alkaline β-naphthol (see p. 124). If a primary aromatic amine is present, the original compound is an aryl mono- or di-substituted thiourea. Only the mono-substituted compounds will have yielded ammonia in test (*b*) above.

If no primary aromatic amine is present, add solid cadmium carbonate to a third portion of the hydrolysed substance, shake well and filter. Acidify the filtrate with dilute sulphuric acid. If a precipitate (other than potassium sulphate) is formed, filter it off and identify it as an aromatic acid (benzoic acid is the most likely one).

If no solid acid is precipitated, distil and test the distillate for a volatile acid. If present, identify it.

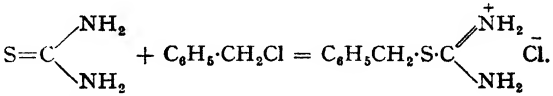
Formation of an organic acid indicates that the original compound is a simple thioamide.



Derivatives

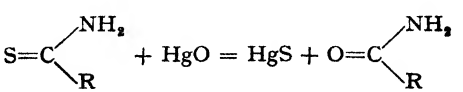
1. **S-benzyl thiuronium chloride** (for thiourea).

Take about 0·5 g. of the substance, add an equal weight of benzyl chloride and about 3 ml. of alcohol. Reflux for 15 min.; cool and filter off the crystalline precipitate. Recrystallize from alcohol.



2. **Amide** (for simple thioamides).

Shake some of the compound with an aqueous or alcoholic suspension of yellow mercuric oxide. Filter, and evaporate off the water or alcohol on a water-bath. Recrystallize the resultant amide from dilute alcohol.

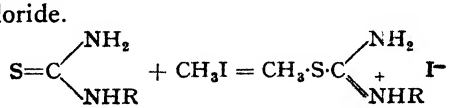


3. **Xanthydrol derivative** (for simple thioamides).

Method as for simple substituted amides (see p. 114).

4. **Addition compounds with methyl iodide** (for monosubstituted thioureas).

Prepared as for Derivative 1 above substituting methyl iodide for benzyl chloride.



5. Di-substituted ureas (for di-substituted thioureas).

Shake about 1 g. of the original substance with an alcoholic suspension of yellow mercuric oxide. Warm gently to accelerate the reaction. Filter off the mercuric sulphide formed together with excess mercuric oxide. Evaporate off the alcohol and recrystallize the di-substituted urea from dilute alcohol.

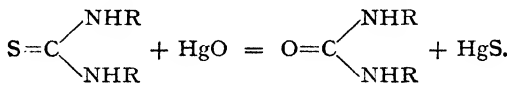


TABLE LXXIII.—THIOUREA, THIOAMIDES, MONO- AND DI-SUBSTITUTED THIOUREAS

	M.P. °C.	Miscellaneous Derivatives
sym-Dimethyl thiourea	61	Nitroso deriv., M.P. 47° C.
unsym-Dipropyl thiourea	67	*unsym*-Dipropyl urea, M.P. 76° C.
sym-Di-*n*-propyl thiourea	67	
sym-Dipropyl thiourea	71	*sym*-Dipropyl urea, M.P. 105° C.
sym-Diethyl thiourea	77	Ethyl iodide in alcohol → addition compound, M.P. 72° C.
Allyl thiourea	78	
n-Butyl thiourea	79	
Thioacetamide	108	
Propyl thiourea	110	
Thiobenzamide	116	
Methyl thiourea	119	
sec-Butyl thiourea	137	
4-Phenylthiosemicarbazide	142	
sym-Diphenyl thiourea (Thiocarbanilide)	153	Carbanilide, M.P. 238° C. Me_2SO_4 and 15 per cent NaOH → S-methyl deriv., M.P. 109° C.
sym-Di-*o*-tolyl thiourea	153	*sym*-Di-*o*-tolyl urea, M.P. 250° C.
Phenyl thiourea	154	Heat with aniline → thiocarbanilide, M.P. 153° C.
unsym-Dimethyl thiourea	159	
tert-Butyl thiourea	165	
Acetyl thiourea	166	
sym-Di-*p*-tolyl thiourea	178	*sym*-Di-*p*-tolylurea, M.P. 268° C.
Thiourea	180	NH_4SCN → addition compound, M.P. 144° C. Xanthydrol deriv., M.P. 226° C. With benzyl chloride in alcohol → S-benzyl thiuronium chloride, M.P. 176° C.
Thiosemicarbazide	182	Hydrochloride, M.P. 188° C. Acetyl deriv., M.P. 165° C.
1-Phenylthiosemicarbazide	200d	1-Phenylsemicarbazide, M.P. 172° C.

GROUP V—CLASS IV

ISOTHIOCYANATES

Classification test.—Heat about 0·5 g. of the given compound with 0·5 g. of yellow mercuric oxide just to the boiling-point of the substance. If black mercuric sulphide is formed, the presence of an isothiocyanate (mustard oil) is indicated. (Allyl isothiocyanate reacts somewhat slowly.)

Confirmatory test.—Mix about 1 g. of the given compound with 10 ml. of hydrochloric acid, add a slight excess of zinc dust and heat under a reflux till reduction has been effected. Thioformaldehyde (CH_2S), with the odour of onions, will be evolved. Cool, make alkaline with caustic soda and distil. Test the distillate for primary aliphatic amine (see p. 110). If present, the original compound is an alkyl isothiocyanate. If no aliphatic amine is found, extract the alkaline liquid with ether, remove the ether by distillation, and test the residue for a primary aromatic amine (see p. 124). A positive result proves that the original compound was an aryl isothiocyanate.

Derivatives

1. Substituted phenylthioureas.—Method as for primary aliphatic amines substituting aniline for the base (see p. 111).

TABLE LXXIV.—ISOTHIOCYANATES

	B.P. °C.	Substituted phenylthiourea	Mono-substituted thiourea	Miscellaneous
Liquids				
Allyl	150	98	74	
Phenyl	220	153	154	Thiourethane (2 isomers), M.P. 72° or 73° C.
o-Tolyl	239	139	151	
Solids	M.P.			
p-Tolyl	26	141	—	B.P. 239° C.
α-Naphthyl	58	158		
m-Nitrophenyl	60	155		
β-Naphthyl	62	182		
4-Diphenylyl	70	—	—	Methylamine → subst. ether, M.P. 142° C.

2. **Monosubstituted thioureas.**—Method as for isothiocyanates of primary aliphatic amines substituting ammonia for the base (see p. 111).

$$R{\cdot}N : C : S + NH_3 = R{\cdot}NH{\cdot}CS{\cdot}NH_2.$$

3. **Thiourethanes.**—Reflux one gram of the substance with 5 ml. of absolute alcohol till the odour of mustard oil disappears. Pour into water, filter, and recrystallize the solid from alcohol.

$$R{\cdot}N : C : S + C_2H_5OH = R{\cdot}NH{\cdot}CS{\cdot}OC_2H_5.$$

GROUP V—CLASS V

SALTS AND ESTERS OF THIOCYANIC ACID

Classification test.—If a metal is present as shown by the preliminary tests, dissolve some of the given substance in water or dilute hydrochloric acid and add ferric chloride solution. A blood-red colour, discharged by mercuric chloride solution, shows the presence of a metallic thiocyanate.

If no metal is present, mix about 0·5 g. of the given compound with 2 ml. of N/2 alcoholic potash and heat in a boiling water bath for 10 min. Cool, make acid with dilute nitric acid and add ferric chloride solution. A blood-red colour shows the presence of an ester of thiocyanic acid.

Confirmatory test.—Mix a small amount of the original compound with dilute hydrochloric acid and add zinc dust. Boil, and lead any volatile products into caustic soda solution. Add excess ferrous sulphate solution, boil well, cool and add a few drops of ferric chloride followed by hydrochloric acid till clear. A blue precipitate (or green solution) as in testing for nitrogen indicates the presence of a thiocyanate.

Derivative (for aryl thiocyanate).

Oxidation to sulphonic acid and preparation of S-benzylthiuronium salt.

Boil one gram of the compound with 5 ml. of concentrated nitric acid under a reflux for 15 min. Cool, dilute to 10 ml. with water, and neutralize with sodium hydroxide. Add 5 g. of S-benzyl thiuronium chloride dissolved in the minimum amount

of water. Cool well and scratch the inside of the tube to induce crystallization. If no crystalline precipitate forms, concentrate by evaporation.

$$Ar{\cdot}S{\cdot}C{:}N + 4HNO_3 = Ar{\cdot}SO_3H + 4NO_2 + HCN + H_2O.$$

TABLE LXXV.—ESTERS OF THIOCYANIC ACID

	B.P. °C.	Miscellaneous
Liquids		
Methyl	130	
Ethyl	145	
iso-Propyl	152	
Allyl	161	
n-Butyl	182	
Phenyl	231	
Solids	M.P.	
Benzyl	141	Nitric acid→benzoic acid, M.P. 122° C.

GROUP V—CLASS VI

SIMPLE SULPHONAMIDES

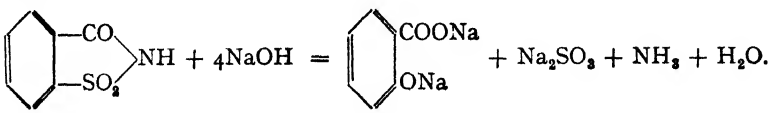
If ammonia has been liberated slowly on boiling with sodium hydroxide in the preliminary examination, and classification tests have shown the absence of urea sulphate, thiourea and mono-substituted thioureas, the substance is probably a simple sulphonamide.

Confirmatory test.—Fuse about one gram of the substance with 3 g. of caustic soda in a nickel crucible. Test for the evolution of ammonia.* Cool, dissolve in water, acidify with dilute hydrochloric acid and extract with ether. Dry the ethereal solution with anhydrous sodium sulphate and remove the ether. Examine the residue for a phenol with ferric chloride (see p. 61).

The presence of a phenol proves that the original compound is a simple sulphonamide.

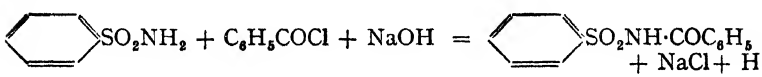
* In the case of sulphanilamide, aniline will also be driven off.

If salicylic acid is formed, the original substance is probably saccharin.



Derivatives

1. **Benzoyl derivative.**—Prepared by the Schotten-Baumann reaction (see p. 131).



2. **Dimethyl derivative.**—Dissolve one gram of the given compound in 10 ml. of 2N sodium hydroxide in a stoppered bottle, warming if necessary. Add 2 ml. of dimethyl sulphate (*caution* —poisonous vapour), and shake vigorously for 5 min. Transfer to a small flask, add a further 10 ml. of sodium hydroxide and boil under a reflux for 10 min. to hydrolyse the excess of dimethyl sulphate. Cool, and shake till the oil that first separates becomes solid. Filter, wash with water and recrystallize from dilute alcohol.

$$ArSO_2NH_2 + 2(CH_3)_2SO_4 + NaOH = ArSO_2N(CH_3)_2 + 2CH_3NaSO_3 + 2H_2O.$$

Note.—In the case of saccharin, Method 2 above will yield a monomethyl derivative.

3. **Xanthydrol derivative.**—As for simple amides (see p. 114).

