CONSTITUTIONAL PROBLEMS IN ORGANIC CHEMISTRY

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Constitutional Problems in Organic Chemistry

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Preface

If any justification of this book is needed it lies in the authors' belief that, despite the many elegant physical methods now available for the elucidation of organic structures, the solution of problems based on the traditional analytical and synthetic approach still provides the best method of consolidating the student's knowledge of organic reactions. Knowledge repeatedly applied is truly assimilated and through the solution of problems the student gains valuable experience in the interpretation of experimental data as well as confidence and satisfaction.

The problems, which have been roughly graded according to difficulty, are preceded by short chapters on organic reactions of diagnostic value which are discussed with special reference to their scope and limitations. Doubtless, much of this information the student will have already encountered but more than likely it will be scattered throughout his notes. In attempting to set forth the chemical background of the problems the authors hope they have achieved something more than a compilation of problems and that the book will make useful supplementary reading in organic chemistry courses in universities and technical colleges.

The standard of the problems ranges from about second year to Honours B.Sc. and Grad. R.I.C. level, most of the second half of the problems being in the latter category.

The authors wish to acknowledge their gratitude and indebtedness to their many friends and colleagues in other Colleges and Universities who have so willingly supplied them with problems and the permission to reproduce them and to the Royal Institute of Chemistry for permission to use problems from Parts I and II of the Royal Institute's examination papers.

The authors also wish to record their thanks to Dr. R. H. Thomson, of the University of Aberdeen, who read the manuscript and suggested some valuable amendments and to their colleague Mr. Robert Buchan who, besides contributing some of the problems, patiently checked the solutions.

Robert Gordon's Technical College, M.B.W.
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Hints on the Solution of Problems

Read through the problem carefully before starting to work on it.

Work out all analysis figures to get empirical or molecular formulae. Be accurate and check all calculations.

Examine molecular formulae. Saturated aliphatic compounds are usually easily recognized from their C/H ratios; hydrocarbons are C_nH_{2n+2}, alcohols are $C_nH_{2n+2}O$, aldehyde and ketones are $C_nH_{2n}O$, and so on.

In the same way olefinic and acetylenic compounds have their characteristic generic formulae, but if the compounds are highly unsaturated their formulae may not be easy to distinguish from those of aromatic compounds. The nature of the degradation products, however, will often resolve this difficulty, e.g. unsaturated aliphatic compounds are not at all likely to be products of an oxidation.

Aromatic compounds can often be recognized from the C/H ratio but are most surely indicated by the appearance, as degradation products, of compounds such as benzoic acid, phthalic acid, phenols, etc.

Always compare the molecular formula of the starting material with that of a reaction product and note the atoms lost or gained. Loss of the elements of water, hydrogen halide, ethyl alcohol or halogen are highly significant and may indicate the formation of a multiple bond or a condensation to form a new carbon-carbon bond. The possibility that such a condensation may form a cyclic compound should always be kept in mind.

The loss of carbon and hydrogen atoms, etc., not otherwise accounted for, usually indicates degradation of a carbon chain. Note particularly that the loss of a single carbon atom is characteristic of the fission of an aromatic methylene ether.

Attention should be paid to the reagents used and to their specific action, if any; these will often give valuable clues to the nature of the reaction or to the nature of the compound acted upon. For example, reagents such as water, aqueous alkali or acid which suggest hydrolysis should immediately evoke the mental question 'What types of compounds are hydrolysable?' If the compound in question contains nitrogen, suspect an amide, nitrile, oxime, etc. If nitrogen is absent then these compounds are immediately eliminated and others should be considered. Many reagents have specific actions and these can give useful information about the substance upon which they are used. For example, a compound oxidized by selenium dioxide will be sure to contain an activated methylene group or a compound reduced by the Wolff-Kishner reaction will certainly contain a carbonyl group.

Intramolecular rearrangements, often effected by acidic or alkaline reagents, should not be overlooked as possible changes during a sequence of reactions.

Remember that in solving a problem the facts are not necessarily used in the order in which they are presented in the statement of the problem.

It is usually best to start with some recognizable product, which may appear anywhere in the reaction sequence described, and to work forwards or backwards from this compound. An equally good starting point is a familiar reaction from which the character of the reactants can be deduced. Even if a piece of information provided appears to be irrelevant or redundant it is unwise to ignore it; alone or in conjunction with some other fact it may be essential to the correct solution of the problem. If a problem has been solved correctly there should be no loose ends; all the facts should be accounted for in the solution.

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Analytical Calculations

Before attempting to elucidate the structure of an organic compound, it is essential to acquire a knowledge of the elements it contains by qualitative analysis. Quantitative microdeterminations are then applied to obtain the molecular weight of the compound, and the percentage of each element present, together with any other relevant quantitative data which may be available.

Carbon and Hydrogen

Carbon and hydrogen are determined by a combustion procedure in which the carbon and hydrogen present in the compound are oxidized to carbon dioxide and water respectively, and weighed as such. The percentages of carbon and hydrogen can then be calculated:

3·251 mg of an organic compound gave 8·452 mg carbon dioxide and 1·951 mg water on combustion. Since $C/CO_2 = 12/44 = 0{\cdot}2727$, and $H_2/H_2O = 2/18 = 0{\cdot}1111$,

$$\%C = \frac{0{\cdot}2727 \times 8{\cdot}452 \times 100}{3{\cdot}251} = 70{\cdot}91$$

$$\%H = \frac{0{\cdot}1111 \times 1{\cdot}951 \times 100}{3{\cdot}251} = 6{\cdot}67.$$

Nitrogen

Nitrogen is commonly determined by two methods. The first, the Dumas method, is a modification of the combustion procedure for carbon and hydrogen, and involves the collection and measurement over caustic potash solution, of gaseous nitrogen. This volume is reduced to S.T.P. and from the fact that 22·4 litres of nitrogen weigh 28·016 g (i.e. 1 ml weighs 1·2507 mg), the percentage of nitrogen can be calculated.

4·250 mg of an organic compound gave 0·3803 ml nitrogen at 25°C and 748 mm pressure.

The volume of N_2 at S.T.P. $= \dfrac{0{\cdot}3803 \times 273 \times 748}{760 \times 298}$ ml

The factor $\dfrac{273}{760} = 0{\cdot}3592$

The weight of N_2 at S.T.P.

$$= \frac{0{\cdot}3803 \times 0{\cdot}3592 \times 748 \times 1{\cdot}2507}{298} \text{ mg}$$

$$\therefore \quad \%\text{N} = \frac{0{\cdot}3803 \times 0{\cdot}3592 \times 748 \times 1{\cdot}2507 \times 100}{298 \times 4{\cdot}250} = 10{\cdot}09.$$

The second method, the Kjeldahl procedure, depends on the conversion of the nitrogen present to ammonium bisulphate by sulphuric acid in the presence of catalysts such as mercury, copper or selenium. Addition of caustic soda containing sodium thiosulphate to the reaction mixture liberates ammonia gas which is distilled into 2% boric acid solution, and titrated directly with hydrochloric acid. Since 1 ml 0·01 N hydrochloric acid ≡ 0·1401 mg nitrogen, the percentage of nitrogen in the original compound can be calculated.

The ammonia obtained by the Kjeldahl treatment of 5·253 mg of a nitrogenous compound required 3·88 ml 0·01 N acid for neutralization,

$$\therefore \quad \%\text{N} = \frac{3{\cdot}88 \times 0{\cdot}1401 \times 100}{5{\cdot}253} = 10{\cdot}35.$$

Halogen

Halogen can be determined by the Carius method in which the organic compound is heated in a sealed tube with fuming nitric acid and silver nitrate crystals. From the weight of the silver halide formed, the percentage halogen can be obtained.

4·060 mg of an organic compound gave 6·480 mg silver bromide.

Since $\dfrac{\text{Br}}{\text{AgBr}} = \dfrac{79{\cdot}916}{187{\cdot}80} = 0{\cdot}4256$

$$\%\text{Br} = \frac{6{\cdot}480 \times 0{\cdot}4256 \times 100}{4{\cdot}060} = 67{\cdot}94.$$

Corresponding factors for chlorine and iodine are respectively

$$\frac{\text{Cl}}{\text{AgCl}} = \frac{35{\cdot}46}{143{\cdot}34} = 0{\cdot}2474, \qquad \frac{\text{I}}{\text{AgI}} = \frac{126{\cdot}91}{234{\cdot}79} = 0{\cdot}5405.$$

Sulphur

Sulphur is also determined by a Carius method similar to that for halogen, but with the omission of silver nitrate. The sulphur present is converted to sulphuric acid. Two variants of the procedure are used to measure the sulphuric acid formed.