TABLE LXXVI.—SULPHONAMIDES

	M.P. °C.	Xanthydrol deriv.	Miscellaneous
Ethane-	58		
Methane-	90		
Benzyl-	105		
m-Toluene-	108		
4-Ethylbenzene-	109	196	
d-Camphor-10-	132		
3 : 5-Dimethylbenzene-	135		
d-Camphor-8-	137		
2 : 4-Dimethylbenzene-	137	188	
p-Toluene-	137	197	Dimethyl deriv., M.P. 80° C. N-benzoyl deriv., M.P. 147° C.
2 : 4 : 6-Trimethylbenzene-	142	204	
3 : 4-Dimethylbenzene-	144	190	
2 : 5-Dimethylbenzene-	148	176	
1-Naphthalene-	150		
o-Toluene-	153	183	
Benzene-	153	206	Dimethyl deriv., M.P. 47° C.
m-Nitrobenzene-	162		
p-Aminobenzene- (Sulphanilamide)	163	208	
2 : 3-Dimethylbenzene-	167		
p-Nitrobenzene-	180		
2 : 4 : 5-Trimethylbenzene-	181		
2-Naphthalene-	212	—	Dimethyl deriv., M.P. 94° C.
1-Nitro-2-naphthalene-	214		
o-Sulphobenzimide (Saccharin)	222	199	Methyl deriv., M.P. 131° C.
2-Methylbenzene-1 : 4-di-	224		
1 : 3-Benzene di-	229	170	
4-Methylbenzene-1 : 2-di-	237		
2 : 7-Naphthalene di-	242		
1 : 5-Anthraquinone di-	246		
1 : 2-Benzene di-	254		
Anthraquinone-β-	261		
1 : 4-Naphthalene di-	273		
1 : 4-Benzene di-	288		
1 : 6-Naphthalene di-	298		
1 : 5-Naphthalene di-	310		
1 : 3 : 5-Benzene tri-	312		
1 : 8-Anthraquinone di-	340		

GROUP V—CLASS VII

AMINOSULPHONIC ACIDS AND THEIR SALTS

Classification test.—Dissolve about 0·2 g. of the substance in dilute sodium carbonate, add about 0·1 g. of sodium nitrite dissolved in a little water, and then dilute hydrochloric acid dropwise until free nitrous acid is shown to be present by the starch/potassium iodide test. Keep the solution *quite cold* during this addition. Pour the resulting solution into a solution of β-naphthol in sodium hydroxide keeping the solution alkaline. Formation of a soluble azo-dye indicates the presence of an aminosulphonic acid.

Confirmatory test for sulphanilic acid (1 : 4-amino-benzene sulphonic acid) or naphthionic acid (1 : 4-amino-naphthalene sulphonic acid).

Mix a little of the substance with manganese dioxide and concentrated sulphuric acid and warm. The characteristic pungent odour of *p*-benzoquinone or α-naphthoquinone will be apparent.

Derivatives

1. **S-benzylthiuronium salt.**—Method as for the corresponding derivative of sulphonic acids (see p. 193).

2. **Equivalent weight.**—As for simple carboxylic (water soluble) acids (see p. 52).

3. **Tribromo derivative** (for sulphanilic acid only).

Dissolve about 0·5 g. of the substance in water with the aid of heat and add a solution of bromine in potassium bromide until a slight excess is present as indicated by the yellow colour of the solution. Filter, wash with cold water and recrystallize from dilute alcohol.

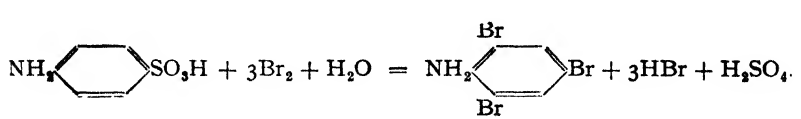


TABLE LXXVII.—AMINO-SULPHONIC ACIDS (SOLIDS)

	Amide	Anilide	S-benzyl thiuronium salt	Miscellaneous
Sulphanilic acid (1 : 4)	163	—	182	*sym*-Tribromo aniline, M.P.119° C.
Metanilic acid (1 : 3)	142	—	148	
Disulphanilic (1 : 2 : 4)				
Naphthionic acid (1 : 4)	—	—	ca.100	
1-Naphthylamine-5-sulphonic acid	—	—	175d	
1-Naphthylamine-8-sulphonic acid	—	—	300d	
2-Naphthylamine-6-sulphonic acid	—	—	184	
o-Aminobenzene sulphonic acid	153		132	
2-Amino-5-methylbenzene-1 : 3-disulphonic acid	257	192		
2 : 4-Diaminobenzene-1 : 5-disulphonic acid	187	236		
2-Naphthylamine-4 : 8-disulphonic acid	—	—	210d	
2-Naphthylamine-6 : 8-disulphonic acid	—	—	276d	

GROUP V—CLASS VIII

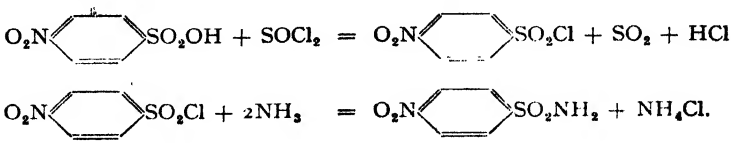
NITROSULPHONIC ACIDS AND THEIR SALTS

Classification test.—Apply the classification test for nitro-compounds (see p. 162). A positive result shows the presence of a nitrosulphonic acid.

Derivatives, etc.

1. **Equivalent weight.**—Method as for simple carboxylic acids (see p. 52).

2. **Amide.**—Prepare the sulphonyl chloride using thionyl chloride, and convert this to the amide by the method given for amides of simple carboxylic acids (see p. 52).



3. **Anilide.**—Method as for anilides of simple carboxylic acids (see p. 52).

4. **S-benzylthiuronium salts.**—Method as for the corresponding derivative of sulphonic acids (see p. 193).

TABLE LXXVIII.—NITRO-SULPHONIC ACIDS

	M.P. °C.	Amide	Anilide	Miscellaneous
m-Nitrobenzene-	48	161	126	S-benzylthiuronium salt, M.P. 146° C.
o-Nitrobenzene-	70*	191	115	*Hygroscopic
2-Nitrotoluene-4-	86	144	109	
p-Nitrobenzene-	95	180	136	
1-Nitronaphthalene-2-	105	214	202	
4-Nitrotoluene-2-	133*	186	148	* Dihydrate
2:5-Dimethyl-4-nitrobenzene	140	198	131	
2 : 4-Dinitro-1-naphthol-7-	150			

GROUP V—CLASS IX

SUBSTITUTED SULPHONAMIDES

Classification test.—To one gram of the original compound add 2 ml. of diethylene glycol and one ml. of syrupy phosphoric acid. Heat just to boiling, and maintain at this temperature for about 2 min. *Allow to cool* in air; add 10 ml. of dilute hydrochloric acid and again boil for 1 min. Cool, and filter if necessary. Make a portion of the solution alkaline with caustic soda, boil, and test the vapour for primary aliphatic amine with 2 : 4-dinitrochlorobenzene test paper. If a positive result is obtained, then the given compound is the sulphonyl derivative of a primary aliphatic amine.

If no primary aliphatic amine is found, make the remainder of the solution alkaline with caustic soda and extract with ether. Remove the ether and examine the residue for (i) secondary amine by the nitrous acid test and by special test on p. 126.

(ii) Primary aromatic amine by the nitrous acid/alkaline β-naphthol test.

A positive test for (i) shows the presence of a sulphonyl derivative of a secondary amine (secondary substituted sulphonamide);

for (ii) shows the presence of a sulphonyl derivative of a primary aromatic amine (primary substituted sulphonamide).

$$ArSO_2NHR + HCl + H_2O = ArSO_2OH + RNH_2{\cdot}HCl$$
$$ArSO_2NRR' + HCl + H_2O = ArSO_2OH + NHRR'{\cdot}HCl.$$

Derivatives (for primary substituted sulphonamides only).

Methyl derivative.—Method as for dimethyl derivative of simple sulphonamides (see p. 242).

$$ArSO_2NHR + (CH_3)_2SO_4 + NaOH = ArSO_2N(CH_3)R + CH_3NaSO_4 + H_2O.$$

For M.P.s of substituted sulphonamides see Tables XIX, XXIII, XXIV, and XXVI (benzene sulphonyl chloride and *p*-toluene sulphonyl chloride derivatives).

CHAPTER VIII

Summary of Classification Tests, Derivatives, etc., for Compounds containing Carbon, Hydrogen, Nitrogen, Halogen, and possibly Oxygen and a Metal

Preliminary examination

1. Physical properties.
2. Ignition on a crucible lid.
3. Solubility and reaction to litmus of water-soluble compounds.
4. Action of hot dilute sulphuric acid.
5. Action of cold and hot concentrated sulphuric acid.
6. Action of cold and hot 30 per cent sodium hydroxide solution.
7. Determination of "mobility" of the halogen atoms and classification of the compound as Class I, II or III.

Class	Classification Tests	Additional Tests	Derivatives, &c.
CLASS I			
Hydrohalides of organic bases, &c. (p. 252)	As for (*a*) Reducing bases (p. 106) (*b*) Primary aliphatic amines, &c. (p. 109) (*c*) Secondary amines (p. 124) (*d*) Primary aromatic amines (p. 128) (*e*) Amino-phenols (p. 130) in the C, H, N (O and metal) group		As for C, H, N and O group of compounds
Hydrohalides of tertiary amines and heterocyclic bases (p. 253)	As for tertiary amines and heterocyclic bases in C, H, N (O) group. Modified for trimethylamine hydrochloride		
Hydrohalides of alkaloids (p. 253)	See Alkaloids (pp. 173–80)		

Class	Classification Tests	Additional Tests	Derivatives, &c.
CLASS I			
Acid chlorides of nitrogen acids (p. 253)	Reduction test with tin and hydrochloric acid for nitro-group	Colour test with acetone and NaOH Special test for chloropicrin Hydrolysis and isolation of 2 : 4-dinitrophenol, picric acid or nitro-carboxylic acid	*For 2 : 4-dinitro halogenated hydrocarbons* 2 : 4-Dinitrophenol 2 : 4-Dinitroanisole *For acid chlorides of nitro-carboxylic acids* As for acid chlorides of C, H and O acids
Quaternary ammonium halides (p. 254)	Silver oxide test		
CLASSES II AND III			
Ammonium salts of halogen-substituted aromatic acids (p. 255)	Zinc or magnesium oxide test		Halogen-substituted aromatic acid
Simple amides of halogen-substituted acids (p. 256)	Nitrous acid test		*For Class II compounds* N-xanthyl amide *For Class III compounds.* Nuclear halogen-substituted acid
Halogen-substituted primary and secondary amines (p. 256)	Nitrous acid test	*For secondary amines.* Liebermann's nitroso reaction on nitrosamine *For primary aromatic amines.* Alkaline β-naphthol test	Acetyl deriv. Benzoyl deriv.
Halogen-substituted tertiary amines and heterocyclic bases	Methyl iodide test		
Halogen-substituted nitriles (p. 257)	Hydroxylaminetest	Hydrogen peroxide and NaOH test Isocyanide testafter reduction	*For Class II compounds* Amide *For Class III compounds* Amide. Acid
N-substituted amides containing halogen(s)	Hydrolysis with HCl/H_3PO_4 in diethylene glycol		Hydrolysis and isolation of acid and base
Halogen-substituted nitro-compounds (p. 258)	Reduction with tin and hydrochloric acid	Reduction with zinc dust and ammonium chloride Acetone and caustic soda test	*For nitro-benzyl halides* Oxidation to nitro-acid Nitro-benzyl phenyl ether *For nitro-halogen-substituted hydrocarbons* Dinitro- deriv.

GROUP VI

COMPOUNDS CONTAINING CARBON, HYDROGEN, NITROGEN HALOGEN(S) AND POSSIBLY OXYGEN AND A METAL

Preliminary examination

1. *Physical properties*

Colourless and deliquescent	Hydrohalides of urea, guanidine, &c.
Colourless when pure but becoming greenish on exposure to air	Hydrohalides of primary and secondary aromatic amines.
Yellow	Halogen-substituted nitro-compounds, acyl chlorides of nitro-acids, hydrohalides of N-nitroso compounds.

Note.—Hydrohalides of amino-phenols and diamines are often brown or dark coloured due to aerial oxidation.

2. *Effect of ignition on a crucible lid*

A residue of a metallic oxide or carbonate remains after strong ignition	A metallic salt of a halogenated nitro-, amino-acid or phenol.

3. *Reaction to litmus of water soluble compounds*

Warm the substance with water and rest the resulting solution with litmus.

Soluble and giving an acid reaction	Hydrohalides of most nitrogen bases and amino phenols.
Sparingly soluble and giving an acid reaction	Halogen-substituted nitro- and amino- carboxylic acids, acyl chlorides of nitro-acids.
Almost insoluble giving a neutral reaction	Halogen-substituted amides, and nitrogen bases.

4. *Action of hot dilute sulphuric acid*

Substance soluble even though insoluble in water	Halogen-substituted aromatic amine.

5. *Action of cold and hot concentrated sulphuric acid*

Halogen hydracid evolved (some bromine or iodine may also be formed	Hydrohalide of urea, guanidine, phenylhydrazine, semicarbazide, aliphatic or aromatic amine, amino-phenol or heterocyclic base.
Odour of acetic acid	Halogen-substituted acetamide, acetyl derivative of halogen-substituted amine.
Carbon monoxide evolved	Formyl derivative of a halogen-substituted amine.