The titrimetric method requires the inclusion in the Carius reaction vessel of sodium or potassium chloride, which is converted to sodium or potassium bisulphate by the sulphuric acid. Excess nitric acid is evaporated, and the bisulphate converted to sulphate by sodium hydroxide solution. Titration of the sulphate solution by 0·01 N barium chloride solution using tetrahydroxybenzoquinone as indicator gives a measure of the sulphur present.

5·863 mg of a sulphur-containing organic compound required 7·72 ml 0·01 N barium chloride solution.

Since $$BaCl_2 \equiv H_2SO_4 \equiv S$$

then $$1 \text{ ml } 0{\cdot}01 \text{ N } BaCl_2 \text{ solution} \equiv 0{\cdot}1603 \text{ mg S}$$

$$\therefore \quad \%S = \frac{7{\cdot}72 \times 0{\cdot}1603 \times 100}{5{\cdot}863} = 21{\cdot}11.$$

The gravimetric method entails the collection and weighing of the precipitated barium sulphate obtained as in the titrimetric method. Alternatively, the sodium chloride used initially in the Carius reaction vessel can be replaced by barium chloride and the precipitated barium sulphate determined by weighing.

4·135 mg of an organic compound gives 6.362 mg barium sulphate.

Since $$\frac{S}{BaSO_4} = \frac{32{\cdot}066}{233{\cdot}426} = 0{\cdot}1374$$

$$\%S = \frac{6{\cdot}362 \times 0{\cdot}1374 \times 100}{4{\cdot}135} = 21{\cdot}13.$$

Oxygen

Oxygen, although determinable by direct methods based on the high temperature decomposition of the organic compound in an inert gas, is nevertheless usually obtained by calculating the difference between 100% and the total of the percentages of the other elements present in the compound.

To find the relative whole numbers of each kind of atom present in a compound, each percentage is divided by the appropriate atomic weight and the resultant figures scaled to the simplest whole numbers. The formula thus obtained is the empirical formula of the compound. To obtain the true or molecular formula, the molecular weight must first be obtained, for example, by freezing-point depression determinations. A whole number factor must then be applied to the empirical formula to give the same molecular weight as that obtained by experiment.

An organic compound is found to contain on analysis 35·60% carbon, 4·95% hydrogen, and 27·70% nitrogen.

Totalling these figures gives 68·25%, therefore 31·75% must be oxygen.

	Carbon	*Hydrogen*	*Nitrogen*	*Oxygen*
Percentages	35·60	4·95	27·70	31·75
At.Wt	12	1	14	16
Divide by At.Wt	2·97	4·95	1·98	1·98

Decreasing these quotients proportionately so that the smallest is 1,

Carbon	*Hydrogen*	*Nitrogen*	*Oxygen*
1·5	2·5	1	1

The empirical formula must therefore be $C_3H_5N_2O_2$ (formula weight 101). A molecular weight determination gives a figure of 202.

The molecular formula of the compound must therefore be $C_6H_{10}N_4O_4$.

Other determinations or estimations which may be useful in the elucidation of the structure of an organic compound are as follows:

Hydroxyl Groups

Acetylation of hydroxyl groups by acetic anhydride and pyridine affords a method of obtaining the number of such groups present in the molecule. Excess of the reagent is hydrolysed with water to acetic acid which is titrated with standard alkali:

$$R.OH + CH_3.CO.O.CO.CH_3 \rightarrow R.O.CO.CH_3 + CH_3.COOH$$

A corrected blank carried out simultaneously gives the volume of alkali equivalent to the acetic acid formed and hence by difference to the acetic acid used in the acetylation.

7·36 mg of a phenol (M.Wt 126) gave a titration difference of 3·51 ml 0·05 N alkali.

Since
$$1000 \text{ ml N NaOH} \equiv 17 \text{ gm OH}$$
$$1 \text{ ml } 0{\cdot}05 \text{ N NaOH} \equiv 0{\cdot}85 \text{ mg OH}$$

$$\therefore \quad \% \text{ hydroxyl group} = \frac{3{\cdot}51 \times 0{\cdot}85 \times 100}{7{\cdot}36} = 40{\cdot}53$$

$$\therefore \quad \text{The number of hydroxyl groups is } \frac{40{\cdot}53 \times 126}{100 \times 17} = 3.$$

Acetyl Groups

Hydrolysis of esters or amides of acetic acid by *p*-toluene sulphonic acid is followed by treatment of the acetic acid produced with excess potassium iodide-potassium iodate solution. The liberated iodine is determined by thiosulphate titration:

$$6CH_3.COOH + KIO_3 + 5KI \rightarrow 6CH_3.COOK + 3H_2O + 3I_2$$

9·324 mg of a compound required 7·61 ml 0·01 N sodium thiosulphate in an acetyl group determination.