Note.—Certain alkaloids (present as hydrohalides) give characteristic colour reactions with concentrated sulphuric acid.

6. *Action of cold and hot* 30 *per cent sodium hydroxide*

Ammonia evolved	Ammonium salt of a halogen-substituted acid, halogen-substituted amide, hydrohalide of urea, guanidine or semicarbazide.
Fishy ammoniacal odour	Hydrohalide of an aliphatic amine.
Separation of an oil or precipitation of a solid on cooling	Hydrohalide of phenylhydrazine, primary or secondary aromatic amine or halogen-substituted derivative of these.
Odour of pyridine or quinoline and (except in the case of pyridine) separation of an oily layer	Hydrohalide of a heterocyclic base.
Soluble with formation of a yellow solution	Acyl chloride of a nitro-acid; halogenated nitro-hydrocarbon.
Formation of a green precipitate	Hydrohalide of a N-nitrosamine.

7. *The following tests must always be applied to determine whether or not the halogen is "mobile", i.e. easily removed from the compound*

Add some of the given compound to distilled water, shake well, warm gently, filter if necessary, and to the filtrate add dilute nitric acid and a solution of silver nitrate.

Precipitate of silver halide	*No precipitate of silver halide*	
(Neglect a faint turbidity)	Reflux about 0·5 g. of the compound with 5 per cent alcoholic potash for 15 min. Cool, acidify with dilute nitric acid, filter if necessary and add silver nitrate solution in excess	
The original compound is probably one of the following: (*a*) The hydrohalide of a base or amino-phenol (*b*) The acyl chloride of a nitro-acid (*c*) A compound containing halogen attached to a carbon atom of a ring in which *both ortho* and *para* positions are occupied by nitro groups (*d*) A quaternary ammonium halide *These will be referred to subsequently as Class I compounds*	*Precipitate of silver halide* The compound is either (*a*) A nitrogen-containing compound with halogen attached to a carbon atom of a chain or (*b*) A compound containing halogen attached to a carbon atom of a ring in which the *ortho* or *para* position is occupied by a nitro group *These will be referred to as Class II compounds*	*No precipitate of silver halide* The compound is one in which the halogen is attached to the carbon atom of a ring with no nitro group in the *ortho* or *para* positions. *These will be referred to as Class III compounds*

If the elements test has shown the presence of more than one halogen, examine the precipitated halide (CLASS I or II) by oxidation with manganese dioxide and concentrated sulphuric acid to discover which halogen is reactive.

Even if only one halogen is present it may be in both a reactive and an unreactive form.

GROUP VI—CLASS I

HYDROHALIDES OF ORGANIC BASES, ETC., ACID CHLORIDES OF NITRO-ACIDS, SOME HALOGENATED NITRO-HYDROCARBONS, QUATERNARY AMMONIUM HALIDES

As indicated in Preliminary Test 7 (p. 251) the above types of compounds give ionized halogen when dissolved in water. Apply the tests given below.

A. Hydrohalides of Organic Bases, etc.

Some indication of the probable presence of such compounds will have been obtained in the preliminary examination with sodium hydroxide solution.

Classification tests.—Examine the given compound for:

(*a*) *Reducing bases* with Fehling's solution, &c. (see p. 106).

(*b*) *Primary aliphatic amines, urea and substituted ureas, guanidine and substituted guanidines* with nitrous acid in 75 per cent sulphuric acid (see p. 109).

(*c*) *Aliphatic and aromatic secondary amines* with nitrous acid (see p. 124).

(*d*) *Primary aromatic amines and diamines* by diazotizing and coupling with β-naphthol (see pp. 128–9).

(*e*) *Amino-phenols* (see p. 130).

If an aromatic base is found to be present, isolate it by the procedure given below, and examine the free base for halogen by the usual elements tests. If found, it will be a nuclear substituted halogen.

Derivatives of the base may generally be prepared directly from the given salt, the procedure being the same as for the corresponding compounds containing carbon, hydrogen, nitrogen (and oxygen) only.

If, however, a sample of the free base (not urea, &c.) is required, treat the given substance with an excess of warm sodium hydroxide (sodium bicarbonate in the case of amino-phenols) and extract the free base with ether. Separate the ether layer and dry over anhydrous sodium sulphate. Evaporate off the ether.

B. Hydrohalides of tertiary amines and heterocyclic bases

If the preliminary tests show the probable presence of aliphatic tertiary amines or of heterocyclic bases, isolate the base by treating an aqueous solution of the hydrohalide with a slight excess of caustic soda and extracting with ether. After drying and distilling off the ether, test the residue with methyl iodide for compounds of this class (see p. 147).

Owing to the very low boiling-point of the base, hydrohalides of trimethylamine cannot be treated thus, and should be classified by treating with caustic soda, warming gently and leading the vapours evolved directly into methyl iodide.

In the case of hydrohalides of aromatic tertiary amines where the *para* position is unoccupied, the nitrous acid test (see p. 124) may be applied to an aqueous solution of the original compound.

C. Hydrohalides of alkaloids

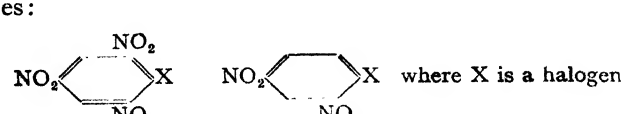
In certain cases the preliminary tests will have indicated the presence of compounds of this class. Direct information from the instructor, or the circumstances calling for identification, will usually show whether examination for alkaloids is necessary. In this case see *Alkaloids*, pp. 173–80.

D. Acid chlorides of nitro-acids and some halogenated nitro-hydrocarbons

Classification tests.—Apply the reduction test for nitro-groups and the colour test for nitro-compounds (see p. 162).

If the reduction test gives a positive result but no colour is formed with acetone and caustic soda, the compound is either the acid chloride of a mono-nitro-acid, or chloropicrin.

If both tests give a positive result, the substance is either the acid chloride of a di- or tri-nitro-acid or conforms to one of the following types:



where X is a halogen

In either case, take one gram of the substance, add about 20 ml. of 2N caustic soda, and boil under reflux for 15 min. Cool. Acidify a portion with dilute hydrochloric acid. If nitrous acid is liberated (test with starch-iodide solution), the original substance is chloropicrin $NO_2 \cdot CCl_3$.

If chloropicrin is proved absent, acidify the remainder of the alkaline solution with concentrated hydrochloric acid and cool well. (Note any marked diminution in colour due to the presence of 2 : 4-dinitrophenol or picric acid.) Filter off the precipitated solid, recrystallize from dilute hydrochloric acid and determine the melting-point.

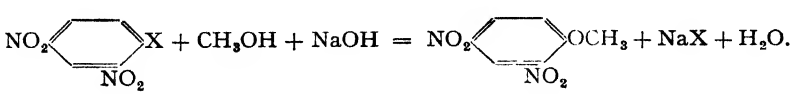
M.P °C.	Shows presence of	Arising from
114° C.	2 : 4-Dinitrophenol	2 : 4-Dinitrohalogenobenzene
122° C.	Picric acid	Picryl chloride

If the product is neither of these compounds, it is probably a nitrocarboxylic acid formed from the acid chloride of such an acid. Reference to the melting-points of these acids (Table XXXIX) will indicate its identity, which should be confirmed by a determination of its equivalent weight, &c.

Derivatives. *For 2 : 4-dinitro-halogenated hydrocarbons.* (For M.P.s of original substances and derivatives, see Table LXXXIV.)

1. 2 : 4-**Dinitrophenol.** See above.

2. 2 : 4-**Dinitroanisole.**—Dissolve 1 g. of the substance in 10 ml. of methyl alcohol, add 0·3 g. of caustic potash and boil under reflux for 15 min. Cool, pour into water, filter off the precipitated solid and recrystallize from alcohol.



For acid chlorides of nitro-carboxylic acids.—See derivatives for acid chlorides of simple carboxylic acids, p. 217.

E. Quaternary ammonium halides

Classification test.—Dissolve a small amount of the original substance in water or neutral alcohol, add excess of silver oxide,

shake well and filter. If the filtrate is strongly alkaline, the original compound is a quaternary ammonium halide.

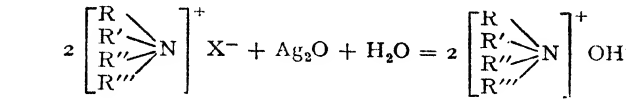


TABLE LXXIX.—ACID CHLORIDES OF NITRO-CARBOXYLIC ACIDS

	M.P. °C	Acid	Amide	Anilide	
m-Nitrobenzoyl chloride	35	141	143	154	
2 : 4-Dinitrobenzoyl chloride	41	179	203		
3-Nitrosalicyloyl chloride	60	125*	145	—	*Anhydrous M.P., 144° C.
o-Nitrocinnamoyl chloride	64	237	185		
3 : 5-Dinitrosalicyloyl chloride	69	173			
3 : 5-Dinitrobenzoyl chloride	74	202	183	234	
p-Nitrobenzoyl chloride	75	241	201	211	
2 : 4 : 6-Trinitrobenzoyl chloride	158	220d	264d		
o-Nitrobenzoyl chloride	—	146	174	155	

GROUP VI—CLASS II AND CLASS III

AMMONIUM SALTS OF HALOGEN-SUBSTITUTED AROMATIC ACIDS, SIMPLE AMIDES OF HALOGEN-SUBSTITUTED ACIDS, PRIMARY AND SECONDARY HALOGEN-SUBSTITUTED AMINES, HALOGEN-SUBSTITUTED NITRILES (CYANIDES), HALOGEN-SUBSTITUTED AMIDES, HALOGEN-SUBSTITUTED NITRO-COMPOUNDS

For the purpose of applying classification tests for functional groups these two classes may be dealt with together. Subsequently, consideration of the results of the preliminary examination for "mobility" of the halogen will indicate the particular type of compound present.

A. Ammonium salts of halogen-substituted aromatic acids

Classification test.—If ammonia was freely evolved in the preliminary test with caustic soda, test for the presence of ammonium salts by mixing intimately a little of the given compound with zinc (or magnesium) oxide, moistening with water and warming very

gently. If ammonia is evolved (test with moist red litmus paper), an ammonium salt is present.

Derivatives.—Boil about 1 g. of the compound with a slight excess of caustic soda till all ammonia is evolved. Cool and acidify with hydrochloric acid. Filter off the precipitated acid, recrystallize and identify by a determination of the equivalent weight and preparation of derivatives (see pp. 52–4).

B. Simple amides of halogen-substituted acids

The presence of these will be indicated by the more gradual evolution of ammonia in the preliminary test with sodium hydroxide and a negative result in the test for ammonium salts.

Confirmatory test.—To 2 ml. of *cold* 75 per cent sulphuric acid add a cold concentrated solution of sodium nitrite dropwise until the solution is blue. To this add a little of the original substance dissolved or suspended in cold 75 per cent sulphuric acid. A sustained and brisk effervescence (due to evolution of nitrogen) indicates the presence of a member of this class.

Derivatives.—If the compound is in Class II, it is the amide of a halogen-substituted aliphatic acid. Prepare a *N-xanthyl amide* as for an amide of a simple carboxylic acid (see p. 114).

If the substance be in Class III, it is the amide of a nuclear halogen-substituted aromatic acid. Isolate and identify the acid as in the case of an ammonium salt above.

C. Halogen-substituted primary and secondary amines

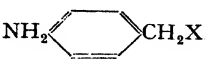
Halogen-substituted secondary amines are only likely to be met with in the form of Class III compounds, but halogen-substituted primary amines may be encountered as Class II or Class III compounds, though the latter are more common.

Classification tests.—To a well-cooled solution of 0·5 g. of the given compound in dilute hydrochloric acid, concentrated hydrochloric acid or glacial acetic acid, add dropwise a cold 2 per cent solution of sodium nitrite with constant shaking until free nitrous acid is present as shown by the starch/potassium iodide test.

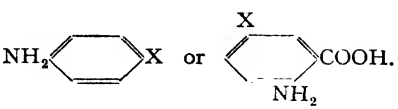
If an oily precipitate or emulsion forms, the original compound is a halogen-substituted secondary amine. Confirm the identity of the oil as a nitrosamine by the Liebermann's nitroso reaction (see p. 125), and prepare derivatives as for unsubstituted secondary amines (see p. 126).

If no oily precipitate or emulsion is formed, pour the cold solution into a solution of β-naphthol in sodium hydroxide. Formation of an azo-dye indicates the presence of a halogen-substituted primary aromatic amine.

If the compound has already been placed in Class II, it is of a type similar to



If in Class III, the substituent halogen (or halogens) is in the nucleus, e.g.



Distinction between these two latter types is simple, since the first is purely basic while the second is acidic in character.

Derivatives.—Those based upon the reactions of the amino group are best, and the acetyl and benzoyl derivatives are recommended, the methods used being unlikely to result in replacement of halogen in Class II compounds.

For methods of preparation, see corresponding derivatives of primary amines, p. 130.

D. Halogen-substituted tertiary amines and Heterocyclic bases

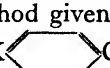
Apply the methyl iodide test as for simple tertiary amines and heterocyclic bases (see p. 147).

E. Halogen-substituted nitriles (cyanides)

Ammonia is very slowly evolved when these compounds are boiled with strong caustic soda solution.

Classification tests.—Apply the hydroxylamine test, the hydrogen peroxide-caustic soda test, and the isocyanide test (p. 155) as in the case of simple nitriles.

Derivatives.—For Class II compounds, e.g. $Cl{\cdot}CH_2{\cdot}CN$, the amide may be prepared by the method given on p. 156.

For Class III compounds, e.g.  , prepare the amide or the acid as for aromatic nitriles (see p. 156).

F. Substituted amides containing halogen(s)

These are only likely to be met with in the form of Class **III** compounds, e.g.

As mentioned on p. 128 such substances may give a positive result in the test for primary aromatic amines due to slight hydrolysis, but they are not basic in character, and a volatile acid (or carbon monoxide in the case of formyl compounds) should have been detected in the preliminary test with warm concentrated sulphuric acid.

Classification test.—To 0·5 g. of the given compound add 1 ml. of diethylene glycol and 0·5 ml. of syrupy phosphoric acid and maintain just at the boil for 2 min. Allow to cool *in air*. Add 5 ml. of dilute hydrochloric acid, boil and cool again. Filter if necessary, and to the well-cooled filtrate add dropwise a 2 per cent solution of sodium nitrite. Pour the solution into a solution of β-naphthol in caustic soda. The formation of a brightly coloured azo-compound indicates the presence of a substituted amide derived from a halogen-substituted primary aromatic amine.

Hydrolysis.—Reflux 1 g. of the given compound with 20 ml. of 50 per cent sulphuric acid till hydrolysis is complete. If the preliminary tests have indicated the probable presence of a derivative of formic or acetic acid, distil and test the distillate for these acids. Otherwise isolate the acid by filtration or ether extraction and identify it. To the residual acid solution add caustic soda till alkaline. Extract with ether and identify the base so extracted.

G. Halogen-substituted nitro compounds

Classification tests.—Apply the following tests:

(i) Reduction with tin and hydrochloric acid (see p. 162).

(ii) Reduction with zinc dust and ammonium chloride (see p. 162).

(iii) Colour test with acetone and sodium hydroxide for poly-nitro-compounds (see p. 162).

A positive result for tests (i) and (ii) indicates the probable presence of an aromatic nitro-halogenohydrocarbon or nitro-derivative of a halogen-substituted aromatic hydrocarbon with halogen in the side chain.

Test (iii) above will indicate whether more than one nitro group is present though compounds of this type are not very common.

If the substance is a Class II compound, it is probably (*a*) a nitrobenzyl halide, or (*b*) a nitro-halogen-substituted benzene with the nitro group in the *ortho* or *para* position.

Boil a small quantity of the substance with concentrated sodium hydroxide solution. If an intense yellow or orange solution results, which on cooling and making acid with hydrochloric acid becomes noticeably paler in colour, the substance is of type (*b*) above.

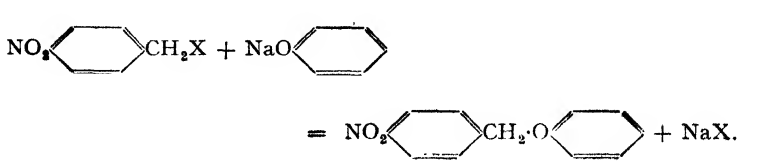
If the above test gives a negative result, mix together 2 g. of the compound, 2·5 g. of potassium permanganate, 40 ml. water and 1 g. of caustic soda, add a few pieces of porous pot and boil under reflux till the colour of the permanganate has disappeared. Filter, cool, add concentrated hydrochloric acid till the solution is acid, and if the solution is not colourless, sufficient sulphurous acid to discharge the colour. If a solid is precipitated, filter it off. If not, extract with ether and isolate the acid. Thus *o*- or *p*-nitrobenzoic acid would result from the oxidation of an *o*- or *p*-nitrobenzyl halide.

If the substance is a Class III compound, it is probably *m*-nitrochloro (or bromo) benzene or 3 : 5-dinitrochloro (or bromo) benzene.

Derivatives

For nitrobenzyl halides.—1. *Oxidation* to the corresponding nitrobenzoic acid as above.

2. *Nitrobenzyl phenyl ether.*—Dissolve 0·5 g. of sodium hydroxide in the minimum amount of water, add 20 ml. of alcohol and 1 g. of phenol. When solution has been effected, add 2 g. of the nitrobenzyl halide. Boil gently under reflux for 20 min. Cool well. If no crystallization occurs, add 10 ml. water and shake well. Filter off the solid, wash well with cold water and recrystallize from alcohol.



For nitro halogen-substituted hydrocarbons.—*Dinitro derivative.*—Mix carefully 5 ml. of concentrated sulphuric acid and 5 ml. concentrated nitric acid (fuming nitric acid for *m*-nitro compounds) and add 1 g. of the given compound. Heat just to boiling and maintain at this temperature for about 1 min. Cool well and pour into 50 ml. of water. When quite cold, filter, wash well with water and recrystallize from alcohol.

Note.—***The greatest possible care must be exercised during such nitrations as they are liable to become violently explosive.***

TABLE LXXX.—AMIDES OF HALOGEN-SUBSTITUTED ACIDS

	M.P. °C.	Acid	Miscellaneous
Bromoacetamide	91		
Iodoacetamide	95		
Dichloroacetamide	96		
Chloroacetamide	120	—	Xanthydrol deriv., M.P. 209° C.
α-Bromopropionamide	123		
m-Chlorobenzamide	134	155	
o-Chlorobenzamide	139	140	
Trichloroacetamide	141		
o-Bromobenzamide	155	148	
m-Bromobenzamide	155	155	
Dibromoacetamide	156		
p-Chlorobenzamide	179	239	
o-Iodobenzamide	184	162	
m-Iodobenzamide	186		
p-Bromobenzamide	189	251	
p-Iodobenzamide	217	270	

TABLE LXXXI.—HALOGEN-SUBSTITUTED PRIMARY AROMATIC AMINES

	B.P. °C.	Acetyl deriv.	Benzoyl deriv.	Benzene sulphonamide	*p*-Toluene sulphonamide	Formyl deriv.	Picrate	Miscellaneous
Liquids								
2-Amino-4-chlorotoluene	134	183						
o-Chloroaniline	207	87	99	129	105	81	134	1 : 3 : 5-Trinitrobenzene deriv., M.P. 135° C.
								Phenyl thiourea, M.P. 156° C.
4-Amino-3-chlorotoluene	223	118	137	110				
m-Chloroaniline	230	73	122	121	138	58	177	1 : 3 : 5-Trinitrobenzene deriv., M.P. 115° C.
4-Amino-3-bromotoluene	240	117	149	—	—	—	—	Phenyl thiourea, M.P. 154° C.
m-Bromoaniline	251	87	136	—	—	63	—	Phenyl thiourea, M.P. 97° C.
Solids	M.P.							
m-Iodoaniline	27	119	157	—	128			
4-Amino-3-bromotoluene	27	117	149	—	—	—	—	Phenyl thiourea, M.P. 154° C.
2-Amino-5-chlorotoluene	29	140	172	125	—	—	—	B.P. 241° C.
o-Bromoaniline	31	99	116	—	—	87	129	Phenyl thiourea, M.P. 146° C.
2-Amino-4-bromotoluene	32	165						Phenyl thiourea, M.P. 158° C.
5-Chloro-4-amino-1 : 2-dimethylbenzene	40	—	148					
2 : 5-Dichloroaniline	50	132	120			147		Phenyl thiourea, M.P. 166° C.
2-Amino-3 : 5-dichlorotoluene	50	) 186						
2 : 5-Dibromoaniline	52	172	—	—	—	—	149	Phenyl thiourea, M.P. 173° C.

[*Contd. over*

TABLE LXXXI—(*contd.*)

	M.P.°C.	Acetyl deriv	Benzoyl deriv.	Benzene sulphon-amide	*p*-Toluene sulphon-amide	Formyl deriv.	Picrate	Miscellaneous
Solids								
2-Chloro-1-naphthylamine	56	191						
o-Iodoaniline	56	110	139	—	—	—	112	
3 : 5-Dibromoaniline	56	231	169	—	—	100	—	Phenyl thiourea, M.P. 163° C.
2-Amino-5-bromotoluene	59	156	115					
4-Amino-3 : 5-dichlorotoluene	60							
1-Chloro-2-naphthylamine	60	147	99	131	—	136	174	
p-Iodoaniline	62	181	210	—	—	109	—	1 : 3 : 5-Trinitrobenzene deriv., M.P. 108° C.
								Phenyl thiourea, M.P. 153° C.
1-Bromo-2-naphthylamine	63	140	—	—	100	—	178	
2 : 4-Dichloroaniline	63	146	117	128	126	153	106	1 : 3 : 5-Trinitrobenzene deriv., M.P. 91° C.
p-Bromoaniline	66	167	204	134	101	119	180	Phenyl thiourea, M.P. 158° C.
p-Chloroaniline	70	179	192	121	95	102	178	1 : 3 : 5-Trinitrobenzene deriv., M.P. 111° C.
								Phenyl thiourea, M.P. 152° C.
2-Chloro-3 : 5-diaminotoluene	73	228						
2 : 4 : 6-Trichloroaniline	77	206	174	—	—	180	83	1 : 3 : 5-Trinitrobenzene deriv., M.P. 94° C.
3 : 5-Dibromo-4-aminotoluene	78	183						

2 : 4-Dibromoaniline	79	146	134	—	134	140	124	1 : 3 : 5-Trinitrobenzene deriv., M.P. 86° C. Phenyl thiourea, M.P. 171° C.
3-Amino-6-chlorotoluene	83	91	119	130				
2-Amino-4-chlorotoluene	83	140						
2 : 6-Dibromoaniline	84	210	—	—	—	—	124	
2 : 4-Diaminochlorobenzene	88	170 (mon) 243 (di)	178	—	215 (di)			
6-Chloro-2 : 4-dibromoaniline	95	227	192					
2 : 4-Di-iodoaniline	96	—	181					
4-Chloro-1-naphthylamine	98	184						
4-Bromo-1-naphthylamine	102	193	—	149	—	172	—	1 : 3 : 5-Trinitrobenzene deriv., M.P. 196° C.
2 : 4 : 6-Tribromoaniline	119	232	198	—	—	222	—	1 : 3 : 5-Trinitrobenzene deriv., M.P. 111° C.
1 : 6-Dibromo-2-naphthylamine	121	212	—	—	—	—	131	1 : 3 : 5 Trinitrobenzene deriv., M.P. 165° C.
2-Chloro-2-aminobenzoic acid	161	207						
3 : 6-Dibromo-2-naphthylamine	187	195	162					
5-Chloro-2-aminobenzoic acid	216	267						
3 : 5-Dibromoanthranilic acid	236	221d	—	—	—	—	—	Amide, M.P. 197° C.
o-Aminobenzyl chloride	—	114	125					
m-Aminobenzyl chloride	—	89						
p-Aminobenzyl chloride	—	155						

TABLE LXXXII.—HALOGEN-SUBSTITUTED SECONDARY AMINES

	B.P. °C.	Acetyl deriv.
Liquids		
N-methyl *o*-chloroaniline	214	
N-methyl *p*-chloroaniline	240	92
N-methyl *p*-bromoaniline	260	
Solids	M.P.	
N-methyl tribromoaniline	39	101