Since $6CH_3.CO \equiv 3I_2 \equiv 6Na_2S_2O_3$ (i.e. 6 equivalents)

$$1 \text{ ml } 0{\cdot}01 \text{ N thiosulphate} \equiv 0{\cdot}4305 \text{ mg } CH_3.CO$$

$$\therefore \quad \% \text{ acetyl group} = \frac{0{\cdot}4305 \times 7{\cdot}61 \times 100}{9{\cdot}324} = 35{\cdot}14\%.$$

If the molecular weight is known, the number of acetyl groups can be calculated in a manner similar to that for hydroxyl groups.

Methoxyl Groups

The determination of methoxyl groups depends on the decomposition of a methyl ether by constant boiling hydriodic acid solution (Zeisel determination). The methyl iodide produced can be estimated by titrimetric or gravimetric methods.

The titrimetric estimation method employs the oxidation of the methyl iodide by bromine in acetic acid to iodic acid which, with acidified potassium iodide solution, liberates iodine. Standard thiosulphate solution is used to estimate the iodine.

$$CH_3OR \rightarrow CH_3I$$

$$CH_3I + Br_2 \rightarrow CH_3Br + IBr$$

$$IBr + 3H_2O + 2Br_2 \rightarrow HIO_3 + 5HBr$$

$$HIO_3 + 5KI + 5/2\ H_2SO_4 \rightarrow 3I_2 + 3H_2O + 5/2\ K_2SO_4$$

5·817 mg of a methyl ether liberates iodine which requires 9·89 ml 0·01 N thiosulphate solution.

From the above equations

$$CH_3O \equiv CH_3I \equiv 3I_2 \equiv 6Na_2S_2O_3 \text{ (i.e. 6 equivalents),}$$

so that $\frac{31{\cdot}035}{6}$ gm $CH_3O \equiv 1000$ ml N $Na_2S_2O_3$

$$\therefore \quad 1 \text{ ml } 0{\cdot}01 \text{ N } Na_2S_2O_3 \equiv 0{\cdot}0517 \text{ mg } CH_3O$$

$$\therefore \quad \%CH_3O = \frac{9{\cdot}89 \times 0{\cdot}0517 \times 100}{5{\cdot}817} = 8{\cdot}79.$$

In the gravimetric estimation, the methyl iodide is volatilized out of the reaction vessel into an alcoholic solution of silver nitrate where it is converted to silver iodide.

9·660 mg of an ether gives 6·422 mg silver iodide.

Since $CH_3O \equiv CH_3I \equiv AgI$

i.e. $31{\cdot}035$ gm $CH_3O \equiv 234{\cdot}79$ gm AgI

$$\therefore \quad \%CH_3O = \frac{6{\cdot}422 \times 31{\cdot}035 \times 100}{9{\cdot}660 \times 234{\cdot}79} = 8{\cdot}79.$$

From a knowledge of the molecular weight, the number of methoxyl groups can be calculated as before.

Active Hydrogen

The reaction between a methyl Grignard reagent (methyl magnesium halide) and active hydrogen atoms in an organic compound produces one mole of methane gas for every active hydrogen present (Zerewitinoff determination). By raising the temperature of reaction, the second active hydrogen of a primary amino-group can be made to give a further mole of methane.

33·2 mg of an alcohol (mol. wt. 92), gave 25·05 ml methane at 15°C and 752 mm pressure.

At S.T.P., this volume of methane will be $\dfrac{25{\cdot}05 \times 752 \times 0{\cdot}3592}{288}$ ml

92 gm of the alcohol will therefore provide

$$\frac{92 \times 25{\cdot}05 \times 752 \times 0{\cdot}3592}{33{\cdot}2 \times 10^{-3} \times 288 \times 10^{3}} = 65{\cdot}10 \text{ litres.}$$

Since each active hydrogen gives 22·4 litres of methane at S.T.P., the alcohol must therefore have 3 active hydrogen atoms.

Lithium aluminium hydride can be used in a similar fashion since it reacts with compounds containing active hydrogen atoms to liberate hydrogen, one mole of hydrogen being produced for every active hydrogen atom present. This method is much more accurate for determining the enol content of a tautomeric mixture because of the greater speed of reaction.