TABLE LXXXIII.—HALOGEN-SUBSTITUTED TERTIARY AMINES AND HETEROCYCLIC BASES

	B.P. °C.	Miscellaneous
Liquids		
Dimethyl *o*-chloroaniline	207	
Dimethyl *p*-chloroaniline	230	
Dimethyl *p*-bromoaniline	265	
Dimethyl 2 : 4 : 6-tribromoaniline	301	
2-Chloropyridine		
Solids	M.P.	
Diethyl *p*-bromoaniline	34	B.P. 270° C.
2-Chloroquinoline	35	
6-Chloroquinoline	41	
Dimethyl *o*-bromoaniline	55	B.P. 264° C. Compound with methyl iodide, M.P. 185° C.
3 : 5-Dibromopyridine	111	
2 : 6-Dibromopyridine	119	

TABLE LXXXIV.—HALOGEN-SUBSTITUTED NITRILES

	B.P. °C.	Acid	Amide
Liquids			
Chloroacetonitrile	124	—	120
γ-Chlorobutyronitrile	197		
β-Chloropropionitrile	60/8 mm.		
o-Chlorobenzonitrile	—	140	139
Solids	M.P.		
p-Chlorobenzonitrile	92	239	179
p-Bromobenzonitrile	112	251	189

Table LXXXV.—Halogen-substituted nitro compounds

	B.P. °C.	Nitro-deriv.	Position of nitro-groups	Benzoyl deriv. of amine	Miscellaneous
Liquids					
Chloropicrin	112				
4-Chloro-3-nitrotoluene	260				
Solids	M.P.				
p-Nitrofluorobenzene	27				
o-Nitrochlorobenzene	32	53	2 : 4	99	
4-Bromo-3-nitrotoluene	33				
2 : 4-Dichloronitrobenzene	33	—	—	117	
4-Chloro-1 : 2-dinitrobenzene	36				
4-Chloro-2-nitrotoluene	38				
o-Nitrobromobenzene	41	72	2 : 4	116	
m-Nitrochlorobenzene	44	72	3 : 4	122	
m-Nitrobenzyl chloride	45	—	—	—	$KMnO_4$ → *m*-nitrobenzoic acid, M.P. 141° C.
4-Bromo-2-nitrotoluene	46				
o-Nitrobenzyl chloride	48	34	2 : 4	—	$KMnO_4$ → *o*-nitrobenzoic acid, M.P. 144° C. Nitrophenyl ether, M.P. 63° C.
o-Nitroiodobenzene	49	—	—	139	
2 : 4-Dinitrochlorobenzene	53	183	2 : 4 : 6	178	KOH in CH_3OH → 2 : 4-dinitroanisole, M.P. 88° C.
Nitro-*p*-dichlorobenzene	54	104	2 : 6	120	KOH in CH_3OH → 2-nitro-4-chloroanisole, M.P. 97° C.
m-Nitrobromobenzene	54	59	3 : 4	136	

[*Contd. over*

TABLE LXXXV—(*contd.*)

	M.P.°C.	Nitro-deriv.	Position of nitro-groups	Benzoyl deriv. of amine	Miscellaneous
Solids					
2-Chloro-3 : 5-dinitrotoluene	64				
m-Nitrobenzal chloride	65				
2 : 4 : 6-Trichloronitrobenzene	68				
p-Nitrobenzyl chloride	71	34	2 : 4	—	$KMnO_4$ → *p*-nitrobenzoic acid, M.P. 241° C.
2 : 4-Dinitrobromobenzene	72	—	—	—	Boiling aq. Na_2CO_3 → 2 : 4-dinitrophenol, M.P. 114° C.
p-Nitrochlorobenzene	83	53	2 : 4	192	
2 : 4 : 6-Trinitrochlorobenzene	83				
Picryl chloride	83	—	—	—	KOH in CH_3OH → trinitroanisole, M.P. 68° C.
2 : 5-Dibromonitrobenzene	85				
2 : 4 : 5-Tribromonitrobenzene	94				
p-Nitrobenzyl bromide	99	—	—	—	$KMnO_4$ → *p*-nitrobenzoic acid, M.P. 241° C.
2 : 4 : 6-Tribromonitrobenzene	125				
p-Nitrobromobenzene	126	72	2 : 4	204	
2 : 4 : 6-Trichloro-1 : 3-dinitrobenzene	130				
2 : 4 : 5-Tribromo-1 : 3-dinitrobenzene	135				
p-Nitroiodobenzene	171	—	—	222	
2-Bromo-3-nitrobenzoic acid	182				
2 : 4 : 6-Tribromo-1 : 3-dinitrobenzene	192				
2-Chloro-3 : 5-dinitrobenzoic acid	199				

CHAPTER IX

Summary of Classification Tests, Derivatives, etc., for Compounds containing Carbon, Hydrogen, Sulphur, Halogen, and possibly Oxygen and a Metal

Preliminary examination

1. Physical properties.
2. Effect of ignition on crucible lid.
3. Reaction to litmus of water-soluble compounds.
4. Action of warm dilute sulphuric acid.
5. Action of cold and hot 30 per cent sodium hydroxide.
6. Action of hot concentrated sulphuric acid.
7. Test for " mobility " of halogen.

Class	Classification Tests	Additional Tests	Derivatives
Bisulphite compounds of halogen-substituted aldehydes and ketones (p. 269)	Dilute sulphuric acid and test for sulphur dioxide	2 : 4-Dinitrophenylhydrazine test on residual liquid	Isolation of aldehyde or ketone followed by preparation of a derivative
Sulphonium halides (p. 269)	Silver oxide test to give an alkaline solution		
Sulphonyl chlorides and bromides (p. 270)	Silver nitrate and nitric acid on warm solution	Zinc dust and dilute hydrochloric acid	Amide Anilide
Halogen-substituted thiophenols or mercaptans (p. 272)	Mercuric chloride		2 : 4-Dinitrophenylthioether Sulphone
Nuclear halogen-substituted sulphonic acids and their salts (p. 272)	Heat with soda-lime	Test for phenol on acidified residue	Amide Anilide S-benzylthiuronium salt

GROUP VII

COMPOUNDS CONTAINING CARBON, HYDROGEN, SULPHUR, HALOGENS, AND POSSIBLY OXYGEN AND A METAL

Preliminary examination

1. *Physical properties*

Hygroscopic	Sulphonium halides.
Fuming red liquid with a suffocating odour	Thiophosgene. (This compound on refluxing with water evolves H_2S, HCl and CO_2; excess aniline → thiocarbanilide, M.P. 153° C.)

2. *Effect of ignition on a crucible lid*

A non-combustible residue remains	A bisulphite compound of a halogen substituted aldehyde or ketone; salt of a halogen-substituted sulphonic acid or thiophenol.

3. *Reaction to litmus of water-soluble compounds*

(*a*) Acid	Halogen-substituted sulphonic acids; sulphonyl halides (on warming).
(*b*) Neutral	Sulphonium halides; esters of halogen-substituted sulphonic acids.

4. *Action of warm dilute sulphuric acid*

Evolution of sulphur dioxide (potassium dichromate test-paper)	Bisulphite compound of halogen-substituted aldehyde or ketone.
Evolution of hydrogen sulphide (lead acetate test-paper)	Halogen-substituted thiophenol.

5. *Action of hot and cold 30 per cent sodium hydroxide*

An odour of an aldehyde or ketone	A bisulphite compound.
Soluble	Halogen-substituted sulphonic acids; sulphonyl halides (on warming).

6. *Action of hot concentrated sulphuric acid*

Evolution of halogen hydracid	Sulphonium halides; sulphonyl halides.

7. Apply test 6, p. 205, to determine whether the halogen is "mobile" or not. The halogen may be present in the compound in both a reactive and an unreactive form, as in *o*-chlorobenzene sulphonyl chloride.

GROUP VII—CLASS I

BISULPHITE COMPOUNDS OF HALOGEN-SUBSTITUTED ALDEHYDES AND KETONES

The preliminary examination with dilute sulphuric acid and ignition on a crucible lid will have indicated the probable presence of a compound of the above type.

Classification test.—Add dilute sulphuric acid to some of the given compound and test for the evolution of sulphur dioxide with potassium dichromate paper. When all sulphur dioxide has been evolved, test for the presence of aldehyde or ketone in the residual liquid by means of 2 : 4-dinitrophenylhydrazine (see p. 36).

Derivatives.—As for bisulphite compounds of aldehydes and ketones, p. 185. The M.P.s and B.P.s of halogen-substituted aldehydes and ketones together with their derivatives are to be found in Tables LXI, LXII and LXVIII.

GROUP VII—CLASS II

SULPHONIUM HALIDES

Such salts dissolve in water to give a neutral reaction.

Classification test.—Dissolve a small amount of the original substance in water, add an excess of silver oxide, shake well and filter. If the filtrate is strongly alkaline, the given compound is probably a sulphonium halide.

$$2\,R''(R')(R''')S^{+}X^{-} + Ag_2O + H_2O = 2\,R''(R')(R''')S^{+}OH^{-} + 2AgX.$$

The more common halides are as follows:

	M.P. °C.	
Trimethyl sulphonium bromide	172	Very hygroscopic
Trimethyl sulphonium chloride	100	
Trimethyl sulphonium iodide	207	

GROUP VII—CLASS III

SULPHONYL CHLORIDES AND BROMIDES

Classification test.—To 3 ml. of distilled water add a small quantity of the given compound. Heat to boiling and continue to boil briskly for 5 minutes. Cool, filter if not clear, and add dilute nitric acid, followed by 1 ml. of silver nitrate solution. A white or yellowish curdy precipitate of a silver halide indicates a substance of this class.

Confirmatory test.—Treat about 0·2 g. of the compound with 5 ml. of dilute hydrochloric acid, add zinc dust and boil. The characteristic odour of a thiophenol will be apparent with a substance of this class.

Derivatives

1. **Sulphonamide.**—To 1 g. of the compound add 10 ml. of concentrated ammonia. Allow to stand for 15 min. then add 20 ml. of water. Boil to remove excess ammonia, and just acidify with dilute hydrochloric acid. If the derivative is insoluble, filter, wash with water and recrystallize from alcohol. If the derivative be water soluble, evaporate down until crystals separate from a cooled portion. Recrystallize from water.

$$RSO_2Cl + 2NH_3 = RSO_2NH_2 + NH_4Cl.$$

2. **Anilide.**—To a suspension of 0·3 ml. of aniline in 5 ml. of 10 per cent sodium hydroxide add 0·5 g. of the sulphonyl halide. Shake vigorously, keeping the solution cool and alkaline. When the reaction is complete, filter, acidify the filtrate with dilute hydrochloric acid, wash the derivative with water and recrystallize from alcohol.

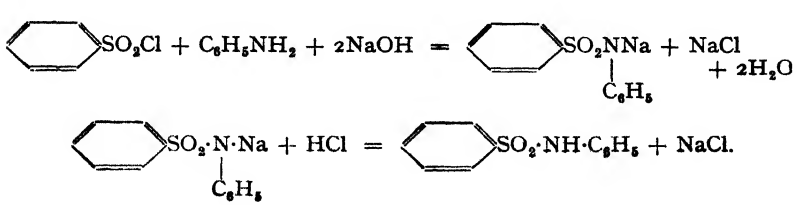


TABLE LXXXVI.—SULPHONYL CHLORIDES

	B.P. °C.	Acid	Amide	Anilide	Miscellaneous
Liquids					
Methane-	—	—	90	99	
Ethane-	—	—	58	58	
o-Toluene-	—	57	153	136	
m-Toluene-	—	—	108	96	
Benzene-	—	66	153	110	M.P. 14° C.
Solids	M.P.				
3 : 4-Dichlorobenzene-	19	—	135		
2 : 5-Dimethylbenzene-	25	48	148		
o-Chlorobenzene-	28	—	188		
2 : 4-Dimethylbenzene-	34	62	137	110	
3 : 4-Dibromobenzene-	34	—	175		
2 : 5-Dichlorobenzene	38	97	181	—	S-benzylthiuronium salt of acid, M.P. 170° C.
2 : 4 : 6-Trichlorobenzene-	40	—	212d		
2 : 3-Dimethylbenzene-	47	—	167		
o-Bromobenzene-	51	—	186		
3 : 4-Dimethylbenzene-	52	64	144		
2 : 4-Dichlorobenzene-	53	—	180		
p-Chlorobenzene-	53	68	144	104	S-benzylthiuronium salt of acid, M.P. 175° C.
2 : 4 : 6-Tribromobenzene-	60	—	220d		
1 : 3-Benzenedi-	63	—	229		
2 : 3 : 4-Trichlorobenzene-	65	—	226d		
d-Camphor-10-	67	193	132	121	
1-Naphthalene-	68	90	150	112	
p-Toluene-	69	92	137	103	
2 : 5-Dibromobenzene-	71	—	194		
p-Bromobenzene-	75	103	166	119	
2-Naphthalene-	76	91	212	132	
2 : 4-Dibromobenzene	79	—	190		
d-Camphor-3-	88	—	143	124	
1 : 2-Ethanedi-	91	104			
Benzyl-	92	—	105	102	
3 : 5-Dimethylbenzene-	94	—	135	119	
4-Chloro-1-naphthalene-	95	—	186	143	
8-Chloro-1-naphthalene-	101	—	199		
1 : 7-Naphthalene di-	122				
1 : 6-Naphthalene di-	128	125	298		
3-Bromocamphor-8-	136	196	145		
1 : 3-Naphthalene di-	138				
d-Camphor-8-	138	—	137		
1 : 4-Benzene di-	139	—	288		
1 : 2-Benzene di-	143	—	254	241	
2 : 7-Naphthalene di-	162	—	242		
1 : 4-Naphthalene di-	166	—	273	179	
1 : 5-Naphthalene di-	183	245	310	249	
1 : 3 : 5-Benzene tri-	187	100d	312	237	
Anthraquinone-β-	197	—	261	193	
Anthraquinone-α-	214	218	—	216	
1 : 7-Anthraquinone di-	232	120	—	238	

GROUP VII—CLASS IV

HALOGEN-SUBSTITUTED THIOPHENOLS OR MERCAPTANS

Classification test.—To a solution of the substance in aqueous alcohol add mercuric chloride solution. Formation of a colourless precipitate while an acid reaction develops in the solution indicates a thiophenol.

Derivatives.—1. 2 : 4-*Dinitrophenyl thioether.* Method as on p. 186.

2. *Sulphone.*—Method as for simple thiophenols, p. 188.

TABLE LXXXVII.—HALOGENATED THIOPHENOLS

	M.P. °C.	2 : 4-Dinitrophenyl thioether	Sulphone
p-Chlorophenyl mercaptan	53	123	170
p-Bromophenyl mercaptan	74	142	190

GROUP VII—CLASS V

NUCLEAR HALOGEN-SUBSTITUTED SULPHONIC ACIDS AND THEIR SALTS

Classification test.—Mix about 1 g. of the given compound with an excess of dry soda-lime in a hard glass test-tube and heat strongly. Cool the residue in the tube and treat with dilute sulphuric acid. Sulphur dioxide, as tested with potasssium dichromate paper, will be evolved in the case of halogen-substituted sulphonic acids and their salts. Further confirmation may be obtained by extracting the acid solution with ether, evaporating off the ether and testing the residue for a phenol by the ferric chloride test (see p. 61).

Derivatives.—1. *Amide*
2. *Anilide*
3. *S-benzylthiuronium salt*

} as for simple sulphonic acids, p. 193.

The melting-points of the above derivatives will be found in Table LXXXVI.

CHAPTER X

GROUP VIII

Compounds containing Carbon, Hydrogen, Oxygen, Nitrogen, Sulphur, Halogen, and possibly a Metal

Preliminary examination

1. *Note physical state, odour and colour*

Odour of chlorine	Compounds of the type of chloramine T.

2. *Effect of ignition on a crucible lid*

A non-combustible residue remains	The compound is probably chloramine T or the sodium salt of halazone.

3. *Solubility in water and reaction of solution towards litmus*

Very sparingly soluble to give an acid reaction	Nitro-sulphonyl halides.
Sparingly soluble	Sulphates of halogen-substituted amines.
Insoluble	Dichloramine T; halazone; sulphonyl derivative of halogen-substituted amine.

4. *Action of cold and hot* 30 *per cent sodium hydroxide*

The formation of a precipitate or an oily emulsion with the odour of an organic base	Sulphate of a halogen-substituted amine.
Readily soluble though sparingly soluble in water	Halazone; benzene and *p*-toluene sulphonyl derivatives of halogen-substituted primary amines.

5. *Soda-lime test* (see p. 21)

Odour of amines	Sulphate of halogen-substituted amine.
Odour of nitro-phenol	Nitro-sulphonyl halide.
Odour of amine and phenol	Sulphonyl derivative of halogen-substituted amine.

GROUP VIII—CLASS I

SULPHATES OF HALOGEN-SUBSTITUTED AMINES

Some indication of the probable presence of these compounds will have been obtained in the preliminary tests with sodium hydroxide and with soda-lime.

Classification test.—Warm the substance with dilute hydrochloric acid, filter if necessary, and add barium chloride solution. A white precipitate of barium sulphate indicates the presence of the sulphate of a halogen-substituted base, probably a primary aromatic amine.

Test the given compound for (*a*) a secondary amine with nitrous acid (see p. 124).

(*b*) A primary aromatic amine by diazotizing and coupling with alkaline β-naphthol (see p. 124).

If the results of these tests are negative, isolate the base by treating with an excess of sodium hydroxide and extracting with ether. Evaporate off the ether and apply the methyl iodide test for tertiary amines and heterocylic bases (see p. 147).

In the case of halogen-substituted secondary or primary aromatic amines, derivatives may often be prepared directly from the original substance using the procedure shown on pp. 130–3, but for certain derivatives isolation of the dry base is a necessary preliminary.

GROUP VIII—CLASS II

AMMONIUM SALTS OF HALOGEN-SUBSTITUTED SULPHONIC ACIDS

In the case of such compounds ammonia will have been evolved in the preliminary tests with caustic soda and with soda-lime.

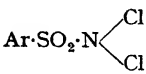
Classification test.—Apply the zinc oxide or magnesium oxide test as for ammonium salts of simple carboxylic acids (see p. 105).

If the test be positive, treat as for the ammonium salt of a sulphonic acid (see p. 235).

GROUP VIII—CLASS III

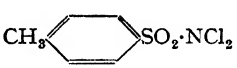
N-CHLOROSULPHONAMIDES (CHLORAMINES)

Classification test.—Add a very small amount of the substance to potassium iodide solution and shake well. Add 1 ml. of carbon tetrachloride and shake again. A violet colour, due to free iodine in the carbon tetrachloride layer, indicates the presence of a compound of this class, i.e.



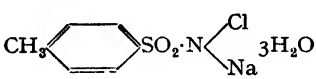
If sodium is absent as shown by the preliminary test, the compound is probably either halazone

or dichloramine T



Halazone is soluble in sodium carbonate with effervescence. Dichloramine T is only sparingly soluble.

If sodium is present, the compound is probably either chloramine T,



or the sodium salt of halazone.

Derivatives, etc.—Treat about 1 g. of the substance with 20 ml. of 10 per cent sodium hydroxide and 20 ml. of 20 vol. hydrogen peroxide and boil for 15 min. Acidify with concentrated hydrochloric acid and again boil till complete solution is effected. Cool well, filter off the crystalline product which separates out and recrystallize from water or very dilute alcohol and determine its melting-point.

If the product melts at 137° C., i.e. it is *p*-toluene sulphonamide, the original substance is chloramine T or dichloramine T. If the product melts with decomposition at 283° C., the given compound is halazone or its sodium salt. M.P. of dichloramine T is 81° C.

GROUP VIII—CLASS IV

ACID CHLORIDES OF NITROSULPHONIC ACIDS

Classification test.—Boil a small amount of the given compound with water, cool, filter if necessary, acidify with dilute nitric acid and add silver nitrate solution. A precipitate of silver chloride shows the presence of a compound of this class.

Confirmation of the presence of the nitro-group may be obtained by applying the reduction test with tin and hydrochloric acid (see p. 162).

Derivatives.

1. Amide
2. Anilide

} as for simple sulphonyl chlorides (see p. 270).

TABLE LXXXVIII.—NITROSULPHONYL CHLORIDES

	M.P. °C.	Acid	Amide	Anilide
m-Nitrobenzene-	63	48	167	126
o-Nitrobenzene-	68	70	191	115
p-Nitrobenzene-	80	95	180	136
1-Nitro-2-naphthalene-	121	105	214	202

GROUP VIII—CLASS V

SULPHONYL DERIVATIVES OF HALOGEN-SUBSTITUTED AMINES

Classification test.—Apply the classification test for substituted sulphonamides (see p. 246).

Derivatives, etc. — *Hydrolysis.* Hydrolyse about 5–10 g. by refluxing with 100 ml. of 25 per cent hydrochloric acid until the liquid becomes clear. In some cases many hours are required to complete the reaction. Cool, add 25 per cent sodium hydroxide till the liquid is alkaline and extract the liberated amine with three small portions of ether. Dry the ethereal solution, distil off the ether and prepare a suitable derivative of the amine (see pp. 130–3).

Make the alkaline liquor almost neutral, leaving it just on the

alkaline side, by the cautious addition of concentrated hydrochloric acid, concentrate by evaporation and from the sodium salt of the sulphonic acid in solution prepare a S-benzyl thiuronium salt (see p. 193). In endeavouring to identify the sulphonic acid through the medium of the melting-point of this derivative it should be borne in mind that while benzene sulphonic acid or *p*-toluene sulphonic acid is the most likely, halogen- or nitro-substituted sulphonic acids may be encountered. For melting-points of some original substance of this class see Table LXXXI (halogen-substituted primary amines).

CHAPTER XI

Miscellaneous Compounds

Compounds containing Carbon, Hydrogen, Oxygen and Phosphorus

The only compounds containing these elements to be considered are alkyl and aryl esters of phosphoric and phosphorous acids.

Confirm the fact that the substance is a member of this class by applying the ester test with alcoholic potash and phenolphthalein as for esters containing carbon, hydrogen and oxygen only (see p. 67).

Derivatives, etc.—*Hydrolysis.* Reflux about 5 g. of the substance with 50 ml. of 50 per cent aqueous caustic potash for about 15 min. or until the liquid becomes homogeneous. Transfer to a distilling flask connected to a water-cooled condenser and distil off about 15 ml. Test this distillate for alcohol as in the case of the corresponding distillate obtained in the hydrolysis of esters containing carbon, hydrogen and oxygen (see p. 68). If an alcohol is proved present, prepare a suitable derivative, i.e. the 3 : 5-dinitrobenzoate or xanthate.

If no alcohol is obtained, acidify the residual alkaline liquid with dilute sulphuric acid and extract the liberated phenol with ether. After drying and distilling off the ether prepare a derivative, e.g. benzoate, of the phenol.

To portions of the acid liquid remaining from the ether extraction apply the following tests for phosphate and phosphite:

Test	Phosphate	Phosphite
1. Add 1 ml. of conc. nitric acid, 5 ml. of ammonium nitromolybdate solution and warm gently	Yellow powdery precipitate	No immediate precipitate On heating a yellow precipitate may form due to oxidation to phosphate
2. Make alkaline with ammonia, add magnesia mixture and shake well	White crystalline precipitate	No precipitate
3. Neutralize with ammonia and add silver nitrate solution	Yellow precipitate soluble in ammonia and in dilute nitric acid	White precipitate turning black in the cold
4. To the acid solution add a few drops of potassium permanganate solution and warm gently	No change	Permanganate colour discharged
5. To the acid solution add mercuric chloride solution and warm	No precipitate	White precipitate of mercurous chloride

TABLE LXXXIX.—ALKYL AND ARYL PHOSPHATES AND PHOSPHITES

	B.P. °C.	Miscellaneous
Liquids		
Trimethyl phosphate	197	
Triethyl phosphate	215	
Triphenyl phosphite	360	
Tripropyl phosphate	138/47 mm.	
Tri-*o*-cresyl phosphate	265/20 mm.	Conc. HNO_3 in glacial acetic → nitro deriv., M.P. 69° C.
Tri-*n*-butyl phosphate	157/10 mm.	
Tri-*m*-cresyl phosphite	235/7 mm.	
Tri-*p*-cresyl phosphite	239/7 mm.	
Solids	M.P.	
Triphenyl phosphate	50	Conc. H_2SO_4 + conc. HNO_3 → tri-nitro deriv., M.P. 155° C.
Tribenzyl phosphate	64	
Diphenyl phosphate	70	Dihydrate, M.P. 51° C.
Tri-*p*-cresyl phosphate	78	
Dibenzyl phosphate	79	
Tri-*o*-phenylphenyl phosphate	113	

COMPOUNDS CONTAINING CARBON, HYDROGEN, NITROGEN, PHOSPHORUS AND POSSIBLY OXYGEN

Preliminary tests

1. *Effect of boiling the substance with* 30 *per cent sodium hydroxide*

Evolution of ammonia	Urea phosphate.
Odour of an organic base	Phosphate of an organic base, e.g. aniline phosphate.
Separation of a white solid; no characteristic odour	Quinine phosphate.

2. *Treat with cold dilute sulphuric acid*

Dissolves to give a solution with blue fluorescence	Quinine phosphate.

In compounds containing both nitrogen and phosphorus, the phosphorus is most likely to be in the form of phosphate ion (other nitrogen/phosphorus-containing compounds being outside the scope of this scheme).

In most cases the nitro-molybdate test for the phosphate ion may be applied directly to an aqueous solution of the original substance, but since quinine interferes with the test, it is better to make a general practice of removing water-insoluble bases before applying it.

Boil about 0·2 g. of the substance with 10 per cent sodium hydroxide solution, cool, filter if necessary, make acid with a little concentrated nitric acid, add about 5 ml. of ammonium nitro-molybdate reagent and warm gently. Formation of a brilliant yellow powdery precipitate proves phosphate present.

Confirmatory tests, e.g. the magnesia mixture test and silver nitrate test as in qualitative inorganic analysis may be applied to the alkaline filtrate.

The presence of urea phosphate will have been indicated by the evolution of ammonia in the preliminary test with caustic soda and may be confirmed by the application of the xanthydrol test and the "biuret" test to the original substance (see pp. 112–3). The sparingly soluble nitrate, oxalate and xanthydrol derivative of urea (see p. 114) may also be prepared without isolation of the free base.

In the preliminary test with sodium hydroxide, the formation of an oil or solid with the characteristic odour of an organic base suggests the presence of the phosphate of a primary aromatic amine (phosphates of other amines are rarely met with).

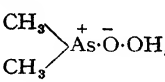
Apply the nitrous acid/alkaline β-naphthol test for aromatic amines (see p. 124).

The methods used for the preparation of derivatives of the base (see pp. 130–3) will indicate whether isolation of the base is a necessary preliminary step or if the original substance may be used.

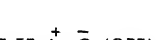
If indications of the presence of quinine phosphate have been obtained, isolate the base by boiling about 1 g. with caustic soda solution, cooling, filtering and washing well and applying tests (see p. 176) for quinine to the solid so obtained.

COMPOUNDS CONTAINING CARBON, HYDROGEN, OXYGEN AND ARSENIC

The only compounds of this group to be dealt with are cacodylic acid (dimethyl arsonic acid—),



and phenyl arsonic acid,



Classification test.—Dissolve 0·2 g. of the substance in 1 : 1 concentrated hydrochloric acid/water. Pass sulphuretted hydrogen. No precipitate of arsenious sulphide should be formed.

Mix 0·2 g. of the substance intimately with soda-lime in an ignition tube, cover with a one inch layer of soda-lime, and heat as in the soda-lime test (p. 21). *This test must be carried out in the fume chamber.* Cool, dissolve the residue in boiling hydrochloric acid, filter if necessary, and pass in hydrogen sulphide. An immediate yellow precipitate of arsenious sulphide is given by arsonic acids.

Derivative.—*S-benzyl thiuronium salt.*—Dissolve about 0·5 g. of the acid in 2N caustic soda, making the solution just alkaline to phenolphthalein, and add 5 ml. of a cold saturated aqueous solution of S-benzyl thiuronium chloride. Filter, wash with cold water and recrystallize from the least possible quantity of alcohol or alcohol and a very little water.

Note.—The derivative from cacodylic acid is very soluble in alcohol and crystallizes somewhat slowly.

Cacodylic acid (M.P. 200° C.) is a colourless crystalline solid, very soluble in water and in alcohol. It dissolves in sodium

carbonate with effervescence. The equivalent weight may be determined by dissolving about 0·3 g. in 25 ml. of water and titrating with standard N/10 sodium hydroxide to phenolphthalein. The theoretical value is 138. M.P. of S-benzyl thiuronium salt 74° C.

Phenyl arsonic acid.—(M.P. 158° C., at which temperature it passes into the anhydride.) M.P. of S-benzyl thiuronium salt 127° C.

The equivalent weight cannot be determined as in the case of cacodylic acid owing to the very indefinite end-point.

COMPOUNDS CONTAINING CARBON, HYDROGEN, OXYGEN, NITROGEN, ARSENIC AND POSSIBLY SODIUM

Quinine arsenate.—This compound is soluble in dilute sulphuric acid to give a solution with blue fluorescence.

On boiling with sodium hydroxide quinine is liberated as a white sparingly-soluble solid. Separate the base by boiling with caustic soda, cooling and filtering. Apply tests for quinine (see p. 176).

To the alkaline filtrate apply the following tests for arsenate: (i) nitro-molybdate, (ii) magnesia mixture, (iii) silver nitrate.

Arsanilic acid (*p*-aminophenyl arsonic acid).—This substance is sparingly soluble in water to give a colourless acid solution. Its sodium salt, known as *atoxyl*, is soluble in water. Both substances give the following test for the primary aromatic amino group:

Dissolve a small quantity of the given substance in dilute hydrochloric acid, cool well, add a few drops of sodium nitrite solution and pour into an alkaline solution of β-naphthol. A soluble red azo-compound is produced.

M.P. of S-benzyl thiuronium salt, prepared as for simple arsonic acid (p. 281), 93° C.

***o*-Nitro-phenyl arsonic acid.**—This substance is a yellow solid, sparingly soluble in water but readily soluble in sodium hydroxide to give a yellow solution.

Dissolve about 0·2 g. of the substance in 5 ml. of 2N sodium hydroxide, add a few drops of a strong solution of ferrous sulphate, boil for 5 min. and filter hot. To the filtrate after cooling well and acidifying with dilute hydrochloric acid apply the nitrous acid/alkaline β-naphthol test as above. A positive result proves the presence of a nitro group in the original substance.

M.P. of S-benzyl thiuronium salt (see p. 281) 125° C.

CHAPTER XII

Mixtures of Organic Compounds

The procedure described below is designed to deal with those artificial mixtures, containing no more than three constituents, which are used as laboratory exercises or examination problems, rather than those which are met with in industrial processes or arise in the course of organic syntheses. In the last two cases the identity of the constituents of the mixture is known or suspected, and accordingly methods of separation can be applied without preliminary investigation.

The assumption is made that no two compounds of the same type, i.e. containing the same functional groups, are present, and therefore extraction of the mixture with a particular reagent will remove one constituent only.

Separation of the mixture into its constituents is an essential preliminary to identification, and on the efficiency of this separation final success will depend. The methods used to effect separation will be determined by the nature of the mixture and no one procedure will serve for all cases. Processes based on the chemical character (acidic—basic—neutral) of the constituents are preferable to those depending on varying solubility or differences in boiling-point; in fact, fractional crystallization or fractional distillation should only be resorted to when other methods are inapplicable. Even with two component mixtures a rapid and complete separation can only be expected from methods based on solubility or boiling-point when either:

(*a*) one component of a solid mixture is readily soluble in a solvent which neither dissolves nor affects the second constituent, or

(*b*) the boiling-points of the components of a liquid mixture are fairly widely separated and no azeotropic mixture is formed, or

(*c*) one readily-volatile constituent can be distilled off leaving a non-volatile substance behind.

PROCEDURE

Preliminary examination.—Examine the mixture for the presence of nitrogen (using Middleton's mixture (p. 16) in preference to metallic potassium). If nitrogen is absent then nitrogen

bases are absent, and no extraction with dilute mineral acid at a later stage will be necessary. Presence of nitrogen does not necessarily mean that a base is present.

For liquid mixtures completely soluble in ether.—In a short-stemmed (or 10 ml.) burette, place water, previously saturated with ether, until the surface is a few ml. above the lowest graduation mark. Add exactly 5 ml. of an ethereal solution containing 2·5 ml. of the original mixture and shake well. Allow the two layers to separate and note the volume of the ethereal layer. If there is no diminution in volume, then water-soluble compounds (soluble in ether) are absent. If the volume of the ethereal layer is less than 5 ml., a compound of this type is present. (It must be remembered that diminution in volume resulting from water-extraction may be due to the removal of acidic or basic constituents soluble or slightly soluble in water.)

Run off the water layer, retaining it if it contains any constituent of the mixture, and add to the burette about 10 ml. of a 10 per cent solution of sodium hydroxide previously saturated with ether. Again shake well and allow separation into two layers (which will be slower than on the previous occasion) to take place. Diminution in the volume of the ethereal layer indicates the presence of an acidic or phenolic constituent, or both. Run off the alkaline layer, conserving it if it contains a sodium salt.

If nitrogen is present in the original mixture, add to the burette about 10 ml. of 5N hydrochloric acid saturated with ether, shaking well after such addition and noting any possible diminution in the volume of the ether layer due to the extraction of a base. If nitrogen has been proved absent, this extraction is unnecessary. If the acid layer contains the hydrochloride of a base, retain it for use at a later stage.

If the residual ether layer measures 2·5 ml. or slightly less, then the original mixture contains no neutral constituent. If more than 2·5 ml., then a neutral compound insoluble in water is present.

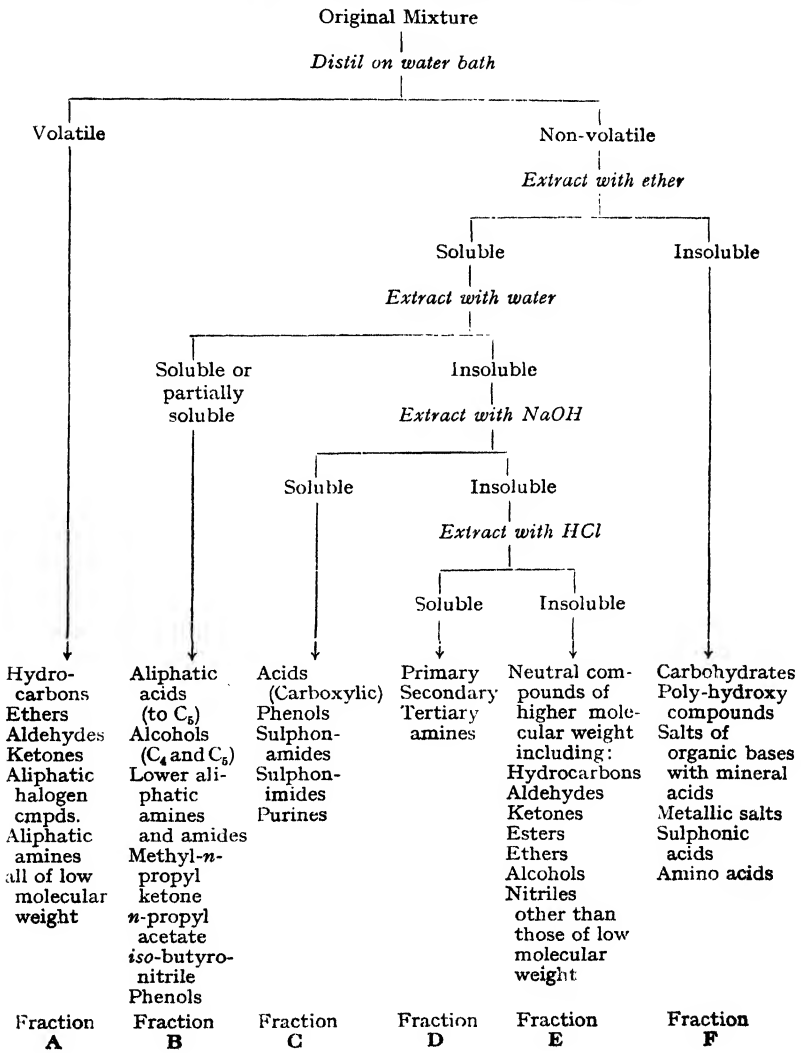
The reserved extracts, including the final ethereal solution, if more than 2·5 ml. in volume, should subsequently be combined with the corresponding ones obtained when working with larger amounts of the original mixture in order to conserve material.

An indication of the amount of each constituent present will be given by the reduction in volume of the ether solution resulting from each extraction and from the final volume of the ethereal layer.

Test the original mixture for the presence of phenols by dis-

solving one drop in a little alcohol and adding to neutral ferric chloride. The colour due to a phenol may be masked to some extent by reaction of the ferric chloride with other constituents of the mixture.

SEPARATION OF THE CONSTITUENTS OF A SOLID OR LIQUID MIXTURE: GENERAL SCHEME



Detailed method of treatment for isolation of the fractions shown in the general scheme

Fraction A.—If the mixture is a liquid, distil from a water-bath using a water-cooled condenser. If a portion distils over, redistil it with a thermometer in the neck of the distilling flask in order to ascertain whether the fraction volatile below 100° C. is a single substance or a mixture. If it distils at a constant temperature, identify it as for a single substance, bearing in mind the possibility that it may be water.

If organic in nature, it is probably a hydrocarbon, ether, alcohol, ketone, aldehyde, ester, aliphatic halogen compound or aliphatic amine and of low molecular weight.

If it boils over an appreciable temperature range, separation methods as given below must be applied.

Fraction F.—Treat the residue in the flask, *or the original mixture if it be a solid*, with about 50 ml. of dry ether. If any solid material is insoluble in the ether, separate it by filtration into a dry flask, and wash the solid with two or three small portions of dry ether, the washings being combined with the main ethereal solution.

If two immiscible layers are formed, separate in a separating funnel and extract the lower layer twice more with small quantities of ether to secure complete separation. All the ethereal extracts are then combined.

The ether-insoluble portion is examined as a single substance bearing in mind the fact that it is likely to be a carbohydrate or other polyhydroxy compound, a salt arising from the combination of an organic base and a mineral acid, a metallic salt of an organic acid, a sulphonic acid or amino-acid.

It will be realized that separation of the remaining constituents is greatly complicated by the presence of substances soluble in both water and ether, because both aqueous acid and alkaline reagents will extract some of this constituent at least, not in virtue of its chemical properties but because of its water-solubility. The most rapid and complete separation will be achieved in those cases where there are present two or more of the following: an acidic, a basic, a neutral compound all soluble in ether, but practically insoluble in water. Most compounds soluble in ether and soluble in water will have been removed by distillation at 100° C.

Fraction B.—If the preliminary examination has indicated the presence of water-soluble compounds, there may remain in the ether solution aliphatic acids (up to C_5), alcohols (C_4 and C_5), certain lower aliphatic amines and amides, methyl *n*-propyl ketone, *n*-propyl acetate, *iso*-butyronitrile and certain phenols.

If the presence of one of these is suspected, add 20 ml. of water to the ethereal solution in the separating funnel, shake well and, after allowing the two layers to separate, run off the lower aqueous layer. Test small portions of this for the classes of compounds mentioned above as follows:

for acids—caustic soda and phenolphthalein test (see p. 50);
for alcohols—ceric ammonium nitrate test (see p. 77);
for amines—2 : 4-dinitrochlorobenzene test (see p. 110);
for amides—nitrous acid test (see p. 109);
for ketones—2 : 4-dinitrophenylhydrazine test (see p. 36);
for esters—alcoholic potash and phenolphthalein test (see p. 67);
for nitriles—hydrogen peroxide/caustic soda test (see p. 155);
for phenols—ferric chloride test (see p. 61).

The test for nitrogen-containing compounds may obviously be omitted if the original mixture has been proved to contain no nitrogen.

If a positive result is obtained in any of the above tests, extract the ethereal solution with two more 10 ml. portions of water and combine these with what remains of the original aqueous extract. If amides are present, remove the water on a water-bath and identify the residual solid. In the case of acids, neutralization with caustic soda before evaporation will yield the sodium salt for the preparation of derivatives, while amines may be retained as hydrochlorides during evaporation.

Alcohols may be identified by conversion to the potassium alkyl xanthate or by oxidation to the aldehyde or ketone, passing this into a solution of 2 : 4-dinitrophenylhydrazine sulphate (or chloride) to form the 2 : 4-dinitrophenylhydrazone. Ketones originally present will yield the latter derivative.

Esters and nitriles can be hydrolysed and the hydrolysis products identified.

By making the aqueous solution of phenol (if present) just alkaline and then concentrating it by evaporation, benzoyl derivatives may be obtained.

Quantitative separation of these water/ether soluble constituents will not be secured by three small-scale extractions, as the solute will distribute itself between the two immiscible solvents, and in the case of simple monohydric phenols the bulk of the material will remain in the ether layer.

Fraction C.—If the preliminary extraction experiments show the presence of an acid constituent after water extraction, add to the ethereal solution in the separating funnel 20 ml. of 10 per cent sodium hydroxide solution, shake well and allow the two layers to separate. Separation in this case will be slow owing to the tendency of an emulsion to persist, and addition of a further small amount of ether may be desirable. Run off the alkaline layer and extract the ether layer with two more 10 ml. portions of alkali combining the alkaline extracts. Shake these combined extracts with 20 ml. of ether to remove basic compounds and add this ether to the main bulk in the separating funnel.

Treatment of the alkaline extract.—If preliminary tests or examination of the water extract have shown the probable presence of a phenol, saturate the alkaline liquid with carbon dioxide, extract three times with ether using 15 ml. for each extraction. Combine the ethereal extracts, dry over anhydrous sodium sulphate, distil off the ether and identify the residual phenol.

Render the aqueous layer just acid by addition of concentrated hydrochloric acid, thus keeping the increase in bulk to a minimum. If a solid acid separates, filter it off, wash with cold water to remove hydrochloric acid and identify it (see pp. 52–4).

If no solid separates, extract the acidified liquor with three 10 ml. portions of ether, combine the ethereal extracts and wash with three 3 ml. portions of water to remove hydrochloric acid. The final wash water should give no more than a very faint reaction for chloride ion. Dry over anhydrous sodium sulphate, distil off the ether and identify the acid.

Fraction D.—If nitrogen has been proved present in the original mixture and the preliminary extraction test has shown a basic constituent to be present, a final extraction of the main ethereal solution with 2N hydrochloric acid will be necessary.

Extract three times using 10 ml. of acid on each occasion, combine the acid extracts and shake with 20 ml. of ether to remove neutral constituents, adding this ether to the main ethereal solution.

Treatment of the acid extract.—Add a concentrated solution of sodium hydroxide until the liquid is definitely alkaline. If a solid

base is precipitated, filter it off, wash with water and dry. Carry out an elements test on the substance and identify it.

If no solid base is formed, extract the alkaline liquid with three 10 ml. portions of ether (slightly more ether may be required to aid the separation into two layers), combine these, wash with three small portions of water, dry over anhydrous sodium or magnesium sulphate, distil off the ether and identify the residual base. An aromatic primary, secondary or tertiary amine is most probable.

Fraction E.—If in the preliminary extraction experiment the volume of the final ethereal solution was greater than 2·5 ml., then a neutral compound is present in the main ethereal solution. Wash this solution with distilled water until the washings are free from chloride ion. Dry the ether layer over anhydrous sodium sulphate and distil off the ether. Carry out an elements test on the compound and complete its identification. A simple or substituted hydrocarbon, ether, ester, aldehyde, ketone, alcohol or nitrile is most probable.

APPENDIX

Some Solutions and Reagents

Ammonium nitro-molybdate solution

Dissolve 125 g. of pure molybdenum trioxide in a mixture of 75 ml. concentrated ammonia and 325 ml. of water. Add 400 g. of ammonium nitrate and make up to 1 litre. Pour this solution slowly into a mixture of 350 ml. concentrated nitric acid and 650 ml. water. Allow to stand in a warm place for a few days. Decant carefully from any separated solid.

Denigès' reagent

Add 10 ml. of concentrated sulphuric acid slowly to 50 ml. of water and dissolve 2·5 g. of mercuric oxide in the hot solution.

2 : 4-Dinitro-phenylhydrazine reagent (for classification test only)

Dissolve 2 g. of 2 : 4-dinitrophenylhydrazine in 15 ml. of concentrated sulphuric acid and, while stirring, add to 150 ml. of 95 per cent alcohol. Dilute to 500 ml. with water. Allow to stand for a few days and filter.

" Ferrox " paper

Dissolve 1 g. of crystalline ferric chloride ($Fe_2Cl_6 \cdot 12H_2O$) and 1 g. of potassium thiocyanate in two separate 10 ml. portions of pure methyl alcohol. Mix and filter. Dip strips of filter paper about 1 cm. wide in the solution and air-dry. More than one dipping is desirable, and the finished paper should have a greenish metallic sheen. Cut the strips into 1 cm. squares and store in a dark-coloured bottle.

Fehling's solution

No. 1.—Dissolve 34·6 g. of crystalline copper sulphate in water and make up to 500 ml.

No. 2.—Dissolve 173 g. of sodium potassium tartrate (Rochelle salt) and 70 g. sodium hydroxide in water and make up to 500 ml.

For use mix equal volumes of solutions Nos. 1 and 2.

Schiff's reagent

To 200 ml. of water saturated with sulphur dioxide add 4 g. of fuchsine and shake until complete solution is effected. Add decolorizing charcoal, shake, and allow to stand overnight. Filter and make up to 2 litres. This solution is free from the yellow colour so often observed in some samples of Schiff's reagent. Store in a well-stoppered dark-coloured bottle.

Nylander's reagent

Dissolve 2 g. of bismuth subnitrate (oxynitrate) and 4 g. of Rochelle salt in 100 g. of 8 per cent sodium hydroxide solution.

Schweitzer's reagent

To a concentrated solution of copper sulphate add concentrated ammonia with stirring till the precipitate first formed completely redissolves.

Nessler's solution

Dissolve 50 g. of potassium iodide in the smallest possible quantity of cold water. Add a saturated solution of mercuric chloride till a very faint permanent precipitate is formed. Add 400 ml. of 50 per cent potassium hydroxide. Allow the precipitate to settle, make up to 1 litre with water, and after standing, decant off the clear solution.

S-benzylthiuronium chloride

126 g. of benzyl chloride, 76 g. of thiourea and 200 ml. of alcohol are boiled gently under a reflux condenser for half an hour. The salt crystallizes out on cooling. The crude product after filtering and washing with a little alcohol is quite satisfactory for the preparation of derivatives, but if a purer product is desired it may be recrystallized from 50/50 concentrated hydrochloric acid/water or from alcohol. M.P. 172–174° C. The salt is dimorphous and a melting-point of 146–148° C. may be obtained, but both forms yield the same derivatives.

Benzene sulphohydroxamic acid

10 g. of hydroxylamine hydrochloride is boiled under a reflux condenser with just enough methyl alcohol to dissolve it, and while still hot a solution of 3 g. of sodium in 60 ml. of ethyl alcohol is

slowly added. After cooling and filtering off the precipitated sodium chloride, 8·5 g. of benzene sulphonyl chloride is added in small portions. Most of the alcohol is distilled off on a water-bath, and after cooling and filtering off the separated hydroxylamine, the solution is made up to 100 ml. with pure ethyl alcohol.

2-Phenyl indole

In a tall 1 litre beaker place a mixture of 53 g. of freshly prepared acetophenonephenylhydrazone (see Derivative, p. 38), and 250 g. of powdered anhydrous zinc chloride. Immerse the beaker in an oil-bath at 170° C. and stir vigorously. After a few minutes white fumes are evolved and the mass becomes liquid. Remove the beaker and stir for a further 5 min. To prevent solidification to a hard mass, stir thoroughly into the reaction mixture 200 g. of clean sand. Dissolve the zinc chloride by digesting the mixture for some hours on a steam-bath with 800 ml. of water and 25 ml. of concentrated hydrochloric acid. Remove the sand and crude 2-phenyl indole by filtration and boil the solid with 600 ml. of 95 per cent alcohol. Treat with decolorizing charcoal and filter. Cool the filtrate and filter off the resulting 2-phenyl indole. Wash three times with 20 ml. of cold alcohol. Dry in a vacuum desiccator. M.P. 188–189° C.

GENERAL INDEX

INDEX OF SUBSTANCES IN TABLES