Equivalent Weight of an Acid by Direct Titrimetry

Acids in aqueous or alcoholic solution are titrated against standard alkali using phenolphthalein as indicator. Care must be taken to exclude carbon dioxide and this can be achieved by carrying out the titration at the boiling point of the acid solution.

8·326 mg of an unknown acid gave a titration of 5·65 ml 0·01 N caustic soda.

Since the equivalent weight in grams of the acid $\equiv 10^5$ ml 0·01 NaOH,

the equivalent weight is $\dfrac{10^5 \times 8{\cdot}326 \times 10^{-3}}{5{\cdot}65} = 147{\cdot}3$.

Equivalent Weight of an Acid by Analysis of Silver Salt

The treatment of the ammonium salts of most organic acids with silver nitrate solution gives an insoluble anhydrous silver salt, which on ignition decomposes to metallic silver. Comparison of the weight of the silver salt before ignition with that of the silver obtained gives the equivalent weight of the silver salt and of the acid.

0·532 gm of the silver salt of an acid gives 0·321 gm silver.

Since the atomic weight of silver is 107·9, the equivalent weight of the silver salt is $\frac{107\cdot9 \times 0\cdot532}{0\cdot321} = 178\cdot8$.

The equivalent weight of the acid will therefore be:

$$\text{Silver salt } (178\cdot8) - \text{Ag}(107\cdot9) + \text{H}(1\cdot0) = 71\cdot9.$$

Saponification Equivalent

Titrimetric evaluation of the weight of ester which is completely saponified by one equivalent of potassium hydroxide gives the equivalent weight of the ester.

A known weight of ester is boiled with excess of standard solution of potassium hydroxide in alcoholic solution until saponification is complete. Back-titration of the excess alkali by standard acid gives the amount of potassium hydroxide consumed in the reaction.

3·840 mg ester is refluxed with 10 ml 0·01 N potasium hydroxide solution. 6·240 ml 0·01 N acid are required to neutralize the excess alkali.

$$3\cdot840 \text{ mg ester} \equiv 10\cdot0 - 6\cdot240 \text{ ml } 0\cdot01 \text{ N alkali}$$

$$\equiv 3\cdot760 \text{ ml}$$

$$\therefore \quad \text{Saponification equivalent} = \frac{3\cdot84 \times 10^{-3}}{3\cdot76 \times 10^{-5}} = 102\cdot1.$$

The simplest ester is methyl formate, H.COOCH$_3$, whose equivalent weight is 60, and if only one ester group is present, 102·1 − 60 gives a value of 42·1 which corresponds to three methylene groups. The ester could therefore be any one of the following:

Butyl formate	$H.COOC_4H_9$
Propyl acetate	$CH_3.COOC_3H_7$
Ethyl propionate	$C_2H_5.COOC_2H_5$
Methyl butyrate	$C_3H_7.COOCH_3$

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Hydrolysis

A wide variety of organic compounds are broken down by hydrolysis to yield two or more simpler compounds which are often more easily identified. It should be noted, however, that the hydrolytic breaking of a bond may be intramolecular so that one new compound only is produced, as for example, in the hydrolysis of cyclic esters (lactones), cyclic amides (lactams), cyclic anhydrides, etc.

The term hydrolysis means a splitting by water but the action of water alone is usually very slow. In practice, since hydrolysis is catalysed by both hydrogen and hydroxyl ions, it is customary to reflux the compound under investigation with aqueous acid or alkali.

That a given compound has undergone hydrolysis is readily revealed by comparing the composition of the original compound with the composition of the product or products. If the former differs from the latter by two hydrogen atoms and one oxygen atom, or a simple multiple of these numbers, always, of course, in the ratio 2H : O, then the reaction has almost certainly been hydrolytic, e.g.,

$$C_{17}H_{19}O_2N + H_2O \rightarrow C_5H_{11}N + C_{12}H_{10}O_3$$

$$C_8H_4O_3 + H_2O \rightarrow C_8H_6O_4$$

$$C_7H_7ON + H_2O \rightarrow C_7H_6O_2 + NH_3$$

Table 1 lists the commoner classes of compounds degraded by hydrolysis, the products formed, and the chemical bond broken.

TABLE 1

Compound	*Products*	*Bond Broken*
Esters	Acids and Alcohols	C—O
Lactones	Hydroxy acids	C—O
Acid Anhydrides	Acids	C—O
Acid Halides	Acids and Hydrogen Halides	C—Hal
Alkyl Halides	Alcohols and Hydrogen Halides	C—Hal

Compound	*Products*	*Bond Broken*
Amides and *N*-substituted Amides	Acids and Ammonia or Amines	C—N
Lactams	Amino acids	C—N
Imides	Acids (often dibasic) and Ammonia or Amines	C—N
Nitriles	Acids and Ammonia	C—N
Isonitriles	Formic acid and Primary Amines	C—N
Ethers	Alcohols or Phenols	C—O
Acetals and Ketals	Alcohols or Glycols and Carbonyl Compounds	C—O
N-Nitroso compounds	Secondary Amines and Nitrous acid	N—N
Oximes, Hydrazones, and Semicarbazones	Carbonyl Compounds	C=N
β-Ketonic Esters	Acids or Ketones	C—C
Metal Alkoxides	Alcohols and Metal Hydroxides	—
Metal Alkyl Halides	Hydrocarbons and Metal Hydroxides	M—C
Metal Alkyls	Hydrocarbons and Metal Hydroxides	M—C

The hydrolysis of five classes of compounds in Table 1 should be noted.

Esters

Esters are hydrolysed by aqueous acids and alkalis to give organic acids and alcohols. If the organic acid can be easily isolated the determination of its neutralization equivalent will often afford a useful indication of its identity.

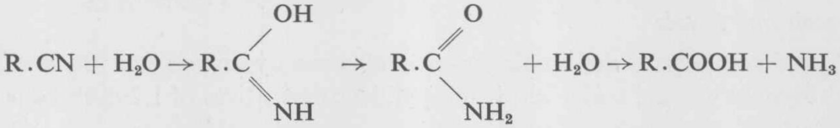
Nitriles

Organic nitriles or cyanides are hydrolysed by both acids and alkalis to yield carboxylic acids and ammonia:

$$R.CN + 2H_2O \xrightarrow{H^+} R.COOH + NH_4^+$$

$$R.CN + 2H_2O \xrightarrow{OH^-} R.COOH + NH_3$$

In both the above reactions hydrolysis proceeds via the amides:



$$R.CN + H_2O \rightarrow R.C\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown\!\!\diagdown NH} \rightarrow R.C\genfrac{}{}{0pt}{}{/\!\!/ O}{\diagdown NH_2} + H_2O \rightarrow R.COOH + NH_3$$

Under suitably controlled conditions the hydrolysis can be arrested at the amide stage. This can be done by dissolving the nitrile in concentrated sulphuric acid and pouring the solution into cold water, or by shaking the nitrile with cold concentrated hydrochloric acid. Sometimes the amide can be obtained by treating the nitrile with alkaline hydrogen peroxide:

$$R.CN + 2H_2O_2 \rightarrow R.CONH_2 + O_2 + H_2O$$

Isonitriles

These compounds are stable towards alkali under normal conditions. Dilute acid in the cold, or water at 180°C, however, hydrolyse them to primary amines and formic acid:

$$R.NC + 2H_2O \rightarrow R.NH_2 + H.COOH.$$

Ethers

Ethers are stable towards alkaline hydrolysis and under ordinary conditions they are also stable towards acids. They are, however, converted into alcohols by heating under pressure with dilute sulphuric acid:

$$R_2O + H_2O \rightarrow 2R.OH$$

Ethers are readily attacked by concentrated hydriodic acid and by concentrated hydrobromic acid, the products depending upon the temperature:

(*a*) *In cold:*

$$R_2O + HI \rightarrow RI + R.OH$$

In mixed ethers the smaller of the two alkyl groups becomes the alkyl halide:

$$CH_3.O.C_2H_5 + HI \rightarrow CH_3I + C_2H_5OH$$

and if both alkyl groups contain the same number of carbon atoms, the less complex group usually forms the alkyl halide. Propyl isopropyl ether, however, is an exception to this rule.

(*b*) *When heated:*

$$R_2O + 2HI \rightarrow 2RI + H_2O$$

Both the above reactions are useful in identifying the groups present in an ether but the most useful application of hydriodic and hydrobromic acids is in the fission of phenolic ethers which yield an alkyl halide and a phenolic compound:

$$Ph.O.CH_3 + HI \rightarrow Ph.OH + CH_3I$$

Acetals and Ketals

These compounds are stable towards alkaline hydrolysis but are readily hydrolysed by dilute acids. The isopropylidene derivatives of 1,2-diols behave similarly: