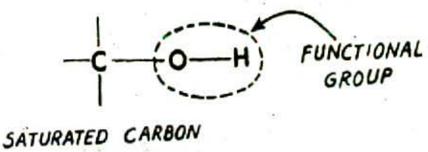
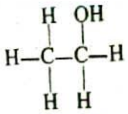
Chapter 16

Alcohols

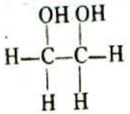
The term alcohol is applied to all organic compounds whose molecules contain a hydroxyl group, —OH, attached to a saturated carbon atom.



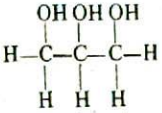
Alcohols containing one such —OH group are called **Monohydric alcohols.** Those with two, three or many C—OH groups are known as **Dihydric alcohols, Trihydric alcohols and Polyhydric alcohols** respectively. Thus,


$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{OH}{\underset{H}{C}}{-}H}$

ethyl alcohol
(monohydric alcohol)


$\mathrm{H{-}\overset{OH}{\underset{H}{C}}{-}\overset{OH}{\underset{H}{C}}{-}H}$

ethylene glycol
(dihydric alcohol)


$\mathrm{H{-}\overset{OH}{\underset{H}{C}}{-}\overset{OH}{\underset{H}{C}}{-}\overset{OH}{\underset{H}{C}}{-}H}$

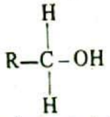
glycerol
(trihydric alcohol)

The —OH group bonded to a saturated carbon is the functional group of alcohol.

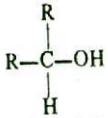
MONOHYDRIC ALCOHOLS

As stated above, monohydric alcohols are those aliphatic compounds which have one hydroxyl group, —OH, bonded to a saturated carbon. Thus they contain the grouping carbon-oxygen-hydrogen in their molecules. They may be represented by the formula R—OH or ROH, where R stands for an alkyl group.

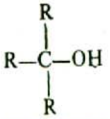
Monohydric alcohols are further classified as primary (1°), secondary (2°), and tertiary (3°) alcohols according as they contain one, two or three alkyl groups attached to the hydroxyl-bearing carbon atom. These alkyl groups may be same or different.


$\mathrm{R{-}\overset{H}{\underset{H}{C}}{-}OH}$

primary alcohol
(1° alcohol)

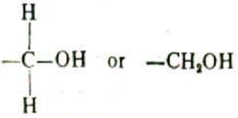

$\mathrm{R{-}\overset{R}{\underset{H}{C}}{-}OH}$

secondary alcohol
(2° alcohol)


$\mathrm{R{-}\overset{R}{\underset{R}{C}}{-}OH}$

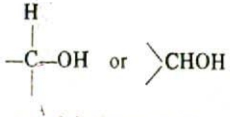
tertiary alcohol
(3° alcohol)

These three types of monohydric alcohols have many similar chemical properties, owing to the presence of the same functional group. However, they also exhibit different behaviour due to the different number of H atoms on the hydroxyl-bearing carbon. In fact the reactive groups or functions in primary, secondary and tertiary alcohols as indicated in bold letters in the above type formulas are



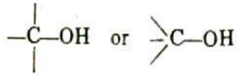
$$-\overset{H}{\underset{H}{C}}-OH \text{ or } -CH_2OH$$

primary alcohol group



$$-\overset{H}{\underset{|}{C}}-OH \text{ or } \rangle CHOH$$

secondary alcohol group



$$-\overset{|}{\underset{|}{C}}-OH \text{ or } \rangle C-OH$$

tertiary alcohol group

ORBITAL STRUCTURE

As in case of water, it is thought that the oxygen atom in the alcohol molecule (ROH) is sp^3 hybridized. The one s orbital and three p orbitals of the valency shell of oxygen mix to form four sp^3 hybrid orbitals

Valency shell

$$1s^2 \quad 2s^2 \quad 2p_x^2 \quad 2p_y^1 \quad 2p_z^1 \quad \xrightarrow{\text{hybridization}} \quad \text{four } sp^3 \text{ orbitals}$$

electronic configuration of O atom

Of the four sp^3 orbitals of oxygen atom, two possess a lone pair each while the remaining two have one electron each. In the formation of the alcohol molecule, one singly filled sp^3 orbital of oxygen atom overlaps with s orbital of H atom to form sp^3-s σ bond. The second singly filled sp^3 orbital overlaps with sp^3 orbital of the carbon atom of alkyl group to form sp^3-sp^3 σ bond.

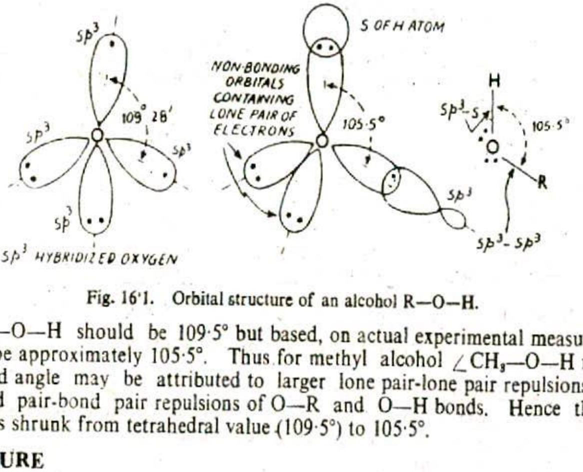


Fig. 16·1. Orbital structure of an alcohol R—O—H.

Normally ∠R—O—H should be 109·5° but based, on actual experimental measurements it has been found to be approximately 105·5°. Thus for methyl alcohol ∠CH_3—O—H is 107°. This decrease in bond angle may be attributed to larger lone pair-lone pair repulsions which overweigh the bond pair-bond pair repulsions of O—R and O—H bonds. Hence the bond angle ∠R—O—H has shrunk from tetrahedral value (109·5°) to 105·5°.

NOMENCLATURE

There are three systems of nomenclature for monohydric alcohols :

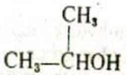
(a) The Common System ; (b) The Carbinol System ; and (c) The IUPAC System.

The recent Chemical Abstracts favour common names for lower members while for the higher and more complex alcohols IUPAC names are used with advantage.

(1) **Common System**. According to the Common System, alcohols (R—OH) are named as 'Alkyl alcohols', the term alcohol designating the —OH group. Thus the common name of an individual alcohol is obtained by writing the name of the alkyl group R linked to —OH group and then adding 'alcohol' as a separate word.

CH_3OH
methyl alcohol

CH_3CH_2OH
ethyl alcohol



$$CH_3-\overset{CH_3}{\overset{|}{C}}HOH$$

isopropyl alcohol

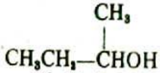
$CH_2=CH-CH_2OH$
allyl alcohol

As we go higher in the series it becomes necessary to indicate whether a particular alcohol is primary (1°), secondary (2°) or tertiary (3°). The prefix secondary is often abbreviated as *sec-* or *s-*, while tertiary as *tert-* or *t-*.

Thus the three butyl alcohols are assigned the following common names.

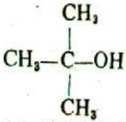
$CH_3CH_2CH_2CH_2OH$

n-butyl alcohol
(1° butyl alcohol)



$$CH_3CH_2-\overset{CH_3}{\overset{|}{C}}HOH$$

sec-butyl alcohol
(2° butyl alcohol)

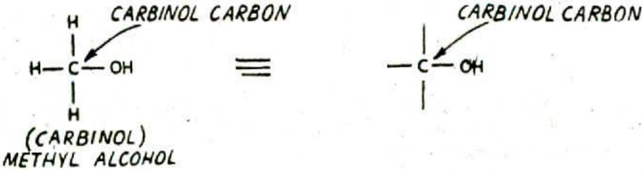


$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH$$

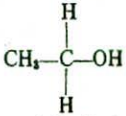
tert-butyl alcohol
(3° butyl alcohol)

Since a normal alkyl alcohol is always a primary alcohol, it is unnecessary to indicate the same by a prefix.

(2) **Carbinol System**. The *Carbinol System* names the alcohols as derivatives of methyl alcohol which is expressed as 'carbinol'. In fact, the word Carbinol designates the carbinol carbon and its attached hydroxyl group. That is,

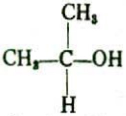


In alcohols each free valency bond of carbonyl carbon shown above is understood to carry an alkyl group or a hydrogen atom. The carbinol name of any alcohol is obtained by naming the alkyl groups attached to the carbinol carbon in alphabatical order and adding the word 'carbinol' as suffix, not as a separate word. Thus the full name of the given alcohol emerges as a continuous one-word name.



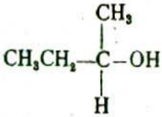
$$CH_3-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH$$

methylcarbinol
(ethyl alcohol)



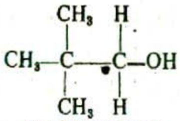
$$CH_3-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH$$

dimethylcarbinol
(isopropyl alcohol)



$$CH_3CH_2-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH$$

ethylmethylcarbinol
(*sec*-butyl alcohol)



$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH$$

tert-butylcarbinol
(neopentyl alcohol)

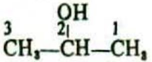
The *Carbinol names* are still used occasionally when alternate names are awkward. The carbinol names convey a mental picture of structure of a rather complex alcohol in a way that IUPAC names do not.

(3) **IUPAC System**. The *IUPAC System* names alcohols as *Alkanols*. The name of an individual alcohol is derived by replacing the final 'e' of the name of the parent alkane, alkene or alkyne by the suffix '*ol*'. Thus methyl alcohol gets the name *methanol* (methane $-e+ol$), while ethyl alcohol has the IUPAC name *ethanol* (ethane $e+ol$).

For naming higher alcohols, the longest continuous carbon chain containing the —OH group is selected as the basic hydrocarbon chain. The positional numbers of the —OH group, other substituent groups and double or triple bonds are obtained by numbering the parent chain from the end nearer the —OH group. Then the systematic name of the given alcohol is written as one word by the usual IUPAC conventions. For example,

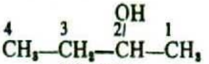
$\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$

1-propanol



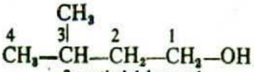
$\overset{3}{CH_3}-\overset{OH}{\overset{|}{\overset{2}{CH}}}-\overset{1}{CH_3}$

2-propanol



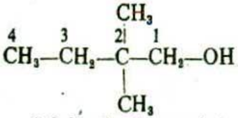
$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{OH}{\overset{|}{\overset{2}{CH}}}-\overset{1}{CH_3}$

2-butanol



$\overset{4}{CH_3}-\overset{CH_3}{\overset{|}{\overset{3}{CH}}}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$

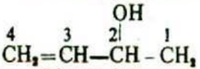
3-methyl-1-butanol



$\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{\overset{2}{C}}}}}-\overset{1}{CH_2}-OH$

2, 2-dimethyl-1-butanol

In case the parent chain of an alcohol contains a double or a triple bond, the positional number of the —OH group is mentioned before the suffix '*ol*'.



$\overset{4}{CH_2}=\overset{3}{CH}-\overset{OH}{\overset{|}{\overset{2}{CH}}}-\overset{1}{CH_3}$

3-butene-2-ol

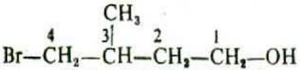
$\overset{5}{CH_3}-\overset{4}{CH}=\overset{3}{CH}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$

3-pentene-1-ol

If atoms or groups other than alkyl groups are attached to the main hydrocarbon chain, the name of such atom or group along with its positional number is prefixed to the overall name of the alcohol.

$Cl-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$

3-chloro-1-propanol



$Br-\overset{4}{CH_2}-\overset{CH_3}{\overset{|}{\overset{3}{CH}}}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$

4-bromo-3-methyl-1-butanol

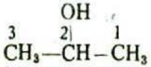
ISOMERISM

Isomerism in alcohols arises from two causes : (*i*) the different structures of the carbon chain, and (*ii*) the different positions of —OH group on the carbon chain. Thus alcohols may show *chain isomerism, positional isomerism*, or both.

n-Propyl alcohol and Isopropyl alcohol offer an example of positional isomerism.

$\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$

n-propyl alcohol,
1-propanol



$\overset{3}{CH_3}-\overset{OH}{\overset{|}{\overset{2}{CH}}}-\overset{1}{CH_3}$

isopropyl alcohol,
2-propanol

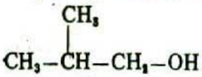
In n-propyl alcohol the —OH group is attached to carbon 1, while in isopropyl alcohol it lies on carbon 2.

The four isomeric butyl alcohols (C_4H_9OH) are :

(1) $CH_3-CH_2-CH_2-CH_2-OH$ n-butyl alcohol; 1-butanol

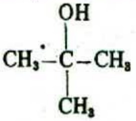
(2) $CH_3-CH_2-CHOH-CH_3$ *sec*-butyl alcohol; 2-butanol

(3)



$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-OH$ isobutyl alcohol; 2-methyl-1-propanol

(4)



$CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$ *tert*-butyl alcohol; 2-methyl-2-propanol

While the alcohols (1) and (2), as also (3) and (4) are positional isomers, the alcohols (1) and (3) are an example of chain isomerism.

Alcohols can show functional isomerism. Thus the molecular formula C_2H_6O represents:

CH_3-CH_2-OH and CH_3-O-CH_3

ethyl alcohol dimethyl ether

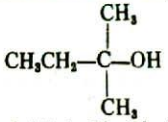
Here the two isomers belong to two different classes of compounds, or for the matter of that, contain different functional groups.

Higher alcohols like amyl alcohol also exhibit optical isomerism.

PHYSICAL PROPERTIES

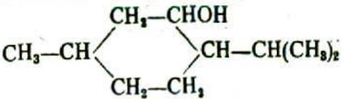
(1) **Odour and Taste**. The lower alcohols are colourless volatile liquids having characteristic 'alcoholic odour' and buning taste. The smell and taste becomes less pronounced with the increase of molecular weight.

Dimethylethylcarbinol, a colourless liquid, has a camphor-like odour and a burning taste. Menthol (a cyclic alcohol) which is a crystalline solid possesses a mintlike odour and produces cool sensation on the tongue which is followod by slight burning.



$CH_3CH_2-C(CH_3)_2-OH$

dimethylethylcarbinol (bp 100°)



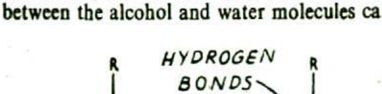
menthol (mp 41- 43°)

(2) **Narcotic Action**. Alcohols as a class have narcotic action. Methyl alcohol is a nerve poison and even in small doses it paralyses the optic nerve and causes blindness. Ethyl alcohol has a stimulant, followed by depressant action, on the central nervous system, causing anaesthesia and lowering of body temperature. The narcotic action of alcohols increases with chain branching so that some of the 3° alcohols (dimethylethylcarbinol) are used as sedatives and hypnotics. In general, the toxic character of liquid alcohols increases with increasing molecular weight.

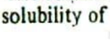
(3) **Solubility**. The lower alcohols are completely miscible with water but as the number of carbon atoms increases solubility decreases.

ALCOHOL	Methyl	Ethyl	n-Propyl	n-Butyl	n-Pentyl	n-Hexyl
SOLUBILITY (g/100 g H_2O)	*miscible*	*miscible*	*miscible*	7·9	2·7	0·59

The solubility of alcohols in water is attributed to association of the two substances by intermolecular hydrogen bonding. We know that due to its high electronegativity (relative to that of carbon or hydrogen) and small atomic volume, the O atom in alcohol (R—O—H) is able to concentrate negative charge effectively, polarizing the C—O and O—H bonds. As a result, the H of OH group carries a partial positive charge and the O atom a partial negative charge. Following the same line of argument, we know that water molecules are also polarized similarly.

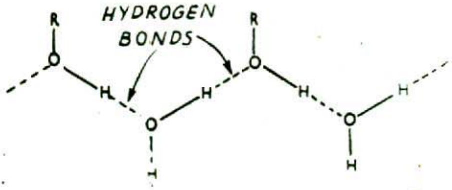


Polarized alcohol molecule



Polarized water molecule

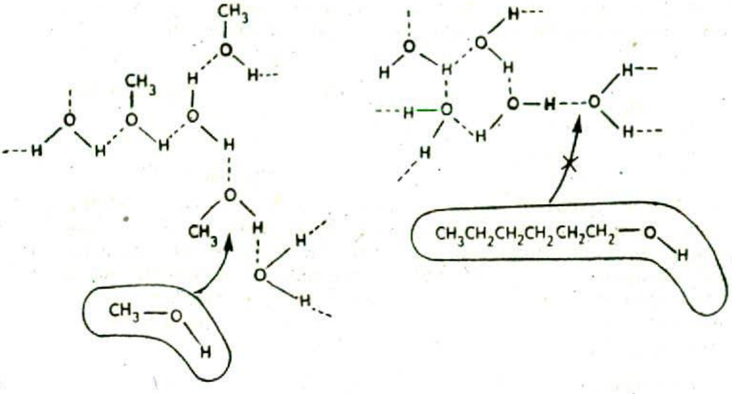
Obviously, the positive H atom of alcohol molecule will be attracted by the negative O atom of water molecule, and H atom of this water molecule will be attracted by O atom of another alcohol molecule ; and so on. The formation of weak electrostatic hydrogen bonds (shown dotted) between the alcohol and water molecules cause the solubility of alcohol in water.



The difference in water-solubility of alcohols can be explained as follows. The alcohol molecule is made of OH group and the alkyl group R. The OH group confers polarity and water-solubility upon the alcohol molecule. On the other hand, the alkane portion R confers nonpolarity and water-insolubility. In a lower alcohol (say CH_3OH or CH_3CH_2OH), the OH group comprises a substantial portion of the total molecule to make it water-soluble. As the size of carbon chain increases, the water-insoluble alkane portion increases and the solubilizing effect of

OH group is gradually overwhelmed. In a higher alcohol such as n-decyl alcohol the OH group becomes totally ineffective in dragging a large alkane portion of the alcohol molecule into water structure. Thus n decyl alcohol is insoluble in water.

$$\underbrace{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2}_{\text{insoluble alkane portion}}—OH$$

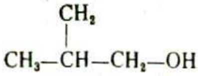
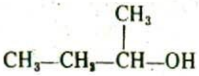
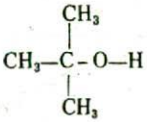


(a) (b)

Fig. 16·2. (a) A short-chain alcohol can easily break into the hydrogen-bonded structure in water and is thus solubilized ; (b) a long-chain alcohol cannot be dragged into water structure and is insoluble.

Since higher alcohols having a large hydrocarbon part are more alkane like, they are soluble in organic solvents as benzene, ether, chloroform, etc.

Table. Solubilities of Butyl alcohols in water

Alcohol	*Formula*	*Solubility g/100 g of water*
n-Butyl alcohol	$CH_3—CH_2—CH_2—CH_2—OH$	7·9
Isobutyl alcohol	 $CH_3—\overset{\overset{CH_3}{\vert}}{C}H—CH_2—OH$	10
sec-Butyl alcohol	 $CH_3—CH_2—\overset{\overset{CH_3}{\vert}}{C}H—OH$	12·5
tert-Butyl alcohol	 $CH_3—\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-O—H$	$\propto$

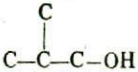
Here different solubilities are a result of different geometrical shapes of the butyl alcohols. The very compact *tert*-butyl alcohol molecules experience weaker intermolecular attractions and are more easily surrounded by water molecules. Hence it has the highest solubility in water of any of its isomers.

(4) **Boiling Points.** (*a*) The boiling points of alcohols increase fairly regularly with the addition of each $—CH_2—$ group to the hydrocarbon chain. This increase is about 20°C among the lower members (*See Table on page 333*).

(*b*) As with alkanes, the boiling points of alcohols decrease with the branching of the carbon chain. Thus boiling points of isomeric alcohols are in the order 1° > 2° > 3°. This is illustrated by taking example of butyl alcohols (C_4H_9OH).

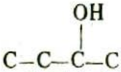
C—C—C—C—OH

n-butyl alcohol (bp 118°)



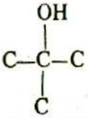
$C-\overset{\overset{C}{|}}{C}-C-OH$

isobutyl alcohol (bp 108°)



$C-C-\overset{\overset{OH}{|}}{C}-C$

sec-butyl alcohol (bp 100°)



$C-\underset{\underset{C}{|}}{\overset{\overset{OH}{|}}{C}}-C$

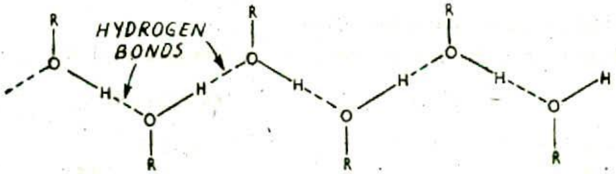
tert-butyl alcohol (bp 80°)

(*c*) Alcohols have much higher boiling points than those of alkanes or most of other compounds of approximately the same molecular weight.

Compound	*Formula*	*Molecular weight*	*Boiling point*
n-Pentane	$CH_3—CH_2—CH_2—CH_2—CH_3$	72	36
Diethyl ether	$CH_3—CH_2—O—CH_2—CH_3$	74	35
n-Propyl chloride	$CH_3—CH_2—CH_2—Cl$	78	46
n-Butyl alcohol	$CH_3—CH_2—CH_2—CH_2—OH$	74	118

Explanation. Let us recall that boiling point is the temperature at which the molecules of a liquid are separated from each other and converted into vapours, so that the vapour pressure becomes equal to the atmospheric pressure. Therefore, naturally the boiling points of alcohols increase with increase of molecular weight as heavier molecules will fly off the liquid surface at a higher temperature.

The fact that alcohols boil at a higher temperature compared to alkanes and other compounds of similar molecular weights is attributed to the hydrogen bonding ability of alcohols. The alcohol molecules are joined to each other through hydrogen bond formation at the polar $\overset{\delta-}{O}—\overset{\delta+}{H}$ group like magnets as shown below.



Although the strengths of the 'electrostatic' hydrogen bonds are much less than those of most conventional chemical bonds, they are still significant (5 to 10 kcal per bond). Thus the boiling points of alcohols are raised compared to those of alkanes and other compounds of comparable molecular weights, due to the extra energy required to break the hydrogen bonds for separating the individual molecules. Alternatively it may be said that association through H-bonds raises the molecular weight and hence reduces volatility, and thus increases the boiling point.

As a rule more compact the molecule, the weaker the forces of attraction between the molecules, since compactness and symmetry mean lower polarity. The molecular compactness and symmetry is maximum in 3° alcohols, less so in 2° alcohol and least in 1° alcohols. Therefore, polarity of O—H bond and hence the hydrogen bonding ability of alcohols is in the order 1° > 2° > 3°. That is why for isomeric alcohols, the primary alcohol boils at a higher temperature than a secondary alcohol ; and the secondary alcohol boils at a higher temperature than the tertiary alcohol.

The melting points of alcohols also increase with rise of molecular weights and for isomeric alcohols they are in the order 3° > 2° > 1°.

Table. Physical Properties of Some Alcohols

Alcohol	*Formula*	*mp °C*	*bp °C*	*Solubility g/100 g H_2O*
Methyl alcohol	CH_3OH	−98	65	∝
Ethyl alcohol	CH_3CH_2OH	−115	78	∝
n-Propyl alcohol	$CH_3CH_2CH_2OH$	−127	97	∝
Isopropyl alcohol	$(CH_3)_2CHCH_2OH$	−81	81	∝
n-Butyl alcohol	$CH_3CH_2CH_2CH_2OH$	−90	118	7·9
Isobutyl alcohol	$(CH_3)_3CHCH_2OH$	−108	108	10·0
sec-Butyl alcohol	$CH_3CH_2CH(OH)CH_3$	−115	100	12·5
tert-Butyl alcohol	$(CH_3)_3COH$	26	83	∝
n-Pentyl alcohol	$CH_3CH_2CH_2CH_2CH_2OH$	−78	138	2·7
Isopentyl alcohol	$(CH_3)_2CHCH_2CH_2OH$	−117	132	2·6
n-Hexyl alcohol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	−52	157	0·59

METHODS OF PREPARATION

Alcohols can be prepared by the following general methods.

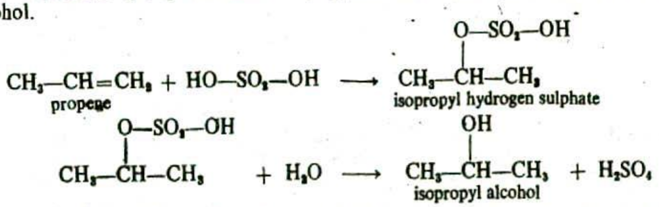
(1) **Hydration of Alkenes.** Alkenes on treatment with concentrated sulphuric acid form alkyl hydrogen sulphates which on subsequent hydrolysis with water or steam yield alcohols. Thus,

$$\underset{\text{ethene}}{CH_2{=}CH_2} + HO{-}SO_2{-}OH \longrightarrow \underset{\text{ethyl hydrogen sulphate}}{CH_3{-}CH_2{-}O{-}SO_2{-}OH}$$

$$CH_3{-}CH_2{-}O{-}SO_2{-}OH + H_2O \longrightarrow \underset{\text{ethyl alcohol}}{CH_3CH_2{-}OH} + H_2SO_4$$

This is the basis for manufacturing ethyl alcohol.

Addition of sulphuric acid to propylene and subsequent hydrolysis gives a secondary alcohol.

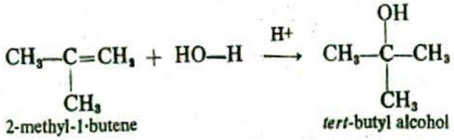


$$\underset{\text{propene}}{CH_3{-}CH{=}CH_2} + HO{-}SO_2{-}OH \longrightarrow \underset{\text{isopropyl hydrogen sulphate}}{CH_3{-}\overset{\overset{\displaystyle O{-}SO_2{-}OH}{|}}{C}H{-}CH_3}$$

$$CH_3{-}\overset{\overset{\displaystyle O{-}SO_2{-}OH}{|}}{C}H{-}CH_3 + H_2O \longrightarrow \underset{\text{isopropyl alcohol}}{CH_3{-}\overset{\overset{\displaystyle OH}{|}}{C}H{-}CH_3} + H_2SO_4$$

Since the addition of sulphuric acid follows the Markovnikov Rule, ethyl alcohol is the only primary alcohol that can be prepared by this method. This method is suitable for the preparation of secondary and tertiary alcohols only.

The above overall procedure involves the addition of water in the presence of sulphuric acid. Alcohols can also be obtained by the direct hydration of alkenes in the presence of an acid. Thus,



$$\underset{\text{2-methyl-1-butene}}{CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2} + HO{-}H \xrightarrow{H+} \underset{\textit{tert}\text{-butyl alcohol}}{CH_3{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CH_3}$$

Alkenes that form secondary and tertiary alcohols by this method, however, can be converted into primary alcohols by hydroboration with diborane ($B_2H_6 = 2BH_3$) followed by oxidation of the alkylborane thus obtained with alkaline hydrogen peroxide.

$$\underset{\text{propene}}{CH_3-CH=CH_2} + H-BH_2 \longrightarrow \underset{\text{n-propylborane}}{CH_3-CH_2-CH_2-BH_2} \xrightarrow{\bar{O}H/H_2O_2} \underset{\text{n-propyl alcohol}}{CH_3-CH_2-CH_2-OH}$$

The hydroboration-oxidation of alkenes follows anti-Markovnikov orientation, and is an extremely valuable process today for producing primary alcohols.

(2) **Hydrolysis of Alkyl halides.** Alkyl halides when treated with dilute aqueous solution of sodium or potassium hydroxide, form alcohols.

$$\underset{\text{alkyl halides}}{R-X} + NaOH \xrightarrow{\text{water}} \underset{\text{alcohol}}{R-OH} + NaX$$

For example,

$$\underset{\text{n-propyl chloride}}{CH_3-CH_2-CH_2-Cl} + NaOH \xrightarrow{\text{water}} \underset{\text{n-propy alcohol}}{CH_3-CH_2-CH_2-OH} + NaCl$$

This method of preparing alcohols is not satisfactory because the alkyl halides may simultaneously undergo dehydrohalogenation to produce alkenes. In order to circumvent this difficulty, mild alkalis like moist silver oxide or aqueous potassium carbonate is used when practicable good yields of alcohols are obtained.

$$R-X + AgOH \longrightarrow R-OH + AgX$$

The order of reactivity of alkyl halides towards hydrolysis is $RI > RBr > RCl$.

Since alkyl halides are relatively unavailable in comparison with alcohols, this method for the preparation of alcohols is used infrequently.

(3) **Hydrolysis of Carboxylic esters.** When heated with a dilute solution of an alkali or a mineral acid, the organic esters are hydrolysed to form the parent carboxylic acids and alcohols.

$$\underset{\text{ester}}{RCOOR} \quad HOH \xrightarrow{\overset{+}{H} \text{ or } \bar{O}H} \underset{\text{carboxylic acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH}$$

Tertiary alkyl halides on hydrolysis with dilute alkalis do not afford good yields of *tert*-alcohols due to their greater tendency to form alkenes by dehydrohalogenation. Satisfactory yields can, however, be obtained by first converting the *tert*-alkyl halide to its ester and then hydrolysing it with dil acid or alkali.

$$\underset{\textit{tert}\text{-alkyl halide}}{R_3C-X} + \underset{\text{silver acetate}}{CH_3COOAg} \longrightarrow \underset{\text{ester}}{R_3C-OOCCH_3} + AgX$$

$$R_3C-OOCCH_3 + HOH \xrightarrow{\overset{+}{H} \text{ or } \bar{O}H} \underset{\textit{tert}\text{-alcohol}}{R_3C-OH} + \underset{\text{acetic acid}}{CH_3COOH}$$

(4) **Reduction of Carbonyl compounds.** Aldehydes, ketones, carboxylic acids and esters when reduced with appropriate reducing agents give alcohols with the same carbon skeleton. The various reducing agents employed are :

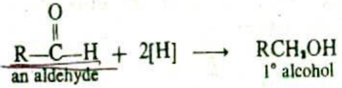
(*a*) *Sodium in alcohol*, can be used for reducing aldehydes, ketones and esters (Bouvealt Blanc Reduction). Such reductions have now been replaced by reductions using metal hydrides.

(*b*) *Hydrogen and metal catalysts* : Such reductions are carried in large scale operations for preparing alcohols from aldehydes and ketones. These may be carried out in inert solvents employing finely divided Ni, Pd or Pt catalysts.

(*c*) *Complex Metal Hydrides* are the best reducing agents for the preparation of alcohols from aldehydes and ketones in the laboratory. Lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) are the most important reducing agents. The expenses of these reagents do not permit their use on large scale. $LiAlH_4$ is used in ether solution to reduce aldehydes, ketones, acids and acid derivatives.

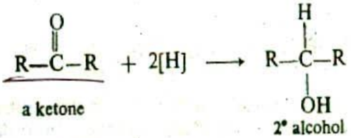
The reductions of the various carbonyl compounds may be illustrated below. The reducing agents which can be employed in each case are shown in brackets.

(*i*) *Reduction of Aldehydes* :



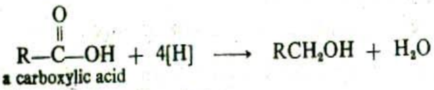
$$\underbrace{R{-}\overset{\overset{O}{\|}}{C}{-}H}_{\text{an aldehyde}} + 2[H] \longrightarrow \underset{1^\circ\text{ alcohol}}{RCH_2OH} \qquad (H_2/Pt\ ;\ NaBH_4 \text{ or } LiAlH_4)$$

(*ii*) *Reduction of Ketones* :



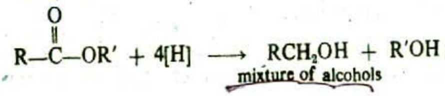
$$\underset{\text{a ketone}}{\underline{R{-}\overset{\overset{O}{\|}}{C}{-}R}} + 2[H] \longrightarrow \underset{2^\circ\text{ alcohol}}{R{-}\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}{-}R} \qquad (H_2/Pt\ ;\ NaBH_4 \text{ or } LiAlH_4)$$

(*iii*) *Reduction of Carboxylic acids* :



$$\underset{\text{a carboxylic acid}}{R{-}\overset{\overset{O}{\|}}{C}{-}OH} + 4[H] \longrightarrow RCH_2OH + H_2O \qquad (B_2H_6\ ;\ LiAlH_4)$$

(*iv*) *Reduction of Carboxylic esters* :



$$R{-}\overset{\overset{O}{\|}}{C}{-}OR' + 4[H] \longrightarrow \underbrace{RCH_2OH + R'OH}_{\text{mixture of alcohols}} \ (LiAlH_4 \text{ or } Na + C_2H_5OH)$$

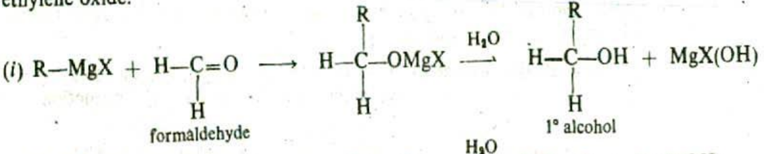
Excellent yields of alcohols are obtained when reductions are carried out with metal hydrides. Here a metal alkoxide is first produced which is then hydrolysed to give the respective alcohol. For example,

$$4\ RCHO + LiAlH_4 \longrightarrow (RCH_2O)_4LiAl \xrightarrow{4H_2O} 4\ RCH_2OH + LiOH + Al(OH)_3$$

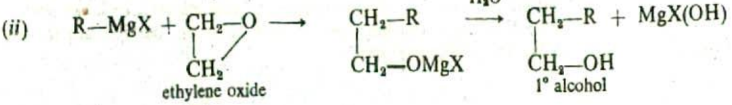
The $LiAlH_4$ reduction of carboxylic acids and esters proceeds by the way of aldehydes. $LiAlH_4$, since it does not reduce a carbon-carbon double bond, is used for the preparation of unsaturated alcohols from unsaturated aldehydes and ketones.

(5) **From Grignard Reagents.** Grignard reagents (RMgX) can be prepared conveniently by the addition of alkyl halides to magnesium suspended in anhydrous ether ($RX + Mg \rightarrow RMgX$). The ethereal solution of RMgX is then treated with aldehydes, ketones and epoxides to form alcohols. As discussed earlier, the initial product so produced in a complex magnesium alkoxide from which the alcohol is liberated by hydrolysis with dilute acid. All the three types of alcohols can be prepared by this method.

(*a*) *Primary Alcohols* are obtained by the action of Grignard reagent with formaldehyde or with ethylene oxide.



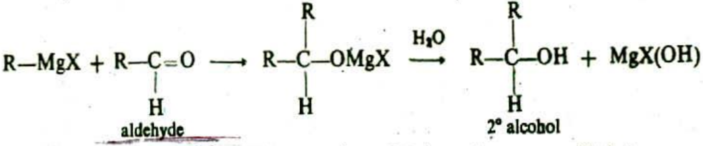
$$(i)\ R{-}MgX + \underset{\text{formaldehyde}}{H{-}\underset{\underset{H}{|}}{C}{=}O} \longrightarrow H{-}\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}{-}OMgX \xrightarrow{H_2O} \underset{1^\circ\text{ alcohol}}{H{-}\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}{-}OH} + MgX(OH)$$



$$(ii)\ R{-}MgX + \underset{\text{ethylene oxide}}{\begin{matrix} CH_2{-}O \\ | \quad / \\ CH_2 \end{matrix}} \longrightarrow \begin{matrix} CH_2{-}R \\ | \\ CH_2{-}OMgX \end{matrix} \xrightarrow{H_2O} \underset{1^\circ\text{ alcohol}}{\begin{matrix} CH_2{-}R \\ | \\ CH_2{-}OH \end{matrix}} + MgX(OH)$$

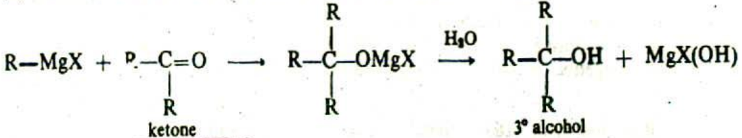
In the second reaction 1° alcohol synthesised has one carbon more than the 1° alcohol produced in reaction (*i*).

(*b*) *Secondary Alcohols* are formed by treating the Grignard reagent with aldehydes other than formaldehyde.



$$R{-}MgX + \underset{\text{aldehyde}}{\underset{H}{\underset{|}{R{-}C{=}O}}} \longrightarrow R{-}\overset{R}{\underset{H}{C}}{-}OMgX \xrightarrow{H_2O} \underset{2^\circ\text{ alcohol}}{R{-}\overset{R}{\underset{H}{C}}{-}OH} + MgX(OH)$$

(*c*) *Tertiary Alcohols* result by the reaction of Grignard reagents with ketones.



$$R{-}MgX + \underset{\text{ketone}}{\underset{R}{\underset{|}{R{-}C{=}O}}} \longrightarrow R{-}\overset{R}{\underset{R}{C}}{-}OMgX \xrightarrow{H_2O} \underset{3^\circ\text{ alcohol}}{R{-}\overset{R}{\underset{R}{C}}{-}OH} + MgX(OH)$$

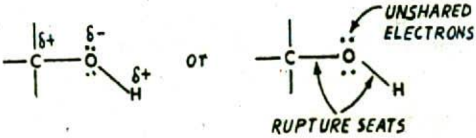
(6) **Fermentation of Carbohydrates.** Alcohols can be prepared by the fermentation of starches and sugars under the influence of suitable microorganisms. Thus,

$$\underset{\text{glucose}}{C_6H_{12}O_6} + \textit{Yeast} \longrightarrow \underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2CO_2\uparrow$$

Similarly n-butyl alcohol is made from starch, $(C_6H_{10}O_5)_n$, by fermentation with *B clostridium acetobutylicum.*

CHEMICAL PROPERTIES

As discussed before, the structure of alcohols can be represented as



Therefore, compared to alkanes which have C—C and C—H nonpolar bonds, alcohols contain ionic C—O and O—H bonds. Moreover, while alkanes have no unshared pairs of electrons, alcohols have them on the oxygen atom. We should, therefore, expect that polar or ionic reagents (NaOH, H_2SO_4, etc.) will be much more successful in interacting with alcohols than with alkanes which possess no 'active centres'. Three types of reactions are shown by alcohols :

(*i*) *Reactions involving rupture of O—H bond*;

(*ii*) *Reactions involving the unshared electrons of oxygen*;

and (*iii*) *Reactions involving rupture of the C—O bond.*

A. REACTIONS INVOLVING O—H BOND

Alcohols show many important reactions in which only the oxygen-hydrogen bond is involved and the carbon-hydrogen bond is left intact.

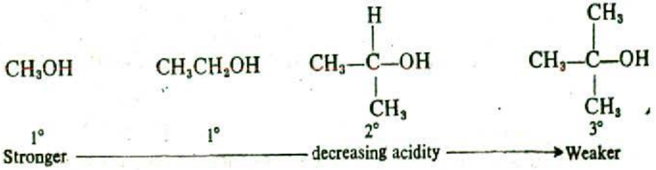
(1) **Acidic character of alcohols ; formation of alkoxides.**

Alcohols behave as weak acids, like water.

$$\underset{\text{alcohol}}{RO{-}H} \rightleftharpoons \underset{\text{alkoxide ion}}{R{-}\bar{O}} + \overset{+}{H}$$

$$\text{e.g.,}\quad \underset{\text{ethyl alcohol}}{CH_3CH_2{-}O{-}H} \rightleftharpoons \underset{\text{ethoxide ion}}{CH_3CH_2{-}\bar{O}} + \overset{+}{H}$$

The acid ionization constant (K_{HA}) of ethyl alcohol is about 10^{-18}, slightly less than that of water which is 10^{-14}. This implies that alcohols are weaker acids than water. The order of acidity of the three types of alcohols is 1°>2°>3°.



$$\underset{1^\circ}{CH_3OH} \qquad \underset{1^\circ}{CH_3CH_2OH} \qquad \underset{2^\circ}{CH_3-\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-OH} \qquad \underset{3^\circ}{CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-OH}$$

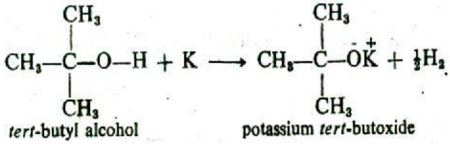
Stronger ——— decreasing acidity ———→ Weaker

It may also be noted from the equilibrium stated on page 386 that alkoxides are strong proton acceptors or bases. The reagents such as alkali metals, metal hydrides, metal amides and Grignard reagents, which are stronger bases than alkoxides, react with alcohols to form metal alkoxides.

(*a*) **Reaction with Alkali metals**. Like water, alcohols react with alkali metals to form alkoxides.

$$HO-H + Na \longrightarrow \underset{\text{sodium hydroxide}}{H\overset{-}{O}\overset{+}{Na}} + \tfrac{1}{2}H_2 \qquad \text{(violent reaction)}$$

$$\underset{\text{methyl alcohol}}{CH_3O-H} + Na \longrightarrow \underset{\text{sodium methoxide}}{CH_3\overset{-}{O}\overset{+}{Na}} + \tfrac{1}{2}H_2 \qquad \text{(moderate reaction)}$$



$$\underset{\textit{tert}\text{-butyl alcohol}}{CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-O-H} + K \longrightarrow \underset{\text{potassium }\textit{tert}\text{-butoxide}}{CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-\overset{-}{O}\overset{+}{K}} + \tfrac{1}{2}H_2 \qquad \text{(extremely slow)}$$

Alkali metal oxides are stronger bases than water. Hence they are not stable in water.

(*b*) **Reaction with Metal hydrides or Metal amides**. Strong bases such as Metal hydrides ($\overset{+}{M}\overset{-}{H}$) or metal amides ($\overset{+}{M}\overset{-}{N}H_2$) react with alcohols to give alkoxides. Thus,

$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} + \underset{\text{sodium hydride}}{\overset{+}{Na}\overset{-}{H}} \longrightarrow \underset{\text{sodium ethoxide}}{CH_3CH_2\overset{-}{O}\overset{+}{Na}} + H_2$$

$$CH_3CH_2-OH + \overset{+}{Na}\overset{-}{N}H_2 \longrightarrow CH_3CH_2\overset{-}{O}\overset{+}{Na} + NH_3$$

(*c*) **Reaction with Grignard reagents**. Alcohols destroy Grignard reagents to form alkoxide salts ($R\overset{-}{O}\overset{+}{Mg}X$).

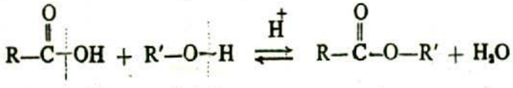
$$\underset{\text{ethyl alcohol}}{CH_3CH_2O-H} + \underset{\text{Grignard reagent}}{R-MgBr} \longrightarrow \underset{\text{alkane}}{R-H} + \underset{\text{ethoxide salt}}{CH_3CH_2\overset{-}{O}\overset{+}{Mg}Br}$$

This reaction is employed for the estimation of lower alcohols present in inert solvents.

Alkoxides are extensively employed for the preparation of ethers in a reaction known as Williamson synthesis.

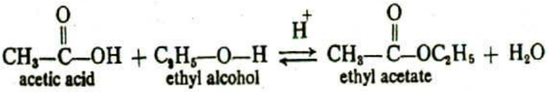
$$\underset{\text{sodium alkoxide}}{R-\overset{-}{O}\overset{+}{Na}} + \underset{\text{alkyl halide}}{R'-X} \longrightarrow \underset{\text{ether}}{R-O-R'} + \overset{+}{Na}\overset{-}{X}$$

(2) **Formation of Esters by reaction with Carboxylic acids.** Alcohols react with carboxylic acids in presence of inorganic acid, say sulphuric acid, as catalyst to form esters. This reaction commonly called **esterification** is accompanied by elimination of a water molecule.



$$\underset{\text{carboxylic acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{alcohol}}{R'-O-H} \overset{\overset{+}{H}}{\rightleftharpoons} \underset{\text{ester}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'} + H_2O$$

e.g.,

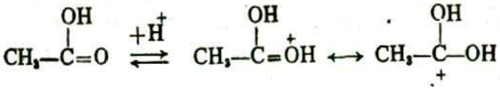


$$\underset{\text{acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{ethyl alcohol}}{C_2H_5-O-H} \overset{\overset{+}{H}}{\rightleftharpoons} \underset{\text{ethyl acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5} + H_2O$$

The esterification reaction is reversible and can be shifted in the forward direction either by using one of the reactants (acid or alcohol) in excess or by removing water as soon as it is formed.

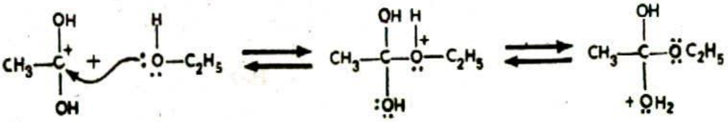
MECHANISM. The mechanism of ester formation as above is illustrated by taking example of the reaction between acetic acid and ethyl alcohol to give ethyl acetate.

(*i*) Protonation of carbonyl oxygen by sulphuric acid and resonance.



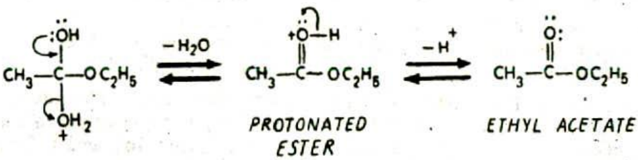
$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=O \overset{+\overset{+}{H}}{\rightleftharpoons} CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=\overset{+}{O}H \longleftrightarrow CH_3-\underset{+}{\overset{\overset{\displaystyle OH}{|}}{C}}-OH$$

(*ii*) Addition of ethyl alcohol by donating electron pair and establishment of equilibrium between the product and its isomer.



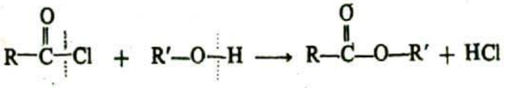
$$CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{\overset{+}{C}}} + :\overset{\overset{\displaystyle H}{|}}{\ddot{O}}-C_2H_5 \rightleftharpoons CH_3-\underset{\underset{\displaystyle :\ddot{O}H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|+}}{\ddot{O}}-C_2H_5 \rightleftharpoons CH_3-\underset{\underset{\displaystyle +\ddot{O}H_2}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-\ddot{O}C_2H_5$$

The elimination of water molecule is accompanied by abstraction of a proton by H_2O resulting in the formation of ethyl acetate.



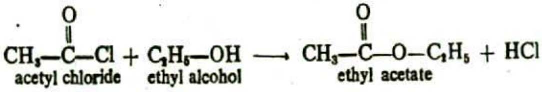
$$CH_3-\underset{\underset{\displaystyle \overset{+}{O}H_2}{|}}{\overset{\overset{\displaystyle :\ddot{O}H}{|}}{C}}-OC_2H_5 \overset{-H_2O}{\rightleftharpoons} \underset{\text{PROTONATED ESTER}}{CH_3-\overset{\overset{\displaystyle +\ddot{O}-H}{\|}}{C}-OC_2H_5} \overset{-\overset{+}{H}}{\rightleftharpoons} \underset{\text{ETHYL ACETATE}}{CH_3-\overset{\overset{\displaystyle \ddot{O}:}{\|}}{C}-OC_2H_5}$$

(3) **Reaction with Acid chlorides.** Alcohols react with acid chlorides to give excellent yields of esters.



$$\underset{\text{acid chloride}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + \underset{\text{alcohol}}{R'-O-H} \longrightarrow \underset{\text{ester}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'} + HCl$$

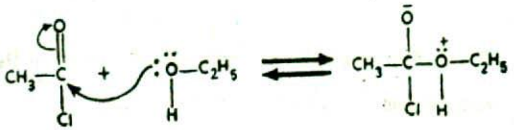
e.g.,



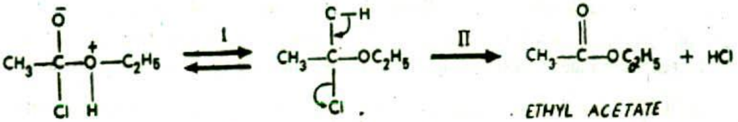
$$\underset{\text{acetyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + \underset{\text{ethyl alcohol}}{C_2H_5-OH} \longrightarrow \underset{\text{ethyl acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5} + HCl$$

The above reaction of alcohols with acetyl chloride is also called acetylation since it involves the replacement of H atom of —OH group by acetyl group (CH_3CO—).

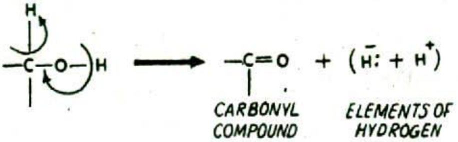
MACHANISM. (*i*) Addition of alcohol to acid chloride by electron-pair donation by O atom.



(*ii*) Intramolecular exchange of a proton (I) with the loss of hydrogen chloride (II) to form ester.



(4) **Oxidation of Alcohols.** The organic chemist often describes oxidation as removal of hydrogen and formation of a new bond between two atoms. In the oxidation of alcohols, hydrogen is removed from the carbon bearing the OH group (α hydrogen) and from the oxygen atom. The new bond formation between carbon and oxygen results in the production of a carbonyl group.

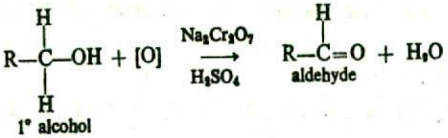


$$(\bar{H}: + \overset{+}{H}) + \underset{\text{from oxidant}}{[O]} \longrightarrow H_2O$$

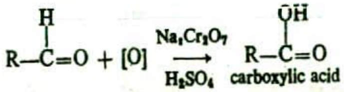
The oxidation involves the breaking of a carbon-hydrogen and an oxygen-hydrogen bond. The elements of hydrogen furnished by the cleavage of the two bonds may either unite to yield hydrogen gas, or in the presence of solutions of oxidising agents form water as shown above.

The most commonly used reagents for the oxidation of alcohols are (*a*) sodium dichromate and sulphuric acid ; (*b*) alkaline potassium permanganate ; (*c*) nitric acid ; and (*d*) heated metal catalysts such as silver and copper. The products of oxidation depend on the type of alcohol under examination as also on the nature of oxidising agents employed.

Oxidation of 1° alcohols. A primary alcohol when treated with sodium dichromate and sulphuric acid is first oxidised to an aldehyde. The aldehyde still possesses an α hydrogen and is readily oxidised to give a carboxylic acid. Both the aldehyde and acid so formed contain the same number of carbon atoms as the parent alcohol.

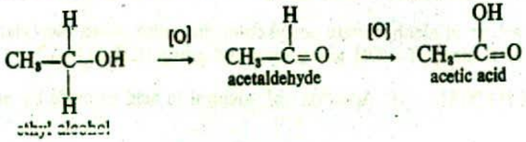


$$\underset{\text{1° alcohol}}{R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH} + [O] \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} \underset{\text{aldehyde}}{R-\overset{\overset{H}{|}}{C}=O} + H_2O$$



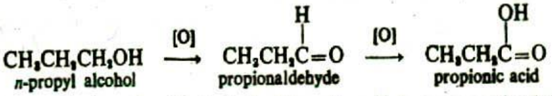
$$R-\overset{\overset{H}{|}}{C}=O + [O] \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} \underset{\text{carboxylic acid}}{R-\overset{\overset{OH}{|}}{C}=O}$$

Thus ethyl alcohol is oxidised to acetaldehyde and then acetic acid.



$$\underset{\text{ethyl alcohol}}{CH_3-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH} \xrightarrow{[O]} \underset{\text{acetaldehyde}}{CH_3-\overset{\overset{H}{|}}{C}=O} \xrightarrow{[O]} \underset{\text{acetic acid}}{CH_3-\overset{\overset{OH}{|}}{C}=O}$$

Similarly n-propyl alcohol yields propionaldehyde and finally propionic acid.



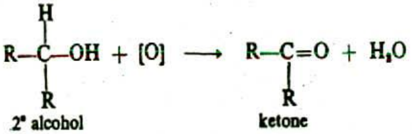
$$\underset{n\text{-propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow{[O]} \underset{\text{propionaldehyde}}{CH_3CH_2\overset{H}{\overset{|}{C}}=O} \xrightarrow{[O]} \underset{\text{propionic acid}}{CH_3CH_2\overset{OH}{\overset{|}{C}}=O}$$

The oxidation of a 1° alcohol with sodium dichromate and sulphuric acid can be stopped at the aldehyde stage by removing the aldehyde as soon as it is produced in the reaction mixture. Since the lower aldehydes (C_1 to C_4) have much lower boiling points than the parent alcohols, they can be distilled continuously from the mixture.

However, oxidation of a 1° alcohol with potassium permanganate converts it all the way to carboxylic acid.

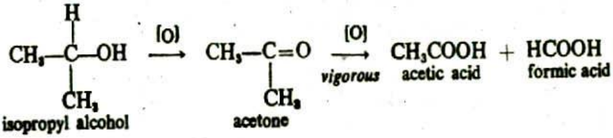
$$RCH_2OH \xrightarrow{KMnO_4} RCOOH$$

Oxidation of 2° alcohols. A secondry alcohol upon oxidation with sodium dichromate and sulphuric acid forms a ketone with the same number of carbon atoms as the original alcohol.

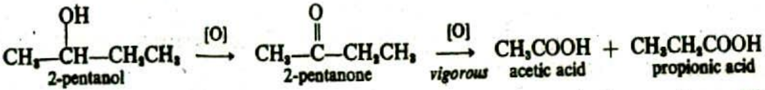


$$\underset{2^\circ\text{ alcohol}}{R-\overset{H}{\overset{|}{\underset{R}{\underset{|}{C}}}}-OH} + [O] \longrightarrow \underset{\text{ketone}}{R-\underset{R}{\underset{|}{C}}=O} + H_2O$$

A ketone has no oxidisable α hydrogen atom and ordinarily it is not expected to undergo further oxidation. However, on vigorous oxidation the carbon skeleton of the ketone is broken to yield a mixture of carboxylic acids, each containing fewer carbon atoms than the original alcohol. Thus oxidation of 2° alcohol upon vigorous oxidation first gives a ketone which is then degraded to form a mixture of two lower carboxylic acids. Thus,

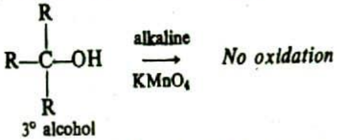


$$\underset{\text{isopropyl alcohol}}{CH_3-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH} \xrightarrow{[O]} \underset{\text{acetone}}{CH_3-\underset{CH_3}{\underset{|}{C}}=O} \xrightarrow[\textit{vigorous}]{[O]} \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{formic acid}}{HCOOH}$$



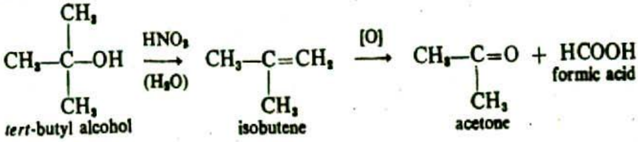
$$\underset{\text{2-pentanol}}{CH_3-\overset{OH}{\overset{|}{C}}H-CH_2CH_3} \xrightarrow{[O]} \underset{\text{2-pentanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3} \xrightarrow[\textit{vigorous}]{[O]} \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{propionic acid}}{CH_3CH_2COOH}$$

Oxidation of 3° alcohols. Tertiary alcohols do not have α hydrogen atoms. Thus in order to oxidise a tertiary alcohol, a carbon-carbon bond must be broken. For this reason, tertiary alcohols are resistant to oxidation in alkaline solution.



$$\underset{3^\circ\text{ alcohol}}{R-\overset{R}{\overset{|}{\underset{R}{\underset{|}{C}}}}-OH} \xrightarrow[KMnO_4]{\text{alkaline}} \textit{No oxidation}$$

However, on drastic oxidation with acid oxidising agents, a tertiary alcohol is degraded to give a mixture of ketone and carboxylic acid, each containing fewer carbon atoms than the original alcohol. Thus the oxidation of *tert*-butyl alcohol with nitric acid to form actone and formic acid. The first step in such oxidation probably involves dehydration of alcohol to alkene which is then oxidised.



$$\underset{tert\text{-butyl alcohol}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH} \xrightarrow[(H_2O)]{HNO_3} \underset{\text{isobutene}}{CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2} \xrightarrow{[O]} \underset{\text{acetone}}{CH_3-\underset{CH_3}{\underset{|}{C}}=O} + \underset{\text{formic acid}}{HCOOH}$$

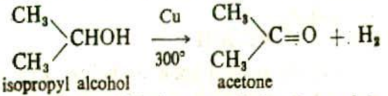
Actually formic acid is further oxidised to give CO_2 and H_2O. Also, the ketone may undergo further oxidation to form a mixture of simpler acids.

Catalytic Dehydrogenation. Alcohols are oxidised by straightaway removal of hydrogen atoms as H_2 (or dehydrogenation etc.) in the presence of a heated metal catalyst (Ag or Cu). Thus when vapours of the three types of alcohols are passed over reduced copper at 300°, primary, secondary and tertiary alcohols behave differently.

(*a*) *A 1° alcohol is dehydrogenated to form an aldehyde.*

$$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[300^\circ]{Cu} \underset{\text{acetaldeyde}}{CH_3CHO} + H_2$$

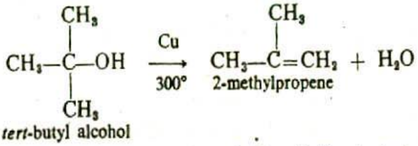
(*b*) *A 2° alcohol is dehydrogenated to form a ketone.*



$$(CH_3)_2CHOH \xrightarrow[300^\circ]{Cu} (CH_3)_2C{=}O + H_2$$

isopropyl alcohol acetone

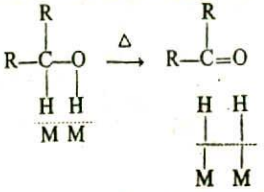
(*c*) *A 3° alcohol is not dehydrogenated but instead is dehydrated to an alkane upon heating.*



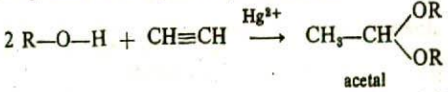
$$CH_3{-}C(CH_3)_2{-}OH \xrightarrow[300^\circ]{Cu} CH_3{-}C(CH_3){=}CH_2 + H_2O$$

tert-butyl alcohol 2-methylpropene

The mechanism of dehydrogenation of 1° and 2° alcohols may be visualised as the reverse of hydrogenation which we discussed under alkenes. The metal (M) can break the C—H and O—H bonds, adsorb the H atoms and then given up as molecular hydrogen.



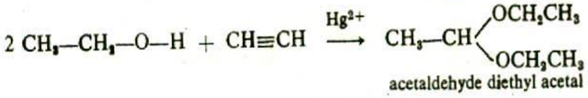
(5) **Reaction with acetylene to form Acetals.** Alcohols combine with acetylene in the presence of mercury compounds as catalysts to yield acetals.



$$2\,R{-}O{-}H + CH{\equiv}CH \xrightarrow{Hg^{2+}} CH_3{-}CH(OR)_2$$

acetal

e.g.,

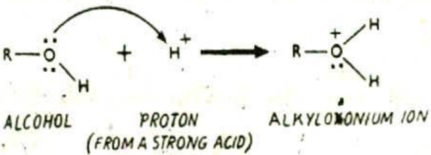


$$2\,CH_3{-}CH_2{-}O{-}H + CH{\equiv}CH \xrightarrow{Hg^{2+}} CH_3{-}CH(OCH_2CH_3)_2$$

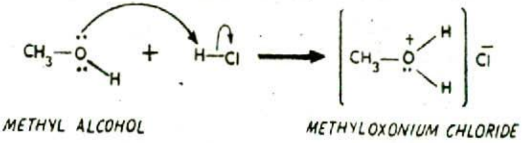
acetaldehyde diethyl acetal

B. REACTIONS INVOLVING UNSHARED PAIRS OF ELECTRONS

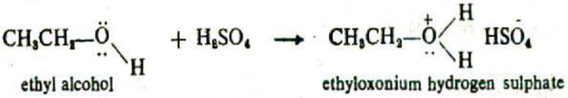
(6) **Behaviour as bases ; formation of alkyioxonium salts.** Because the oxygen atom of the hydroxyl group has two lone pairs of electrons, it is possible for alcohols to accept a proton (H^+) from a mineral acid. In other words alcohols behave as bases.



For example, methyloxonium chloride is formed by passing HCl gas through methyl alcohol.



Similarly, ethyloxonium hydrogen sulphate is obtained by treating ethyl alcohol with concentrated sulphuric acid.



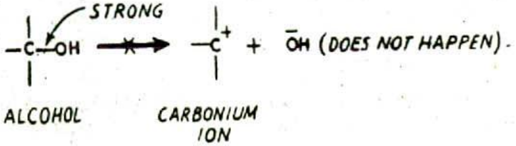
$$CH_3CH_2-\ddot{O}-H + H_2SO_4 \rightarrow CH_3CH_2-\overset{+}{\ddot{O}}H_2 \; H\bar{S}O_4$$

ethyl alcohol — ethyloxonium hydrogen sulphate

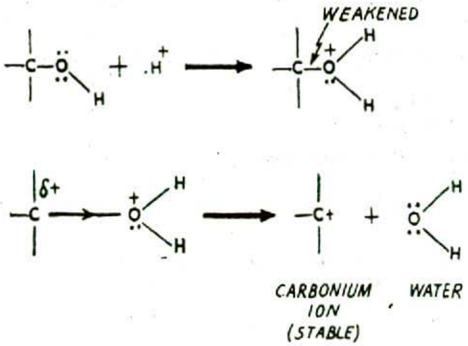
Most alkyloxonium salts exist only in solution and cannot be isolated as pure compounds.

C. REACTIONS INVOLVING RUPTURE OF C—O BOND

While discussing the structure of alcohols, we noted that the $sp^3—sp^3$ bond formed between carbon and oxygen (C—OH) is strong. Therefore, alcohols do not ionise as follows :



However, interaction with a strong acid puts a positive charge on the oxygen atom of OH group and the C—O bond is considerably weakened. This is so because the positively charged oxygen attracts the pair of electrons shared with the carbinol carbon much more strongly toward the oxygen than before. Thus the C—O bond in alcohols can be ruptured under favourable conditions : (*i*) in the presence of a strong acid, (*ii*) among 3° alcohols which give the most stable carbonium ions, and (*iii*) in the presence of nucleophiles which are attracted by the developing positive charge on the carbonium carbon.



For the reasons stated above alcohols give two types of reactions :

(*a*) Nucleophilic substitution reactions where OH is replaced by halogens ; and

(*b*) Elimination reactions whereby an alcohol is converted to alkene by kicking out a water molecule.

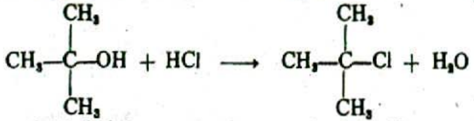
(7) **Formation of Alkyl halides** : (*a*) **Reaction with Hydrogen halides**. Alcohols can be converted to alkyl halides by reaction with hydrogen halides (HX).

$$\underset{\text{alcohol}}{R\text{—}OH} + H\text{—}X \longrightarrow \underset{\text{alkyl halide}}{R\text{—}X} + H_2O$$

where X=Cl, Br, I.

For example,

$$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} + HBr \longrightarrow \underset{\text{ethyl bromide}}{CH_3CH_2Br} + H_2O$$



$$CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}OH + HCl \longrightarrow CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}Cl + H_2O$$

tert-butyl alcohol *tert*-butyl chloride

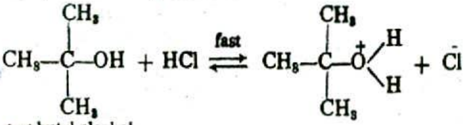
3° alcohols in general react rapidly with halogen acids ; the 2° alcohols are slower and the 1° alcohols are slower still. The order of reactivity of alcohols is the same as the order of stability of the corresponding carbonium ions. The order of reactivity of hydrogen halides is in the order HI > HBr > HCl.

A solution of zinc chloride in conc hydrochloric acid (*Lucas Reagent*) is widely used, in fact, to differentiate between the lower 1°, 2° and 3° alcohols. 3° alcohols react at once to give an oily layer of alkyl chloride at room temperature ; 2° alcohol do so in several minutes ; whereas 1° alcohols form chlorides only on heating.

MECHANISM. The nucleophilic substitution of OH by halogen in primary alcohols follows the S_N2 mechanism, while in secondary and tertiary alcohols it proceeds by S_N1 mechanism.

S_N1 *mechanism for 3° and 2° alcohols* proceeds by the following three steps.

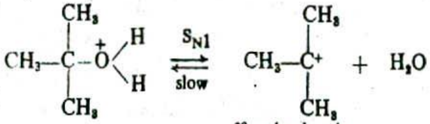
(*i*) The alcohol is protonated by the acid.



$$CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}OH + HCl \overset{\text{fast}}{\rightleftharpoons} CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}\overset{+}{O}\begin{matrix}H\\H\end{matrix} + \bar{Cl}$$

tert-butyl alcohol

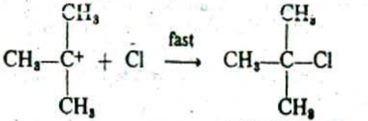
(*ii*) The C—O bond is now much weaker and ruptures to form a carbonium ion.



$$CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}\overset{+}{O}\begin{matrix}H\\H\end{matrix} \underset{\text{slow}}{\overset{S_N1}{\rightleftharpoons}} CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C^+}} + H_2O$$

3° carbonium ion
(*stable*)

(*iii*) The carbonium ion combines with a halide ion.



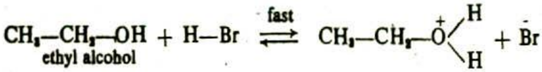
$$CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C^+}} + \bar{Cl} \xrightarrow{\text{fast}} CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}Cl$$

tert-butyl chloride

The slow step (*ii*) is rate determining and since it involves a change in one molecule only, $(CH_3)_3C\text{—}\overset{+}{O}H_2$, the entire reaction is called unimolecular or S_N1 process.

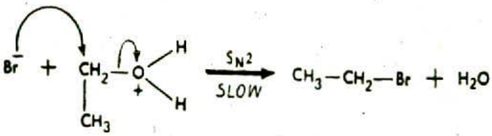
S_N2 *mechanism for 1° alcohols* takes place by two steps.

(*i*) **The alcohol is protonated by the acid.**



$$\underset{\text{ethyl alcohol}}{CH_3{-}CH_2{-}OH} + H{-}Br \overset{\text{fast}}{\rightleftharpoons} CH_3{-}CH_2{-}\overset{+}{O}H_2 + \bar{Br}$$

(*ii*) **The nucleophile $\bar{Br}$ attacks the carbon holding the oxygen.**

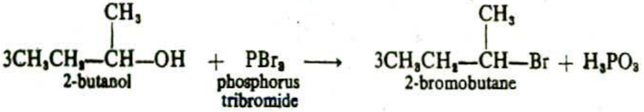


The step (*ii*) is slow and is rate determining. Because two particles ($\bar{Br}$ and $CH_3CH_2\overset{+}{O}H_2$) participate in this step, the overall process is bimolecular or S_N2.

(*b*) **Reaction with Phosphorus halides.** Alcohols can be converted to alkyl iodides by reacting them with phosphorus and iodine *i.e.*, PI_3 formed *in situ*.

$$\underset{\text{methyl alcohol}}{6CH_3OH} + 3I_2 + 2P \longrightarrow \underset{\text{methyl iodide}}{6CH_3{-}I} + 2H_3PO_3$$

Alkyl bromides and alkyl chlorides are obtained from alcohols when they are reacted upon with PBr_3 and PCl_3 or PCl_5 respectively.

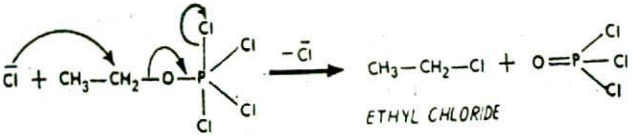


$$\underset{\text{2-butanol}}{3CH_3CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H{-}OH} + \underset{\text{phosphorus tribromide}}{PBr_3} \longrightarrow \underset{\text{2-bromobutane}}{3CH_3CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H{-}Br} + H_3PO_3$$

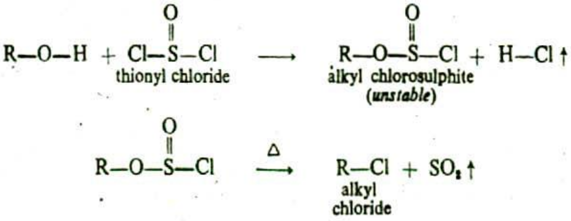
$$\underset{\text{ethyl alcohol}}{CH_3{-}CH_2{-}OH} + \underset{\text{phosphorus pentachloride}}{PCl_5} \longrightarrow \underset{\text{ethyl chloride}}{CH_3{-}CH_2{-}Cl} + POCl_3 + HCl$$

MECHANISM. The ester of the type $R{-}OPX_2$ or $R{-}OPX_4$ are first formed and these subsequently react with the halide ion $\bar{X}$.

$$CH_3{-}CH_2{-}OH + PCl_5 \longrightarrow \underset{\textit{intermediate}}{CH_3{-}CH_2{-}O{-}PCl_4} + \bar{Cl} + \overset{+}{H}$$



(*c*) **Reaction with Thionyl chloride.** A useful reagent for converting alcohols to alkyl chlorides is thionyl chloride, $SOCl_2$. The reaction proceeds through the formation of an intermediate alkyl chlorosulphite which eliminates SO_2 spontaneously, or upon heating, to yield the alkyl chloride free from any impurities.



$$R{-}O{-}H + \underset{\text{thionyl chloride}}{Cl{-}\overset{\displaystyle O}{\overset{\|}{S}}{-}Cl} \longrightarrow \underset{\substack{\text{alkyl chlorosulphite}\\ (\textit{unstable})}}{R{-}O{-}\overset{\displaystyle O}{\overset{\|}{S}}{-}Cl} + H{-}Cl\uparrow$$

$$R{-}O{-}\overset{\displaystyle O}{\overset{\|}{S}}{-}Cl \xrightarrow{\Delta} \underset{\substack{\text{alkyl}\\ \text{chloride}}}{R{-}Cl} + SO_2\uparrow$$

For example,

$$\underset{\text{ethyl alcohol}}{CH_3{-}CH_2{-}OH} + SOCl_2 \longrightarrow \underset{\text{ethyl chloride}}{CH_3{-}CH_2{-}Cl} + SO_2 + HCl$$

(8) **Formation of Alkyl nitrates and Alkyl hydrogen sulphates** : Alcohols, much like the reaction with HCl, react with nitric acid and sulphuric acid when the OH is replaced by NO_2 and HSO_4 respectively.

(*a*) $$\underset{\text{ethyl alcohol}}{CH_3{-}CH_2{-}OH} + \underset{\text{nitric acid}}{HO{-}NO_2} \longrightarrow \underset{\text{ethyl nitrate}}{CH_3{-}CH_2{-}O{-}NO_2} + H_2O$$

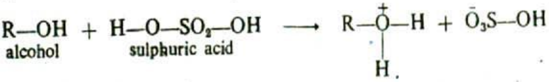
(*b*) $$CH_3{-}CH_2{-}OH + \underset{\text{sulphuric acid}}{HO{-}SO_2OH} \longrightarrow \underset{\text{ethyl hydrogen sulphate}}{CH_3{-}CH_2{-}O{-}SO_2OH} + H_2O$$

$$\underset{\text{second molecule}}{CH_3{-}CH_2{-}OH} + CH_3{-}CH_2{-}O{-}SO_2OH \longrightarrow \underset{\text{diethyl sulphate}}{CH_3{-}CH_2{-}O{-}SO_2{-}O{-}CH_2{-}CH_3} + H_2O$$

Thus ethyl alcohol reacts with sulphuric acid to form ethyl hydrogen sulphate which reacts with another molecule of alcohol (if present in excess), yielding diethyl sulphate.

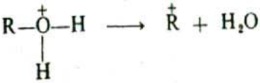
MECHANISM :

(*i*) Protonation of alcohol by sulphuric acid.



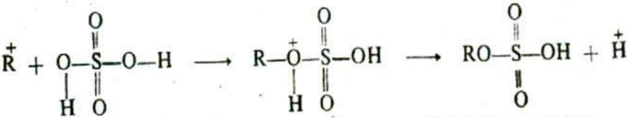
$$\underset{\text{alcohol}}{R{-}OH} + \underset{\text{sulphuric acid}}{H{-}O{-}SO_2{-}OH} \longrightarrow R{-}\underset{\substack{|\\ H}}{\overset{+}{O}}{-}H + \overset{-}{O}_3S{-}OH$$

(*ii*) Formation of the carbonium ion.



$$R{-}\underset{\substack{|\\ H}}{\overset{+}{O}}{-}H \longrightarrow \overset{+}{R} + H_2O$$

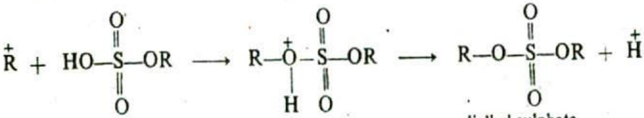
(*iii*) Reaction of carbonium ion with a sulphuric acid molecule.



$$\overset{+}{R} + \underset{\substack{|\\ H}}{O}{-}\overset{\substack{O\\ \|}}{\underset{\substack{\|\\ O}}{S}}{-}O{-}H \longrightarrow R{-}\underset{\substack{|\\ H}}{\overset{+}{O}}{-}\overset{\substack{O\\ \|}}{\underset{\substack{\|\\ O}}{S}}{-}OH \longrightarrow RO{-}\overset{\substack{O\\ \|}}{\underset{\substack{\|\\ O}}{S}}{-}OH + \overset{+}{H}$$

alkyl hydrogen sulphate

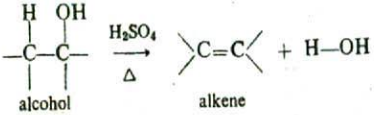
(*iv*) Reaction of a second carbonium ion with alkyl hydrogen sulphate.



$$\overset{+}{R} + HO{-}\overset{\substack{O\\ \|}}{\underset{\substack{\|\\ O}}{S}}{-}OR \longrightarrow R{-}\underset{\substack{|\\ H}}{\overset{+}{O}}{-}\overset{\substack{O\\ \|}}{\underset{\substack{\|\\ O}}{S}}{-}OR \longrightarrow R{-}O{-}\overset{\substack{O\\ \|}}{\underset{\substack{\|\\ O}}{S}}{-}OR + \overset{+}{H}$$

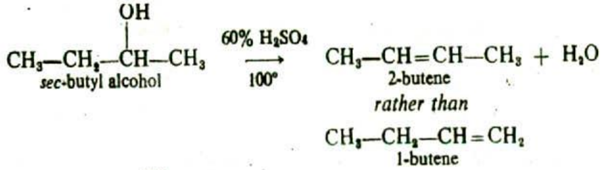
dialkyl sulphate

(9) **Dehydration; Formation of alkenes**. Alcohols which possess at least one H atom on the carbon adjacent to the one holding the OH group, undergo dehydration (elimination of water) when heated with concentrated sulphuric acid.



Examples :

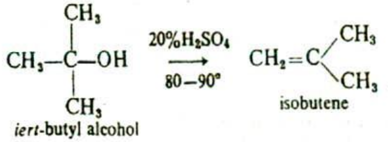
$$\underset{\text{ethyl alcohol}}{CH_3{-}CH_2{-}OH} \xrightarrow[170-180^\circ]{95\%\ H_2SO_4} \underset{\text{ethene}}{CH_2{=}CH_2} + H_2O$$



$$\underset{\textit{sec}\text{-butyl alcohol}}{CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3} \xrightarrow[100^\circ]{60\%\ H_2SO_4} \underset{\text{2-butene}}{CH_3-CH{=}CH-CH_3} + H_2O$$

rather than

$$\underset{\text{1-butene}}{CH_3-CH_2-CH{=}CH_2}$$

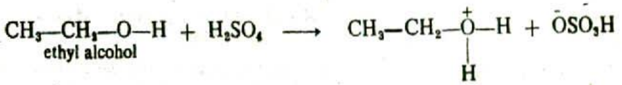


$$\underset{\textit{tert}\text{-butyl alcohol}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH} \xrightarrow[80-90^\circ]{20\%H_2SO_4} \underset{\text{isobutene}}{CH_2{=}C(CH_3)_2}$$

As clear from the sulphuric acid concentration and the temperature required in the above reactions, 3° alcohols dehydrate more readily than 2° alcohols, and 2° alcohols dehydrate more readily than 1° alcohols. Furthermore, whenever it is possible for more than one alkene to form, the principal product is the more substituted alkene at the C=C system. This is illustrated above by the example of dehydration of *sec*-butyl alcohol which forms predominantly 2-butene rather than 1-butene.

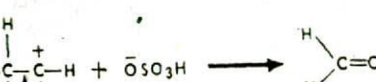
MECHANISM. The mechanism of dehydration of alcohols follows the following pathway which is illustrated by taking example of ethyl alcohol.

Step 1. Sulphuric acid protonates the OH of alcohol.



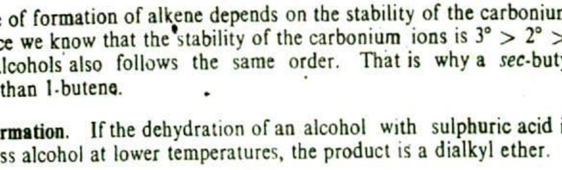
$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-O-H} + H_2SO_4 \longrightarrow CH_3-CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{+}{O}}-H + \overset{-}{O}SO_3H$$

Step 2. A water molecule is eliminated to give a stable carbonium ion.



$$CH_3-CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{+}{O}}-H \longrightarrow \underset{\text{carbonium ion}}{CH_3-\overset{+}{C}H_2}$$

Step 3. A proton is removed from the carbonium ion to yield a more stable alkene. Here $\overset{-}{O}SO_3H$ obtained from step (1) acts as the proton acceptor and pulls it out from the carbonium ion.



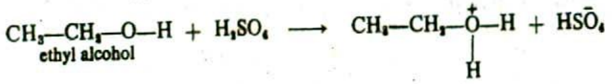
The ease of formation of alkene depends on the stability of the carbonium ion produced in step (2). Since we know that the stability of the carbonium ions is 3° > 2° > 1°, the ease of dehydration of alcohols also follows the same order. That is why a *sec*-butyl alcohol gives 2-butene rather than 1-butene.

Ether formation. If the dehydration of an alcohol with sulphuric acid is carried in the presence of excess alcohol at lower temperatures, the product is a dialkyl ether. Thus,

$$\underset{\text{ethyl alcohol}}{2CH_3-CH_2-OH} \xrightarrow[\text{conc } H_2SO_4]{130^\circ} \underset{\text{diethyl ether}}{CH_3CH_2-O-CH_2CH_3} + H_2O$$

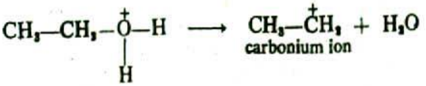
Here two molecules of alcohol eliminate one molecule of water.

MECHANISM. (*i*) Protonation of alcohol by sulphuric acid.



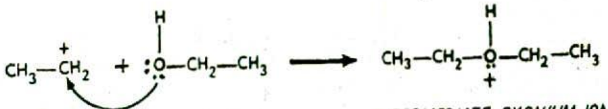
$$\underset{\text{ethyl alcohol}}{CH_3{-}CH_2{-}O{-}H} + H_2SO_4 \longrightarrow CH_3{-}CH_2{-}\underset{\displaystyle H}{\overset{+}{O}}{-}H + H\bar{S}O_4$$

(*ii*) Removal of a water molecule to form carbonium ion.



$$CH_3{-}CH_2{-}\underset{\displaystyle H}{\overset{+}{O}}{-}H \longrightarrow \underset{\text{carbonium ion}}{CH_3{-}\overset{+}{C}H_2} + H_2O$$

(*iii*) Carbonium ion attacks a second molecule of alcohol to give intermediate oxonium ion.

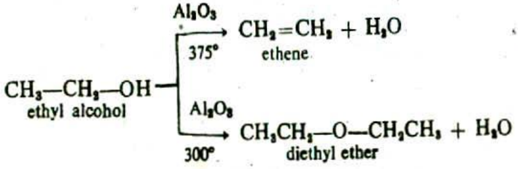


INTERMEDIATE OXONIUM ION

(*iv*) Abstraction of a proton by $H\bar{S}O_4$.

$$CH_3CH_2{-}\underset{+}{\overset{\displaystyle H}{O}}{-}CH_2CH_3 + H\bar{S}O_4 \longrightarrow \underset{\text{diethyl ether}}{CH_3CH_2{-}O{-}CH_2CH_3} + H_2SO_4$$

Most alcohols will also dehydrate at fairly high temperatures to give alkenes or ethers in the presence of a solid catalyst as aluminium oxide (Al_2O_3). For example,



TESTS FOR OH GROUP

There are three tests which may be applied to detect the presence of a hydroxyl group in an unknown organic compound. For these tests, take the liquid substance or a solution of the solid substance in an inert solvent such as dry ether or benzene.

(1) Add to it small pieces of Sodium metal. If bubbles of hydrogen are given off, the compound contains an OH group.

$$2ROH + 2Na \longrightarrow 2RONa + H_2$$

(2) Add to it Phosphorus pentachloride. If the mixture becomes warm with evolution of hydrogen chloride gas, the given substance is hydroxy compound.

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl\uparrow$$

(3) Add acetyl chloride or benzoyl chloride to the substance. The separation of an oily layer of the ester and evolution of HCl gas indicates the presence of an OH group. It may be noted that if the substance was taken in an organic solvent the oily ester may dissolve in it and thus limiting the test to the evolution of HCl gas only.

HOW TO DISTINGUISH BETWEEN 1°, 2° AND 3° ALCOHOLS

The following tests are applied for distinguishing primary, secondary and tertiary alcohols from each other.

(1) **Oxidation Test**. The mode of oxidation of three types of alcohols is characteristic of each type.

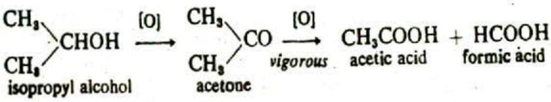
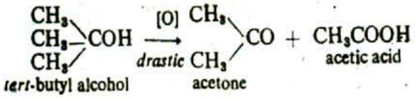
(*a*) A 1° alcohol on oxidation gives an aldehyde, and this on oxidation gives a carboxylic acid containing the same number of carbon atoms as the original alcohol.

(*b*) A 2° alcohol on oxidation first gives a ketone with the same number of carbon atoms as the original alcohol, and the ketones on prolonged action with oxidising agents yields mixture of acids, each containing fewer carbons than the original alcohol.

(*c*) A 3° alcohol is resistant to oxidation in alkaline solution, but is readily oxidised by acid oxidising agents (dil HNO_3) to form a mixture of ketone and acid, each containing fewer carbons than the original alcohol.

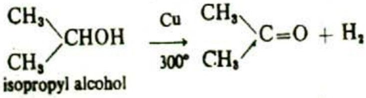
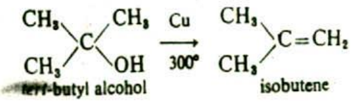
Thus the identification of products of oxidation of a given alcohol indicates whether it was 1°, 2° or 3°.

Table. Oxidation of Alcohols

Type of Alcohol	*Oxidation Steps*	*Product/Products*
1°	$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{acetic acid}}{CH_3COOH}$	*Acid* : contains same number of C atoms as original alcohol.
2°	 $\underset{\text{isopropyl alcohol}}{(CH_3)_2CHOH} \xrightarrow{[O]} \underset{\text{acetone}}{(CH_3)_2CO} \xrightarrow[\text{vigorous}]{[O]} \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{formic acid}}{HCOOH}$	*Mixture of acids* . each contains fewer C atoms than original alcohol.
3°	 $\underset{\text{tert-butyl alcohol}}{(CH_3)_3COH} \xrightarrow[\text{drastic}]{[O]} \underset{\text{acetone}}{(CH_3)_2CO} + \underset{\text{acetic acid}}{CH_3COOH}$	*Mixture of a ketone and acid* : each contains fewer carbons than original alcohol.

(2) **Action of hot Reduced Copper**. The vapours of the given alcohol are passed over reduced copper catalyst at 300° and the product obtained is identified. A 1° alcohol dehydrogenates to give an aldehyde, while a 2° alcohol dehydrogenates to form a ketone. A 3° alcohol under the same conditions dehydrates to yield an alkene.

Table. Action of hot Reduced Copper

Type of alcohol	*Alcohol vapour passed over Cu at 300°*	*Product*
1°	$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[300°]{Cu} \underset{\text{acetaldehyde}}{CH_3CHO} + H_2$	aldehyde
2°	 $\underset{\text{isopropyl alcohol}}{(CH_3)_2CHOH} \xrightarrow[300°]{Cu} (CH_3)_2C{=}O + H_2$	ketone
3	 $\underset{\text{tert-butyl alcohol}}{(CH_3)_3C{-}OH} \xrightarrow[300°]{Cu} \underset{\text{isobutene}}{(CH_3)_2C{=}CH_2}$	alkene

(3) **Victor Meyer Test**. This test is based on the different behaviour of the nitroalkanes obtained from 1°, 2° and 3° alcohols. It is carried by the following steps.

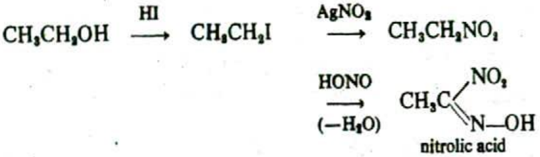
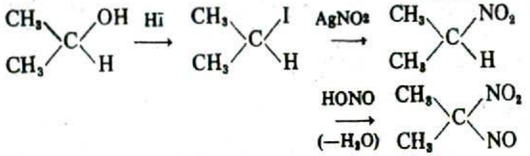
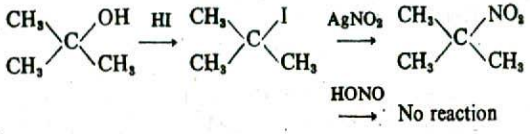
(*i*) *The given alcohol is converted to iodide by treatment with cold hydrogen iodide or red phosphorus and iodine.*

(*ii*) *The iodide is then treated with silver nitrite so as to get the corresponding nitroalkane.*

(*iii*) *The nitroalkane is finally treated with nitrous acid* ($NaNO_2$+*dil* H_2SO_4) *and the solution is made alkaline.*

If the blood red colour is produced in this way the original alcohol is primary ; if a blue colour is produced, the alcohol is secondary ; and if there is no colour obtained, it is a tertiary alcohol.

Table. Victor Meyer Test for Alcohols

Type of alcohol	*Various steps involved*	*Colour produced when the final solution alkalified*
1°		Blood red
2°		Blue
3°		Colourless

(4) **Lucas Test**. This test for distinguishing between the three types of alcohols is based on the fact that the ease of formation of chloride follows the order 3° alcohol >2° alcohol >1° alcohol. When the unknown alcohol is heated with concentrated hydrochloric acid containing anhydrous zinc chloride, the rate of formation of the chloride from a 1°, 2° and 3° alcohol is so well marked that it gives a clear indication of the type of alcohol.

$$\underset{\text{alcohol}}{ROH} + HCl \xrightarrow{ZnCl_2} \underset{\substack{\text{alkyl chloride}\\ (\textit{insoluble})}}{RCl} + H_2O \qquad (\text{Rate}: 3^\circ > 2^\circ > 1^\circ)$$

This test known as *Lucas Test* is carried as follows.

A small quantity of the given alcohol is added to concentrated hydrochloric acid containing anhydrous zinc chloride (1 mole : 1 mole) at room temperature (26—27°). When the mixture is shaken, the insoluble alkyl chloride that commences to form produces a cloud in the test-solution. The time taken for the appearance of cloudiness which markes the formation of the chloride is noted :

a 3° alcohol produces cloudiness immediately ;

a 2° alcohol produces cloudiness within five minutes ;

a 1° alcohol shows no cloudiness at room temperature and it does so only upon heating.

(5) **Ester Test**. Alcohols react with carboxylic acids to form esters. The ease of formation of ester follows the order 1°alcohol > 2°alcohol > 3°alcohol. The difference in the rate of esterification is so marked that it shows the type of alcohol under examination.

The unknown alcohol is heated for one hour at 154° in a sealed tube with an equivalent quantity of acetic acid. The ester so formed is isolated and the percentage of alcohol converted into ester calculated. Approximately 47 per cent of 1°, 22 per cent of 2°, and 1·5 per cent of 3° alcohol is changed into the ester under these conditions.

(6) **Dehydration Test**. When excess of the given alcohol is treated with concentrated sulphuric acid,

a 1° alcohol gives ether very readily :
a 2° alcohol does not give ether readily ;
a 3° alcohol does not give ether at all, but alkene.

INDIVIDUAL MEMBERS

METHYL ALCOHOL, *Methanol*, CH_3OH

Methyl alcohol is the first member of the homologous series of saturated monohydric alcohols. It occurs in nature in the form of esters. *Oil of Winter green* is known to contain methyl salicylate. Since it was formerly prepared from wood by destructive distillation, methyl alcohol is also named as *Wood Spirit* or *Wood Naphtha*.

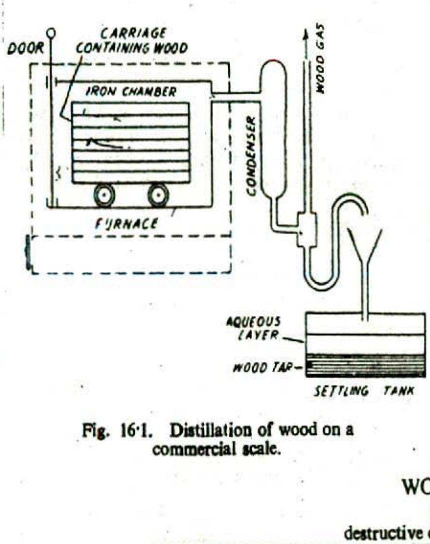
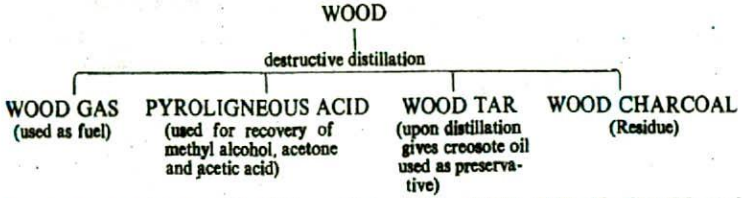


Fig. 16·1. Distillation of wood on a commercial scale.

MANUFACTURE. Methyl alcohol can be prepared by any of the general methods described before. For the large scale production of methyl alcohol, the following three methods are commonly employed.

(*i*) *Destructive distillation of Wood*,
(*ii*) *Synthesis from Water gas*, and
(*iii*) *From Natural gas.*

1. Destructive distillation of Wood. Until recently this was the only source for the manufacture of methyl alcohol. When wood is heated to about 400° in iron retorts in the absence of air (destructive distillation), the products obtained are :



(*i*) *A gaseous mixture* or **Wood Gas**, which consists of CH_4, C_2H_6, H_2, CO, CO_2 and N_2. It is used as a fuel for heating the iron retorts in wood distillation.

(*ii*) *An aqueous distillate* or **Pyroligneous acid** (*Pyro*=heat, *ligneous*=of wood). In addition to water it contains :

Methyl alcohol 3% ; Acetone 0·5% ; Acetic acid 10%.

Pyroligneous acid is further treated for the recovery of these substances.

(*iii*) *A thick black liquid* or **Wood Tar** that separates from the aqueous distillate. On further distillation it yields a mixture of cresols known as '**Creosote**' which is used as preservative for timber.

(*iv*) *A solid residue* or **Wood Charcoal** left in iron retorts. It consists mainly of carbon and is a popular domestic fuel.

The process of wood distillation can be nicely illustrated in the laboratory with the help of apparatus shown in Fig. 16·2.

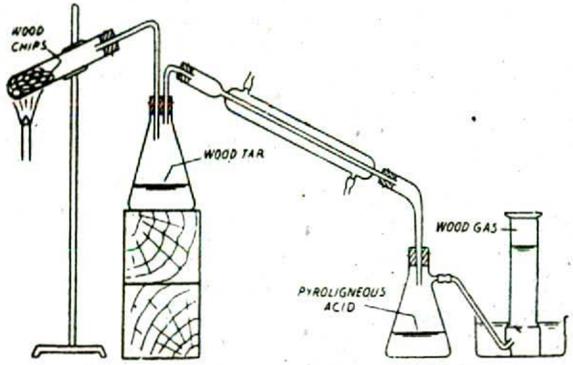


Fig. 16·2. Laboratory illustration of Wood distillation.

RECOVERY OF METHYL ALCOHOL FROM PYROLIGNEOUS ACID

As mentioned above pyroligneous acid contains methyl alcohol, acetone, acetic acid and water. Methyl alcohol is isolated from it by the following steps.

Removal of Acetic acid. Acetic acid is removed from pyroligneous acid by treating it with milk of lime and subsequent distillation. Methyl alcohol and acetone distil over leaving calcium acetate in the retort. Solid calcium acetate thus obtained is then treated with concentrated sulphuric acid, when acetic acid is regenerated which is recovered by distillation.

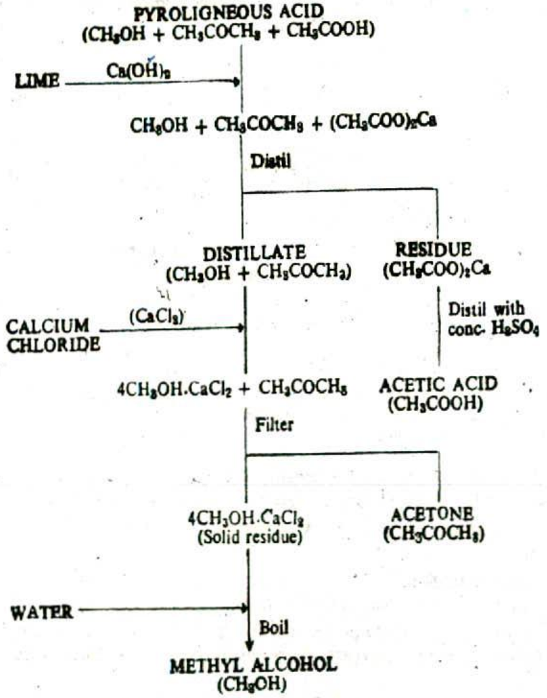
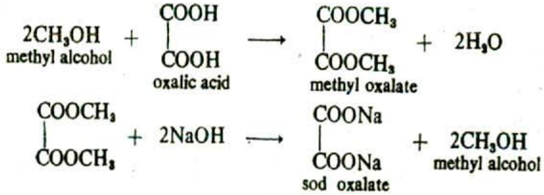


Fig. 16·3. Methyl alcohol from Wood distillation (*Flowsheet*).

Removal of Acetone. The mixture of methyl alcohol and acetone obtained from the previous step is fractionally distilled. The fraction received at about 56°C contains most of acetone and the one at about 65°C has most of methyl alcohol. The latter fraction is then treated with concentrated solution of calcium chloride. The methyl alcohol forms a crystalline compound, $CaCl_2.4CH_3OH$, which is separated and decomposed by boiling with water to give free alcohol. Finally it is dried over quick lime and redistilled.

Alternatively, the mixture is heated with anhydrous oxalic acid. Methyl alcohol is converted to methyl oxalate, leaving behind free acetone. Methyl oxalate upon boiling with alkali solution gives back methyl alcohol.



$$\underset{\text{methyl alcohol}}{2CH_3OH} + \underset{\text{oxalic acid}}{\begin{array}{c}COOH\\ |\\ COOH\end{array}} \longrightarrow \underset{\text{methyl oxalate}}{\begin{array}{c}COOCH_3\\ |\\ COOCH_3\end{array}} + 2H_2O$$

$$\begin{array}{c}COOCH_3\\ |\\ COOCH_3\end{array} + 2NaOH \longrightarrow \underset{\text{sod oxalate}}{\begin{array}{c}COONa\\ |\\ COONa\end{array}} + \underset{\text{methyl alcohol}}{2CH_3OH}$$

With her vast forest resources, India has a bright future for 'Wood Distillation Industry'. At present it is carried chiefly at Bhadravati in Karnatak State.

2. **Synthesis from Water gas** (*Patart Process*, 1923). This method has almost entirely replaced the wood distillation process. Steam is blown through red hot coke to obtain water gas.

$$C + \underset{\text{(steam)}}{H_2O} \longrightarrow \underbrace{CO + H_2}_{\text{water gas}}$$

It is mixed with half its volume of hydrogen, compressed to about 300 atmospheres and passed over a catalyst ($4ZnO.CrO_3$) heated at 300°.

$$CO + 2H_2 \longrightarrow \underset{\text{methyl alcohol}}{CH_3OH}$$

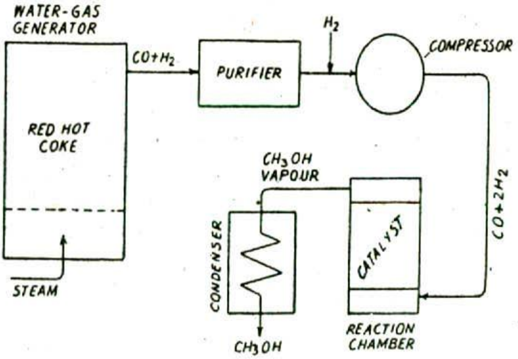


Fig. 16·4. Synthesis of Methyl alcohol from Water gas.

Methyl alcohol thus produced is condensed and the unreacted gases are sent for recirculation along with a fresh charge of hydrogen and carbon monoxide.

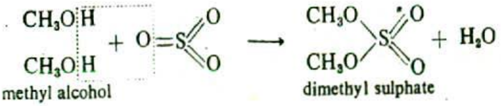
Because of the high purity of synthetic methyl alcohol and low cost of production, this method is becoming increasingly important.

3. **From Natural gas**. In U.S.A. methyl alcohol is prepared on the industrial scale from methane obtained from natural gas. Methane is mixed with oxygen and passed over a catalyst under a pressure of 100 atmospheres at 260°.

$$\underset{\text{methane}}{CH_4} + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{methyl alcohol}}{CH_3OH}$$

Properties. It is a colourless liquid boiling at 65° and having specific gravity 0·8. It has a sharp wine-like odour and a burning taste. It is miscible with water in all proportions, mixing being attended by a contraction in volume. When taken internally, it acts as a poison causing blindness and even death. It is an excellent solvent for fats, oils, shellac, etc. It is inflammable and its vapours form explosive mixtures with air.

Chemically it behaves like a typical monohydric primary alcohol and gives all the general reactions mentioned before. It absorbs sulphur trioxide at low temperatures to produce dimethyl sulphate.



Uses. Methyl alcohol is used .

(1) as fuel ; (2) as a solvent for fats, oils, gums, shellac, celluloid, etc ; (3) for dry cleaning ; (4) to *denature* (render unfit for drinking) industrial alcohol ; (5) as antifreeze for automobile radiators ; and (6) as starting material for the manufacture of methyl chloride, dimethyl sulphate, methyl esters, and formaldehyde.

ETHYL ALCOHOL, *Ethanol*, C_2H_5OH

It is most important and the earliest known representative of the class and is popularly referred to as simply '*alcohol*'. It is the exhilarating principle of all wines and is also named as **Spirit of Wine** Technically it is known as **Grain alcohol**, since it is often manufactured from starchy grains.

Manufacture. Ethyl alcohol is prepared commercially by different methods depending upon the raw materials available.

(1) **Fermentation of Sugars.** Ethyl alcohol has been made for centuries by the fermentation of sugars in presence of yeast.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\textit{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\textit{Zymase}} \underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

Molasses is a rich and cheap source of glucose, fructose and sucrose and it forms an excellent source of ethyl alcohol.

(2) **From Starchy materials.** Ethyl alcohol is also produced from cheap starchy materials such as potatoes, maize and barley. The starchy material is first converted into sugar which is then fermented by yeast.

(3) **From Saw dust.** In Germany ethyl alcohol is obtained from saw dust (cellulose) by digesting with dilute sulphuric acid and steam under pressure.

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_x} + xH_2O \longrightarrow \underset{\text{glucose}}{xC_6H_{12}O_6}$$

The resulting solution is fermented by the yeast after neutralisation with lime.

(4) **Synthetic Methods.** (*i*) In USA ethyl alcohol is made by absorbing ethylene from petroleum refinery gases in 95% sulphuric acid and then hydrolysing the resulting hydrogen sulphate by boiling with water.

$$\underset{\text{ethylene}}{H_2C{=}CH_2} + H_2SO_4 \xrightarrow{100^\circ} \underset{\text{ethyl hydrogen sulphate}}{C_2H_5HSO_4}$$

$$C_2H_5HSO_4 + H_2O \longrightarrow \underset{\text{ethyl alcohol}}{C_2H_5OH} + H_2SO_4$$

The alcohol thus produced is recovered by distillation.

(*ii*) **Hydration of Ethylene.** Recently the manufacture of ethyl alcohol has been achieved by direct hydration of ethylene obtained by cracking of naphtha.

$$CH_2{=}CH_2 + H_2O \xrightarrow{H_3PO_4} CH_3CH_2OH$$

Ethylene gas and distilled water (1 : 0·6 molar ratio) are preheated to 300°C and then passed under high pressure into the reactor. The reactor is a stainless steel vessel containing phosphoric acid catalyst. The reaction products are then cooled and passed into the scrubber where ethyl alcohol is dissolved in water. The aqueous solution of alcohol is sent to the distillation unit to get pure alcohol.

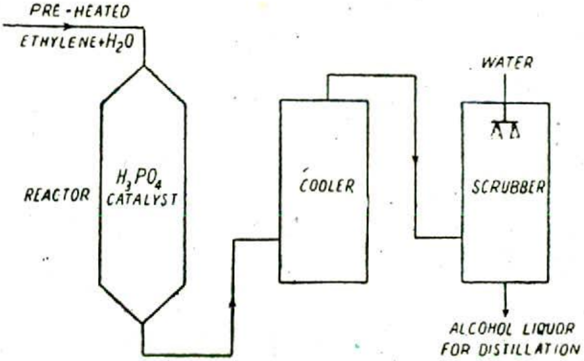


Fig. 16·5. Industrial preparation of Ethyl alcohol.

(*iii*) **Reduction of Acetaldehyde.** In Switzerland, ethyl alcohol is produced industrially by converting acetylene to acetaldehyde which is then reduced to alcohol by catalytic hydrogenation over reduced copper or nickel.

$$\underset{\text{acetylene}}{HC{\equiv}CH} + H_2O \xrightarrow{H_2SO_4} \underset{\text{acetaldehyde}}{CH_3CHO}$$

$$CH_3CHO + 2H \xrightarrow{H_2SO_4} \underset{\text{ethyl alcohol}}{CH_3CH_2OH}$$

Properties. (*Physical*). Ethyl alcohol is colourless liquid with a rather pleasant odour and a burning taste. It boils at 78·5° ; freezes at —114° and has specific gravity 0·789 at 20°. It is miscible with water in all proportions with the evolution of heat and contraction in volume. Thus 52 volumes of ethyl alcohol when mixed with 48 volumes of water, produce a contraction of 8·7 volumes. Ethyl alcohol is an excellent solvent for fats, resins, and inorganic substances like caustic soda, caustic potash, sulphur, phosphorus, etc. When taken orally in small dozes, ethyl alcohol is a good stimulant and heat producer owing to oxidation in blood. If taken in large amounts, it acts as a strong poison.

(*Chemical*). Ethyl alcohol responds to all the general reactions of the class described before.

(1) It burns in air with a clear blue flame producing considerable heat.

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + 6O \longrightarrow 2CO_2 + 3H_2O + 328 \text{ kcal}$$

(2) Sodium and potassium react upon it forming ethoxide and hydrogen

$$\underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{sod ethoxide}}{2C_2H_5\bar{O}\overset{+}{Na}} + H_2$$

(3) Ethyl alcohol reacts with Grignard reagents to form alkanes.

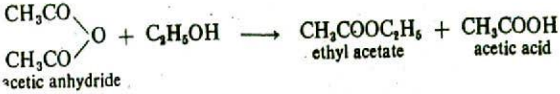
$$CH_3CH_2OH + \underset{\text{methylmag. bromide}}{CH_3{-}MgBr} \longrightarrow \underset{\text{methane}}{CH_4} + \underset{\text{ethoxymag. bromide}}{Mg(OC_2H_5)Br}$$

(4) If reacts with carboxylic acids in presence of inorganic acids as catalysts to produce esters.

$$CH_3CH_2OH + \underset{\text{acetic acid}}{CH_3COOH} \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

(5) It also forms esters with acid chlorides and acid anhydrides.

$$\underset{\text{acetyl chloride}}{CH_3COCl} + C_2H_5OH \longrightarrow \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + HCl$$



$$\underset{\text{acetic anhydride}}{(CH_3CO)_2O} + C_2H_5OH \longrightarrow \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{acetic acid}}{CH_3COOH}$$

(6) Upon oxidation with potassium dichromate and sulphuric acid, it first forms acetaldehyde and then acetic acid.

$$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{acetic acid}}{CH_3COOH}$$

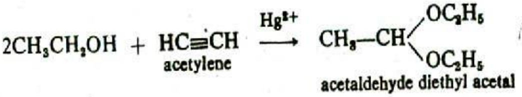
However, with halogens oxidation occurs yielding acetaldehyde.

$$CH_3CH_2OH + Cl_2 \longrightarrow \underset{\text{acetaldehyde}}{CH_3CHO} + 2HCl$$

(7) When ethyl alcohol vapours are passed over hot Cu at 300°, it dehydrogenates to yield acetaldehyde.

$$CH_3CH_2OH \xrightarrow[300°]{Cu} \underset{\text{acetaldehyde}}{CH_3CHO} + H_2$$

(8) It reacts with acetylene in presence of mercury compounds as catalyst to yield *acetals*.



$$2CH_3CH_2OH + \underset{\text{acetylene}}{HC{\equiv}CH} \xrightarrow{Hg^{2+}} \underset{\text{acetaldehyde diethyl acetal}}{CH_3{-}CH(OC_2H_5)_2}$$

(9) Ethyl alcohol reacts with halogen acids to produce alkyl halides.

$$CH_3CH_2OH + HBr \longrightarrow \underset{\text{ethyl bromide}}{CH_3CH_2Br} + H_2O$$

(10) It reacts with phosphorus halides to produce ethyl halides.

$$CH_3CH_2OH + PCl_5 \longrightarrow \underset{\text{ethyl chloride}}{CH_3CH_2Cl} + POCl_3 + HCl$$

$$3CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$

(11) With thionyl chloride ($SOCl_2$) it gives ethyl chloride.

$$CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2 + HCl$$

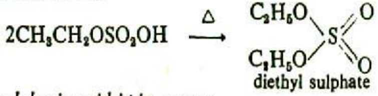
(12) Ethyl alcohol reacts with HNO_3 and H_2SO_4 to produce ethyl nitrate and ethyl hydrogen sulphate respectively.

$$CH_3CH_2OH + \underset{\text{nitric acid}}{HONO_2} \longrightarrow \underset{\text{ethyl nitrate}}{CH_3CH_2ONO_2} + H_2O$$

$$CH_3CH_2OH + \underset{\text{sulphuric acid}}{HOSO_2OH} \longrightarrow \underset{\text{ethyl hydrogen sulphate}}{CH_3CH_2OSO_2OH} + H_2O$$

The ethyl hydrogen sulphate thus produced reacts further to give a variety of products depending upon the reaction conditions.

(*i*) *When heated alone,*



(*ii*) *When sulphuric acid is in excess,*

$$\mathrm{CH_3CH_2OSO_2OH \xrightarrow{170^\circ} \underset{ethene}{H_2C{=}CH_2} + H_2SO_4}$$

(*iii*) *When ethyl alcohol is in excess,*

$$\mathrm{CH_3CH_2OSO_2OH + HOCH_2CH_3 \xrightarrow{140^\circ} \underset{diethyl\ ether}{CH_3CH_2OCH_2CH_3} + H_2SO_4}$$

(13) When passed over alumina at 240°, diethyl ether is produced.

$$\mathrm{2CH_3CH_2OH \xrightarrow[300^\circ]{Al_2O_3} \underset{diethyl\ ether}{(CH_3CH_2)_2O} + H_2O}$$

However at 300°, ethyl alcohol undergoes dehydration to produce ethylene.

$$\mathrm{CH_3CH_2OH \xrightarrow[375^\circ]{Al_2O_3} \underset{ethene}{H_2C{=}CH_2} + H_2O}$$

(14) When warmed with aqueous potassium hydroxide solution and iodine, ethyl alcohol yields iodoform.

$$\mathrm{CH_3CH_2OH + 4I_2 + 6\overset{+}{K}\overset{-}{O}H \longrightarrow \underset{iodoform}{CHI_3} + HCO\overset{-}{O}\overset{+}{K} + 5\overset{+}{K}\overset{-}{I} + 5H_2O}$$

Uses. Ethyl alcohol is used : (1) as a fuel for lamps and stoves. For the sake of convenience in transportation, it is converted into solid state (**Solid alcohol**) by dispersion in saturated calcium acetate and a little stearic acid ; (2) as a substitute of petrol in internal combustion engines ; (3) as a solvent for drugs, tinctures, oils, perfumes, inks, dyes, varnishes etc. ; (4) as a beverage ; (5) as a preservative for biological specimens ; (6) as an antifreeze for automobile radiators ; (7) as a low freezing (*fp* —11·7°) and mobile fluid in scientific apparatus such as thermometers and spirit level ; (8) as a raw material for large number of organic compounds including ethylene, ether, acetic acid, iodoform, chloroform, chloral etc. ; and (9) for manufacture of *terylene* and *polythene*.

ALCOHOL INDUSTRY

WHAT IS FERMENTATION ?

A solution of glucose in distilled water remains unchanged almost indefinitely. If, however, to this solution some yeast* is added, after sometime the whole liquid begins to froth and looks like boiling. On testing it is found that glucose has been converted to ethyl alcohol and the boiling appearance is, in fact, due to the brisk evolution of carbon dioxide during the reaction.

$$\mathrm{\underset{glucose}{C_6H_{12}O_6} \xrightarrow{yeast} \underset{ethyl\ alcohol}{2C_2H_5OH} + 2CO_2}$$

This process of conversion of sugars to ethyl alcohol under the influence of yeast was known since the remotest times and was named **Fermentation** (*Ferver*=to boil). Pasteur suggested that the fermentation of sugar to alcohol was brought about by the physiological action of yeast cells. This view was later on contradicted by Buchner who demonstrated that if yeast cells are killed by grinding with sand and then squeezed, the resulting extract was capable of changing sugar into ethyl alcohol. It is believed that some 'non-living' complex organic compounds present in yeast

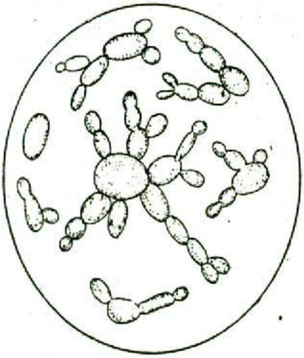


Fig. 16·6. Yeast cells.

---

*Yeast is a single-celled living plant. It grows and multiplies rapidly under suitable conditions.

cells are responsible for this change. These complex compounds bring about fermentation by playing the role of catalyst.

It has been shown further that numerous other decomposition reactions are similarly brought about by complex organic compounds supplied by yeast or other living organisms. The term fermentation in its modern form covers all such reactions which involve slow decomposition of big molecules of certain organic compounds into simpler ones under catalytic influence of non-living complex substances called **Ferments**. Since a number of ferments are present in yeast, they are also termed as **Enzymes** (meaning, *in yeast*).

To distinguish it from other fermentation reactions, the conversion of sugar into ethyl alcohol by yeast has been termed as **Alcoholic fermentation**. This has formed the basis of the alcohol industry for centuries and most of the ethyl alcohol that we use today is still prepared by this method.

RAW MATERIALS FOR ALCOHOL INDUSTRY

In alcohol fermentation, glucose or cane sugar are the fermenting materials. Therefore, any natural product which contains these sugars or can be easily transformed into them, is a potential source of ethyl alcohol. The raw materials for alcohol industry are :

(1) **Substances containing Fermentable Sugars** *e.g.*, cane juice, dry dates, beets, molasses, fruit juices, etc.

(2) **Materials containing Starch or Cellulose** *e.g.*, potatoes, rice, barley, maize or wood. These are first treated to convert the starch or cellulose into sugars which are then fermented by yeast.

MANUFACTURE OF ETHYL ALCOHOL FROM MOLASSES

In India most of the ethyl alcohol is prepared from *molasses* which is the mother liquor left after the crystallisation of cane sugar from concentrated juice. It is a dark coloured thick syrupy mass that still contains about sixty per cent of fermentable sugars, mostly sucrose, glucose, and fructose. Thus molasses forms an excellent cheap source of industrial ethyl alcohol.

Molasses is converted to ethyl alcohol by the following steps :

(1) **Dilution**. Molasses is first diluted with water to bring down the concentration of sugars to about 8 to 10 per cent. Thus, the usual dilution is five volumes of water to one volume of molasses.

(2) **Addition of Ammonium salts and Acidification**. Molasses usually contains enough nitrogenous matter to act as food for yeast during fermentation. If the nitrogen content of the molasses is poor, it may be fortified by the addition of ammonium sulphate or ammonium phosphate.

To the dilute sugar solution is also added a small amount of sulphuric acid to render it acidic. Acidity is favourable to the growth of yeast but unfavourable to most other bacteria. Care should be taken to avoid excess of acid as the yeast may be killed.

(3) **Addition of Yeast ; Fermentation**. The solution from step (2) is received in large 'fermentation tanks' and yeast is added to it. The mixture is maintained at about 30° for a few days. During this period the enzymes *invertase* and *zymase* present in yeast bring about the conversion of sugars into ethyl alcohol.

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\textit{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\textit{Zymase}} \underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

During the process the liquor froths owing to the evolution of carbon dioxide which is recovered and used for preparing aerated waters. The fermented liquid is technically called *WASH*.

(4) **Distillation of Wash.** The fermented liquid containing 15 to 18 per cent alcohol and the rest water is now subjected to fractional distillation. Since the boiling points of alcohol and water are not widely different, it becomes necessary to use a special device for this purpose. The distillation of the *wash* is carried in a unit shown in Fig. 16·7. The fractionating column is fitted with shelves each of which has a baffle plate on the central hole and a side-tube. When the wash is admitted at one of these shelves, it flows down through the side-tube to the next shelf below. As the wash in the still is heated, steam along with volatile components of the wash passes up through the central holes of the shelves. Thus the steam as it bubbles through the wash contained in the shelf, carries with it the more volatile constituents leaving the less volatile ones behind. This process of distillation takes place at each shelf. Ultimately the vapours of ethyl alcohol and some acetaldehyde (also present in wash) reach the head of the column where these are drawn and passed through a condenser. On the other hand, the higher-boiling constituents move down from shelf to shelf and are drawn out near the base. The *spent wash* collects at the bottom of the still. Thus as a result of the fractional distillation we have :

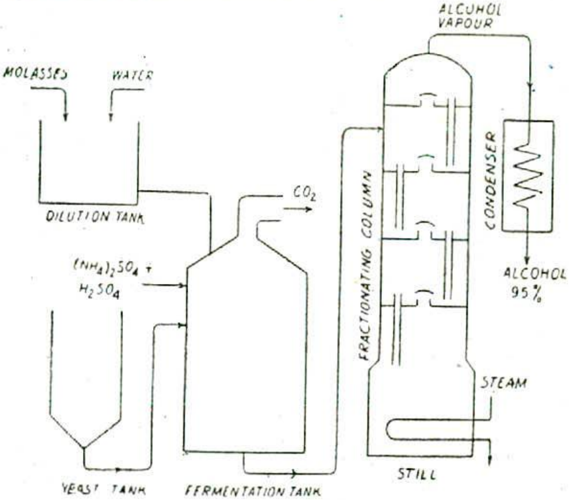


Fig. 16·7. Flowsheet of alcohol manufacture from molasses.

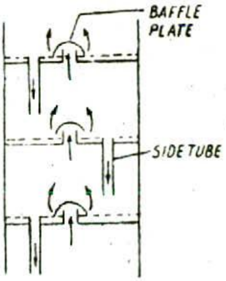


Fig. 16·8. The process in the fractionating column.

(*i*) The first runnings (or fraction) drawn from the head of the column. This consists of **Acetaldehyde** which is an important by-product.

(*ii*) The main fraction drawn near the top is 90-95% ethyl alcohol and is placed in the market as **Rectified Spirit.**

(*iii*) The high boiling fraction (125 -140°) drawn near the base is called **Fusel oil.** This is mostly amyl alcohol and is used as a solvent in the preparation of paints, varnishes and lacquers.

(*iv*) The residue in the still is **Spent wash.** It is rich in nitrogen content and is used as cattle fodder or manure.

MANUFACTURE OF ALCOHOL FROM STARCH

The important raw materials containing starch are potatoes, rice, maize, barley and other cereals. Of these potatoes are commonly employed for the manufacture of ethyl alcohol. The process involves the following steps.

(1) **Liberation of Starch.** Potatoes are cut into slices and crushed. The crushed mass is then steamed at 140-150° under pressure. In this way the cell walls containing starch particles are broken and starch brought into solution. The resulting solution is called *MASH*.

(2) **Hydrolysis of Starch to Maltose.** The enzyme *diastase* is needed to hydrolyse starch to maltose. It is present in small amounts in barley and can be developed considerably upon germination. For this purpose, barley is steeped in water at a temperature of 10–13°C for a couple of days. This is then taken out and allowed to germinate in dark at about 15°. Barley is then heated to 60° to stop germination. The dried and germinated barley is technically known as *MALT*.

To the '*mash*' obtained from step (1) is now added '*malt*' and temperature raised to 50—60°. Within half an hour *diastase* present in the malt converts the starch to maltose.

$$2\,\underset{\text{starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\textit{Diastase}} n\,\underset{\text{maltose}}{C_{12}H_{22}O_{11}}$$

(3) **Fermentation of Maltose to Alcohol.** To the solution of maltose obtained from the previous step is now added yeast. It furnishes the enzymes *maltase* and *zymase*. While the former converts maltose into glucose, the latter enzyme converts glucose into alcohol.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\textit{Maltase}} \underset{\text{glucose}}{2C_6H_{12}O_6}$$

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\textit{Zymase}} \underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

(4) **Distillation.** The fermented liquid or '*Wash*' obtained above is then distilled in the unit as described before. The product is 85 per cent ethyl alcohol or Rectified spirit.

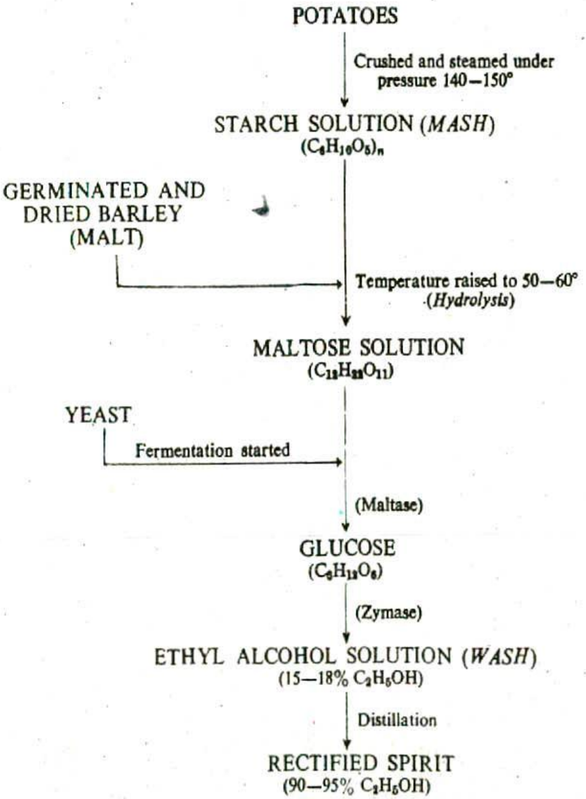


Fig. 16·9. Flowsheet of production of Rectified spirit from Potatoes.

Alternative Method. According to another method starch may be hydrolysed to glucose by heating with dilute sulphuric acid. The excess of acid is then neutralised with lime and the resulting liquid fermented as described before. This new method eliminates the use of malt.

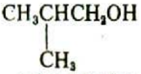
By-products of Alcohol Industry. The important by-products of alcohol manufactured by the fermentation processes are :

(1) *Carbon dioxide.* Large quantities of carbon dioxide are evolved during fermentation of sugars. It is stored under pressure in iron cylinders and used for making aerated waters or is sold as *dry ice.*

(2) *Acetaldehyde.* It is present in the more volatile fractions obtained during alcohol distillation. They are collected and pure acetaldehyde recovered.

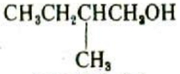
(3) *Fusel Oil.* It is obtained as the last runnings between 125° and 140°. It is a bright yellow, oily liquid with nauseating odour. It consists of a mixture of mainly isoamyl alcohol, isobutyl alcohol and ***n***-propyl alcohol :

$CH_3CH_2CH_2OH$
n-propyl alcohol



$$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_2OH$$

isobutyl alcohol



$$CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_2OH$$

isoamyl alcohol

These alcohols are not produced by the fermentation of sugars. But rather the yeast takes proteins present in the original raw material and throws out these alcohols as non-assimilate products of metabolism.

Fusel oil is used technically for the preparation of amyl acetate which is valuable solvent for varnishes ; it is also used in confectionary and fruit essences. Thus fusel oil fetches much higher price than even ethyl alcohol.

(4) *Spent Wash.* The residual liquor from which ethyl alcohol has been removed by distillation, is called '*spent wash*'. It contains nitrogenous matter originally present in the raw material and is used as fodder for cattle, or for watering land to increase its fertility.

(5) *Potassium acid tartarate.* Being insoluble in alcohol, it is thrown down during the fermentation of grape juice. It is used for the manufacture of tartaric acid and Rochelle salt.

Absolute alcohol. Rectified spirit obtained by the distillation of *wash* contains about 95 per cent ethyl alcohol. Since a mixture of 95·6 per cent alcohol with water boils at lower temperature (78·1°) than the boiling point of pure alcohol (78·5°), it is impossible to get an alcohol of higher concentration by fractional distillation of rectified spirit. Anhydrous or absolute alcohol can be obtained by digesting the rectified spirit over quicklime for several days and then distilling. The first and the last runnings are rejected, and the main portion of the distillate is 100 per cent or absolute alcohol.

A modern process is the *azeotropic distillation* of rectified spirit with benzene. When distillation is carried after addition of a certain amount of benzene, at first *ternary* mixture of water, alcohol and benzene comes over at 65° till all the water is thus removed. Then the boiling point rises and the remaining benzene comes over as *binary* mixture with alcohol at 68°. Finally absolute alcohol distils at 78·5°.

Denatured alcohol. The manufacture and sale of ethyl alcohol is government controlled. Heavy excise duty is levied on the sale of alcoholic beverages. For industrial purposes alcohol is duty free. Therefore, the industrial alcohol is denatured, by the addition of poisonous substances like methyl alcohol, acetone or pyridine. A common practice is to add about 4 per cent of impure methyl alcohol together with traces of pyridine and some colouring matter. The product is often sold in the market under the name '*Methylated Spirit*'. In India rectified spirit is denatured by the addition of light cautchoucine and pyridine bases. Methylated spirit is extensively used for the preparation of varnishes, and tinctures for external use.

Power alcohol. In non-petroleum countries alcohol mixed with petrol and benzene is now used as motor fuel. Alcohol thus used for the generation of power is popularly known as '*power alcohol*'. Rectified spirit alone does not mix with petrol, hence the need of the third ingredient : ether, benzene or tetraline. In a country like India with meagre petroleum resources, the use of power alcohol is a dire necessity. We can make large quantities of cheap alcohol from molasses which could be used to prepare power alcohol.

Alcoholic Beverages. When taken internally in small quantities, alcohol stimulates the human system without any apparent injurious effect. However, its continuous use leads to immoderation and induces other vices. Already the governments in certain states have schemes of prohibition in hand. Anyhow, the fact remains that alcohol is consumed in large quantities as *alcoholic liquors* or *beverages*, especially in European countries.

Alcoholic beverages are of two types : (*a*) Undistilled ; (*b*) Distilled.

UNDISTILLED BEVERAGES. These are produced simply by the fermentation process from fruit juice or grains. The beverages prepared from grape juice or other fruit juices are called **Wines**. Wine containing 18-20 per cent alcohol and produced by natural fermentation are called *Natural Wines*. Weak natural wines are made stronger by adding pure alcohol from outside and are named as *Fortified Wines*.

DISTILLED BEVERAGES. If the fermented liquids are distilled, most of the alcohol along with other volatile products *viz.*, flavours, essential oils, esters and higher alcohols, pass over as distillate. The distilled liquors have a high alcohol content which may go up to 50 per cent or even more.

The colour, flavour and taste of a particular beverage is largely determined by the materials employed and the subsequent treatment of the fermented liquor.

The description of some of the commonly used beverages is given in the table below.

Beverage	*Source*	*Alcohol content per cent by volume*
UNDISTILLED BEVERAGES :		
Claret	Grape juice	7 to 13
Port	Grape juice	15 to 24 (*fortified*)
Sherry	Grape juice	18 to 24 (*fortified*)
Champagne	Grape juice	8 to 10
Cider	Apple juice	3 to 6
Beer	Barley	3 to 5
DISTILLED BEVERAGES :		
Whiskey	Barley	40 to 50
Brandy	Peeches, apples and cherries	40 to 50
Holland	Rye	40
Rum	Molasses	45 to 55
Gin	Barley	40 to 45

Alcoholometry. A heavy tax is levied on alcohol and all alcoholic preparations. Thus it is necessary to estimate the percentage of alcohol in a certain sample. Chemical methods of analysis can be employed but these take much time. A simpler method commonly used consists in determining the specific gravity of the sample by means of a hydrometer and then finding the exact percentage of alcohol from *ready reference tables*. The determination of the percentage of alcohol goes by the name of alcoholometry.

In old days, it was customary to adjudge the alcohol content by pouring the sample of alcohol on gun powder and then setting fire to it. If the liquor contained much alcohol, it burnt away leaving the gun powder dry enough to catch fire. On the contrary, if it contained much water, it damped the gun powder which now refused to catch fire. A sample of spirit which was just strong enough to fire the powder, was called **Proof spirit**. Stronger spirits were called *'Over Proof'* (*O.P.*) and the weaker ones 'Under Proof' (*U.P.*). Proof spirit is now legally defined as an alcohol-water mixture having specific gravity 0·91976 at 15°C, and contains 57·1 per cent alcohol by weight. For excise purpose there are used special types of hydrometers graduated so as to read directly the percentage of alcohol on the scale in terms of proof spirit. The strength of any liquor is expressed as degrees *O.P.* or *U.P.*

PROPYL ALCOHOLS, *Propanols*, C_3H_7OH

Both the propyl alcohols theoretically possible are known.

n-**Propyl alcohol**, *1-Propanol*, $CH_3CH_2CH_2OH$. It occurs in fusel oil from which it is obtained by fractional distillation. It is a colourless liquid, bp 97°, resembling ethyl alcohol in taste and odour. It is used as a solvent.

Isopropyl alcohol, *2-Propanol*, $CH_3CHOHCH_3$. It may be made by the catalytic reduction of acetone. In USA it is prepared in large amounts from propylene obtained by cracking of petroleum during distillation. Propylene is absorbed in concentrated sulphuric acid and the isopropyl hydrogen sulphate thus produced is treated with steam.

$$CH_3CH{=}CH_2 + H_2SO_4 \longrightarrow \underset{\substack{\text{isopropyl hydrogen}\\ \text{sulphate}}}{(CH_3)_2CH{-}HSO_4}$$

$$(CH_3)_2CH{-}HSO_4 + H_2O \longrightarrow \underset{\text{isopropyl alcohol}}{(CH_3)_2CH{-}OH} + H_2SO_4$$

Isopropyl alcohol is a colourless liquid with an odour somewhat like that of acetone. It is known commercially as *Petrohol*. It is also used as a solvent in the preparation of perfumes, nail polish, and lacquers. It is also used for the industrial production of acetone by catalytic dehydrogenation.

BUTYL ALCOHOLS, *Butanols*, C_4H_9OH

There are four isomeric butyl alcohols :

(1) *n*-Butyl alcohol, *1-butanol*, $CH_3CH_2CH_2CH_2OH$, bp 117°.

(2) *sec*-Butyl alcohol, *2-Butanol*, $CH_3CH_3CHOHCH_3$, bp 99°.

(3) Isobutyl alcohol, *2-methyl propanol*, $(CH_3)_2CHCH_2OH$, 107°.

(4) *tert*-Butyl alcohol, *2-methyl-2-propanol*, $(CH_3)_3COH$, mp 26°.

Of all the butyl alcohols, n-butyl alcohol is by far the most important. It is prepared industrially by the fermentation of grain, potatoes or molasses with *Bacillus clostridium acetobutylicum*. The resulting mixture of ethyl alcohol, acetone and butyl alcohol is separated by fractional distillation. In USA butyl alcohol is produced commercially from acetaldehyde by condensation and subsequent hydrogenation.

$$\underset{\text{acetaldehyde}}{2CH_3CHO} \longrightarrow \underset{\text{aldol}}{CH_3CH(OH)CH_2CHO} \xrightarrow[(-H_2O)]{\Delta} \underset{\text{crotonaldehyde}}{CH_3CH{=}CHCHO} \xrightarrow[-H_2O]{+2H_2} \underset{\text{butyl alcohol}}{CH_3CH_2CH_2CH_2OH}$$

n-Butyl alcohol is a colourless liquid, bp 117°. It is a valuable solvent and is used for the technical production of butyl acetate and butyl phthalate both of which are employed as solvent for paints, lacquers and enamels. Butyl acetate is also in demand as a fruit essence.

AMYL ALCOHOLS, *Pentanols*, $C_5H_{11}OH$

All the eight isomeric amyl alcohols are known. A mixture of amyl alcohol is produced commercially by the chlorination of pentanes, obtained from the gaseous fraction of petroleum, and subsequent hydrolysis of the chlorides with aqueous sodium hydroxide. It is sold in the market under the name *Pentasol.* The chief ingredients of pentasol are 2-methyl-1-butanol. (bp 128°) and 1-pentanol (bp 138°). Another source of amyl alcohols is fusel oil which contains mainly 3-methyl-1-butanol (bp 132°) and 2-methyl-1-butanol. The last named alcohol is of interest as it offers the simplest case of optical isomerism and is, therefore, also called *active amyl alcohol.*

Commercial amyl alcohol is used in the manufacture of amyl acetate which is an excellent solvent for lacquers.

UNSATURATED ALCOHOLS

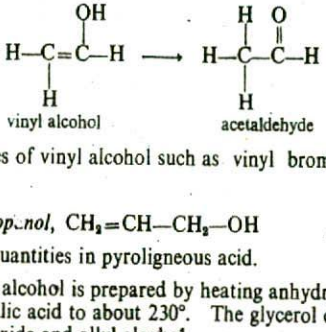
Unsaturated monohydric alcohols are of two types according as the OH is attached to a carbon which is singly or doubly-linked to another carbon. The simplest representatives of these alcohols are :

$$\underset{\text{vinyl alcohol}}{CH_2{=}CH{-}OH} \qquad \underset{\text{allyl acohol}}{CH_2{=}CH{-}CH_2{-}OH}$$

In general, the first type of compounds resemble aromatic phenols while the second type resemble aliphatic alcohols.

VINYL ALCOHOL, $CH_2{=}CH{-}OH$

All attempts to prepare vinyl alcohol result in the formation of acetaldehyde. This is due to the fact that this compound shows keto-enol tautomerism. The vinyl alcohol as soon as it is produced, ketonises to form acetaldehyde.



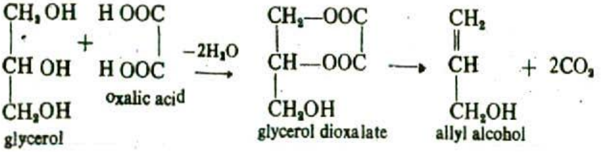
$$\underset{\text{vinyl alcohol}}{H{-}\underset{H}{C}{=}\overset{OH}{C}{-}H} \longrightarrow \underset{\text{acetaldehyde}}{H{-}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H}$$

However, derivatives of vinyl alcohol such as vinyl bromide and vinyl acetate are quite stable.

ALLYL ALCOHOL, *3-Propenol,* $CH_2{=}CH{-}CH_2{-}OH$

It occurs in small quantities in pyroligneous acid.

Preparation. Allyl alcohol is prepared by heating anhydrous glycerol with about twice its weight of crystalline oxalic acid to about 230°. The glycerol dioxalate first produced at once decomposes into carbon dioxide and allyl alcohol.



$$\underset{\text{glycerol}}{\begin{matrix}CH_2OH\\ |\\ CH\,OH\\ |\\ CH_2OH\end{matrix}} + \underset{\text{oxalic acid}}{\begin{matrix}HOOC\\ |\\ HOOC\end{matrix}} \xrightarrow{-2H_2O} \underset{\text{glycerol dioxalate}}{\begin{matrix}CH_2{-}OOC\\ |\qquad\quad |\\ CH{-}OOC\\ |\\ CH_2OH\end{matrix}} \longrightarrow \underset{\text{allyl alcohol}}{\begin{matrix}CH_2\\ \|\\ CH\\ |\\ CH_2OH\end{matrix}} + 2CO_2$$

Allyl alcohol is now manufactured by the hydrolysis of allyl chloride obtained by the chlorination of propylene.

$$\underset{\text{allyl chloride}}{CH_2{=}CH{-}CH_2Cl} + NaOH \longrightarrow \underset{\text{allyl alcohol}}{CH_2{=}CH{-}CH_2OH} + NaCl$$

Properties. Allyl alcohol is a colourless liquid, bp 96°, with a pungent odour. It has a mild lachrymatory effect. It is completely miscible with water, alcohol and ether in all proportions.

The molecule of allyl alcohol contains an ethylenic linkage and a primary alcohol group and shows reactions characteristic of these groups.

Reactions of Ethylenic linkage

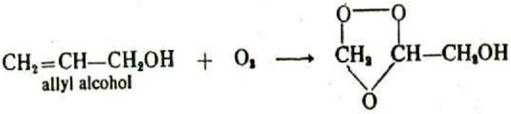
(1) Allyl alcohol forms addition compounds with hydrogen, halogens and hydrogen halides.

$$\underset{\text{allyl alcohol}}{CH_2=CH-CH_2OH} + H_2 \longrightarrow \underset{\text{1-propanol}}{CH_3-CH_2-CH_2OH}$$

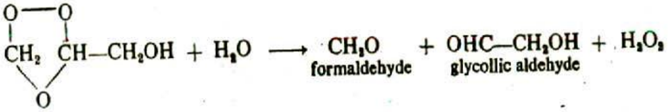
$$CH_2=CH-CH_2OH + Br_2 \longrightarrow \underset{\text{2, 3-dibromo-1-propanol}}{CH_2Br-CHBr-CH_2OH}$$

$$CH_2=CH-CH_2OH + HBr \longrightarrow \underset{\text{2-bromo-1-propanol}}{CH_3-CHBr-CH_2OH}$$

(2) With ozone it forms the ozonide which on hydrolysis forms glycollic aldehyde and formaldehyde.



ozonide



This reaction proves the structure of allyl alcohol.

(*b*) On careful oxidation with permanganate solution, allyl alcohol gives glycerol.

$$CH_2=CH-CH_2OH + H_2O + [O] \longrightarrow \underset{\text{glycerol}}{CH_2OH-CHOH-CH_2OH}$$

Reactions of CH_2OH Group

(4) Allyl alcohol reacts with sodium giving sodium allylate.

$$\underset{\text{allyl alcohol}}{CH_2=CH-CH_2OH} + Na \longrightarrow \underset{\text{sod. allylate}}{CH_2=CH-CH_2ONa} + \tfrac{1}{2}H_2$$

(5) It forms esters with organic and inorganic acids.

$$\underset{\text{allyl alcohol}}{CH_2=CH-CH_2OH} + CH_3COOH \longrightarrow \underset{\text{allyl acetate}}{CH_2=CH-CH_2OOCCH_3} + H_2O$$

$$\underset{\text{allyl alcohol}}{CH_2=CH-CH_2OH} + HCl \longrightarrow \underset{\text{allyl chloride}}{CH_2=CH-CH_2Cl} + H_2O$$

(6) On mild oxidation with ammoniacal silver oxide, allyl alcohol is oxidised to acrylic aldehyde and then acrylic acid.

$$\underset{\text{allyl alcohol}}{CH_2=CH-CH_2OH} \longrightarrow \underset{\text{acrylic aldehyde}}{CH_2=CH-CHO} \longrightarrow \underset{\text{acrylic acid}}{CH_2=CH-COOH}$$

Upon oxidation with sodium dichromate and sulphuric acid, a split at the double bond may result in the formation of formic acid and oxalic acid.

IR SPECTRA OF ALCOHOLS

Alcohols absorb infrared light and the absorption can be measured with the help of an infrared spectrophotometer. IR spectra of alcohols in the vapour phase or in dilute solutions in a nonpolar solvent like carbon tetrachloride, show a sharp band around 3700-3600 cm^{-1}. In the vapour phase, isolated OH groups exist and the absorption in this region is caused due to their presence. If, however, IR spectra of pure alcohols are examined, they exhibit a broad band around 3400-3200 cm^{-1}, instead of a sharp band. This shift of about 300 cm^{-1} is ascribed to the presence of hydrogen bonded OH groups.

The energy absorbed by alcohols in the vapour phase is due to exciting a stretching vibration of the O—H bond, Fig. 16·10 (*a*). On the other hand, the broad absorption band of a pure alcohol is also due to a similar motion of the H atom in OH groups that absorb at slightly different frequencies because they are involved in hydrogen bonds between two alcohol molecules.

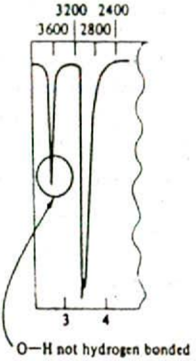


Fig. 16·10. (*a*) IR spectrum of ethyl alcohol in the vapour phase when the isolated OH groups absorb radiation at 3700 cm^{-1}.

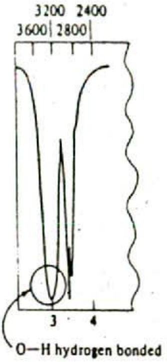


Fig. 16·10. (*b*) IR spectra of pure ethyl alcohol in dilute carbon tetrachloride solution when hydrogen bonded OH groups absorb radiation at 3300 cm^{-1}.

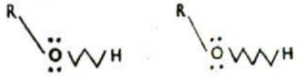


Fig. 16·11. Stretching vibration of O – H bond in isolated alcohol molecules.

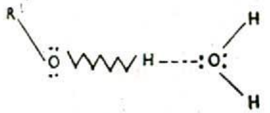


Fig. 16·12. Stretching vibration of O—H bond influenced by hydrogen bonding with another molecule.

The attraction of H nucleus of OH of an alcohol molecule for the oxygen electrons of the second alcohol molecule, makes it easier to pull the hydrogen further away from the O atom (Fig. 16·11). Thus a less energetic vibration of O—H will be caused in a pure alcohol due to hydrogen bonding. This less energetic vibration would in turn need a less energetic photon of light. This accounts for the shifted position of the OH bond in the IR spectrum of a pure alcohol in contrast to that of alcohol in dilute solution.

QUESTIONS

1. Outline the methods of preparation and properties of monohydric alcohols.
2. How is ethyl alcohol manufactured ? (*Jammu BSc, 1993*)
3. How is Absolute alcohol obtained from Rectified spirit ? What is Proof spirit ? (*Sambalpur BSc Hons, 1993*)
4. How does 1-butanol react with :

   (*a*) Na ; (*b*) conc H_2SO_4 ; (*c*) PCl_5 ; (*d*) Cu/300°C ; (*e*) conc HBr ; (*f*) $K_2Cr_2O_7/H_2SO_4$ (*Goa BSc, 1994*)
5. How will you distinguish between :
   - (*a*) 1-Butanol and 2-Butanol
   - (*b*) 2-Butanol and *tert*-Butyl alcohol
   - (*c*) 1-Butanol and 2-Hexyne

Hint. (*a*) 2-Butanol reacts with Lucas reagent ($HCl/ZnCl_2$) to produce cloudiness after about 5 minutes. 1-Butanol does not react with Lucas reagent at room temperature; (*b*) *tert*-Butyl alcohol reacts with Lucas reagent to produce cloudiness immediately. 2-Butanol reacts only after 5 minutes ; and (*c*) 2-Hexyne decolourises red colour of Br_2 in carbon tetrachloride.

6. How will you synthesise isopropyl alcohol from : (*i*) acetone, and (*ii*) propene. (*Osmania BSc Hons, 1994*)

7. How will you synthesise butane from *n*-butyl alcohol ? (*Saugar BSc ,1994*)

8. How will you synthesise :
   - (*a*) 1-Phenylethanol from styrene
   - (*b*) 2-Phenylethanol from styrene (*Dibrugarh BSc, 1993*)

Hint. Styrene is $C_6H_5CH{=}CH_2$. (*a*) H_2O/H^+ ; (*b*) (i) B_2H_6, and (ii) H_2O_2 / OH^-.

9. How will you synthesise the following compounds from the indicated starting materials :
   - (*a*) Isopropyl alcohol from *n*-propyl alcohol
   - (*b*) 2-Methyl-2-butanol from acetone
   - (*c*) 3-Methyl-2-butanol from 2-methyl-2-butene
   - (*d*) Ethanol from methanol
   - (*e*) Methanol from ethanol.

Hint. (a) (*i*) conc H_2SO_4/heat, and (*ii*) H_2O/H^+/heat ; (*b*) (*i*) CH_3CH_2MgBr, and (*ii*) H_2O/H^+ /heat ; (*c*) (*i*) B_2H_6, and (*ii*) H_2O_2/OH^- ; (*d*) (*i*) HI, (*ii*) Mg/ether, (*iii*) $H_2C = O$, and (*iv*) H_2O/H^+ ; and (*e*) (*i*) conc H_2SO_4/heat, (*ii*) O_3, (*iii*) Zn/H_2O, and (*iv*) $LiAlH_4$ *or* H_2/Ni.

10. Write a note on: Hydrogen bonding in alcohols. (*Udaipur BSc, 1993*)

11. Explain: Alcohols are higher boiling liquids as compared to alkanes. (*Karnataka BSc, 1994*)

12. Explain: Methyl alcohol boils at a much lower temperature than water though it possesses higher molecular weight. (*Delhi BSc, 1994*)

13. Explain : The boiling point of 1-butanol (117°C) is much higher than that of methyl propyl ether (39°C) even though they have the same molecular weight (they are isomers).

14. Explain : Lower alcohols are soluble in water. (*Delhi BSc, 1994*)

15. Arrange each group of compounds in order of increasing boiling points. Explain your reasoning.
   - (*a*) Butane; 1-Propanol; 2-Propanol
   - (*b*) Ethanol ; 1-Propanol ; 1-Butanol
   - (*c*) 1-Pentanol; 2-Pentanol; 2-Methyl-2-butanol.

Answer. (*a*) (*Lowest*) Butane < 2-Propanol < 1-Propanol (*Highest*)
(*b*) (*Lowest*) Ethanol < 1-Propanol < 1-Butanol (*Highest*) ;
(*c*) (*Lowest*) 2-Methyl-2-butanol < 2-Pentanol < 1-Pentanol (*Highest*)

16. Given a step-by-step mechanism for the reaction of ethyl alcohol with conc H_2SO_4 at 170°C to form ethylene. (*Madras BSc, 1994 ; North Bengal BSc, 1994*)

17. Write a step-by-step mechanism for the reaction of ethyl alcohol with conc H_2SO_4 at 130°C to form diethyl ether. (*Calcutta BSc, 1994*)

18. Write a step-by-step mechanism for the reaction of ethyl alcohol with acetic acid in the presence of H_2SO_4 catalyst to form ethyl acetate.

19. Identify compound (*A*), $C_4H_{10}O$, from the following data :

(1) $(A) + Br_2/CCl_4 \rightarrow$ No Reaction; (2) $(A) + Na \rightarrow$ Bubbles; (3) $(A) + HCl/ZnCl_2 \rightarrow$ Immediate Cloudiness

Answer. (*A*) is *tert*-Butyl alcohol

20. Compound (*A*), $C_6H_{14}O$, liberates hydrogen gas when treated with sodium metal; (*A*) does not react with NaOH, and gives a positive Lucas test in several minutes. When (*A*) is treated with PBr_5, compound (*B*), $C_6H_{13}Br$, is formed. When (*B*) is treated with alcoholic KOH, compound (*C*) and (*D*) both having the formula C_6H_{12}, are formed; (*C*) is the major reaction product while (*D*) is a minor product. When (*C*) is treated with ozone, followed by hydrolysis, only a single ketone is obtained. This ketone can be shown to be identical to the compound produced by hydration of propyne in the presence of sulphuric acid and mercuric sulphate. From the above information, deduce and write the correct structural formulas of compounds (*A*) through (*D*).

Answer. (*A*) is 2,3-Dimethyl-2-butanol
(*B*) is 2-Bromo-2, 3-dimethylbutane
(*C*) is 2,3-Dimethyl-2-butene (*cis or trans*)
(*D*) is 2,3-Dimethyl-1-butene

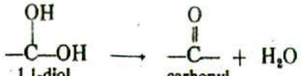
Chapter 17

Polyhydric Alcohols

The compounds which contain more than one hydroxyl group per molecule are given the general name of *Polyhydric alcohols*. They are further classified according to the number of OH groups present in the molecule. The compounds containing two OH groups are referred to as **Dihydric alcohols** or **Diols**. Those containing three OH groups are called **Trihydric alcohols** or **Triols.**

DIHYDRIC ALCOHOLS OR DIOLS

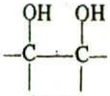
The IUPAC name of dihydric alcohols is *diols*, while their older 'common name' is **Glycols** (Greek, *glycys*=sweet), since they have a sweet taste. The two OH groups in diols may be present on the same carbon or different carbons. The diols having the OH groups bonded to the same carbon are unstable and undergo spontaneous decomposition to yield a carbonyl compound (aldehyde or ketone),



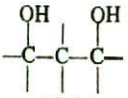
$$-\overset{OH}{\underset{|}{C}}-OH \longrightarrow -\overset{O}{\overset{\|}{C}}- + H_2O$$

1,1-diol (*unstable*) carbonyl compound

Therefore, in this chapter we will limit our study to stable diols only.



1,2-diol (*stable*)



1,3-diol (*stable*)

NOMENCLATURE

The *Common Names* are assigned to individual diols after the name of the corresponding alkene or the polymethylenes from which they could be obtained by direct hydroxylation. Their *IUPAC Names* are derived by adding the suffix *diol* to the name of the parent alkane and using numbers to indicate the positions of the two OH groups.

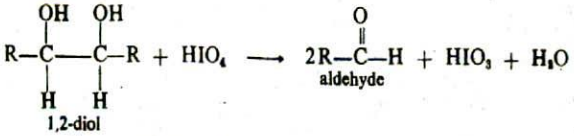
Formula	*Common Name*	*IUPAC Name*
$HOCH_2CH_2OH$	ethylene glycol	1,2-ethanediol
$HOCH_2CH(OH)CH_3$	propylene glycol	1,2-propanediol
$HOCH_2CH_2CH_2OH$	trimethylene glycol	1,3-propanediol
$HOCH_2CH_2CH_2CH_2CH_2OH$	pentamethylene glycol	1,5-pentanediol

Glycols are designated as α, β, γ etc., according to the relative positions of the two OH groups. Thus α-glycols are 1,2-diols; β-glycols are 1,3-diols; γ-glycols are 1,4-diols; and so on. α-Glycols are the commonest and the most important.

PROPERTIES

The lower diols are colourless, viscous liquids which are soluble in water. Their boiling points are very much higher than those of monohydric alcohols of similar molecular weight. Thus the boiling point of ethylene glycol (m wt=62) is 197° while that of 1-propanol (m wt=60) is 97°. This is because the presence of two OH groups in the molecule gives rise to extensive hydrogen bonding. This also explains the high viscosity because the molecules of liquid diol being associated by hydrogen bonds, cannot move freely relative to each other. The high solubility of diols is due to their ability to form hydrogen bonds at both the OH groups at one time with water molecules.

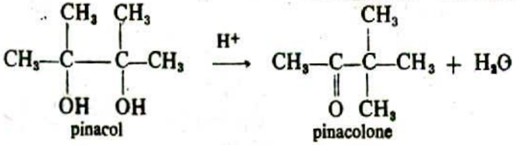
Diols give the same reactions as monohydric alcohols at the two OH groups separately, although the second of these groups reacts under more vigorous conditions. Thus they undergo ester formation, halide formation, oxidation etc., twice over. However, when oxidised with periodic acid (HIO_4) diols undergo oxidation by cleavage to form aldehydes or ketones. Monohydric alcohols do not display such oxidative cleavage.



$$\underset{\text{1,2-diol}}{R-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-R} + HIO_4 \longrightarrow \underset{\text{aldehyde}}{2R-\overset{O}{\overset{\|}{C}}-H} + HIO_3 + H_2O$$

1,3- or 1,4-diols do not undergo oxidative cleavage as above.

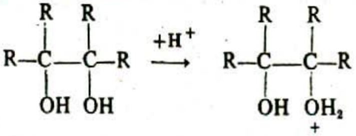
Pinacol Rearrangement. Completely substituted 1,2-diols such as 2,3-dimethyl-1,2,3-butanediol, are known as *pinacols*. They undergo dehydration and rearrangement in acid to form ketones. This reaction is called *Pinacol pinacolone rearrangement*. For Example,



$$\underset{\text{pinacol}}{CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3} \xrightarrow{H^+} \underset{\text{pinacolone}}{CH_3-\underset{O}{\underset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3} + H_2O$$

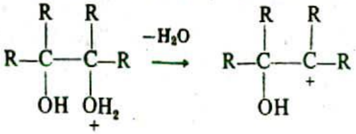
MECHANISM. The mechanism of pinacol rearrangement involves the following steps.

(*i*) Protonation of the 1, 2-diol.



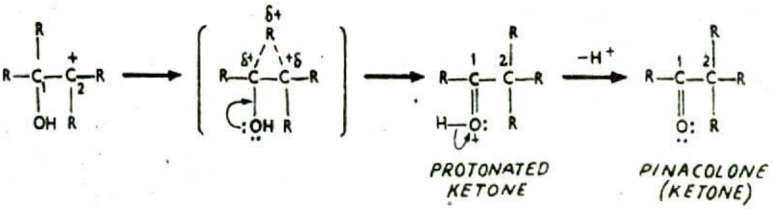
$$R-\underset{OH}{\overset{R}{C}}-\underset{OH}{\overset{R}{C}}-R \xrightarrow{+H^+} R-\underset{OH}{\overset{R}{C}}-\underset{\overset{+}{OH_2}}{\overset{R}{C}}-R$$

(*ii*) Generation of carbonium ion by loss of a molecule of water.



$$R-\underset{OH}{\overset{R}{C}}-\underset{\overset{+}{OH_2}}{\overset{R}{C}}-R \xrightarrow{-H_2O} R-\underset{OH}{\overset{R}{C}}-\underset{+}{\overset{R}{C}}-R$$

(*iii*) 1,2-shift of alkyl group to form a ketone.



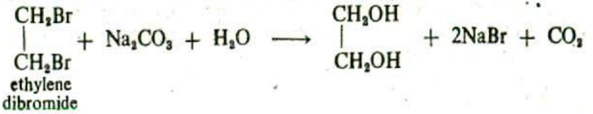
ETHYLENE GLYCOL, *1, 2-Ethanediol*, CH_2OH-CH_2OH

It is the simplest and the most important member of the class. It is often referred to as **glycol**.

Preparation. (1) *Hydroxylation of Ethylene.* Ethylene glycol may be prepared by passing ethylene into cold dilute potassium permanganate made alkaline with sodium carbonate.

$$\underset{\text{ethylene}}{CH_2{=}CH_2} + H_2O + [O] \xrightarrow{KMnO_4} \underset{\text{ethylene glycol}}{CH_2OH{-}CH_2OH}$$

(2) *Hydrolysis of Ethylene Dibromide.* In the laboratory glycol may be obtained by boiling ethylene dibromide with aqueous sodium carbonate.

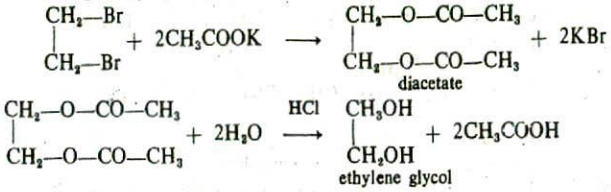


$$\underset{\text{ethylene dibromide}}{\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array}} + Na_2CO_3 + H_2O \longrightarrow \begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} + 2NaBr + CO_2$$

The yield is low (50 %) due to the conversion of some ethylene dibromide into vinyl bromide

$$BrCH_2{-}CH_2Br + Na_2CO_3 \longrightarrow \underset{\text{vinyl bromide}}{CH_2{=}CH{-}Br} + NaHCO_3$$

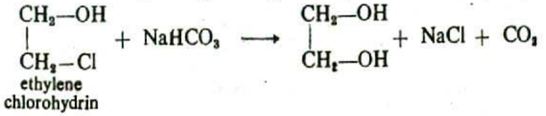
A quick laboratory method which gives excellent yield is by heating ethylene dibromide with potassium acetate in glacial acetic acid, and subsequent hydrolysis of the diacetate thus produced with hydrogen chloride in methanolic solution.



$$\begin{array}{l}CH_2{-}Br\\ |\\ CH_2{-}Br\end{array} + 2CH_3COOK \longrightarrow \underset{\text{diacetate}}{\begin{array}{l}CH_2{-}O{-}CO{-}CH_3\\ |\\ CH_2{-}O{-}CO{-}CH_3\end{array}} + 2KBr$$

$$\begin{array}{l}CH_2{-}O{-}CO{-}CH_3\\ |\\ CH_2{-}O{-}CO{-}CH_3\end{array} + 2H_2O \xrightarrow{HCl} \underset{\text{ethylene glycol}}{\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}} + 2CH_3COOH$$

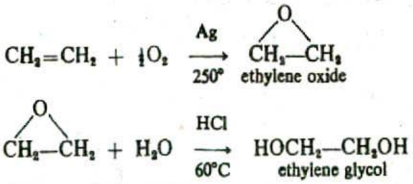
(3) *Hydrolysis of Ethylene Chlorohydrin.* Ethylene glycol is prepared commercially by hydrolysing ethylene chlorohydrin by boiling with aqueous sodium hydrogen carbonate.



$$\underset{\text{ethylene chlorohydrin}}{\begin{array}{l}CH_2{-}OH\\ |\\ CH_2{-}Cl\end{array}} + NaHCO_3 \longrightarrow \begin{array}{l}CH_2{-}OH\\ |\\ CH_2{-}OH\end{array} + NaCl + CO_2$$

Ethylene chlorohydrin required in the process is made by passing ethylene, obtained by cracking of petroleum or by catalytic dehydration of ethyl alcohol into aqueous hypochlorous acid.

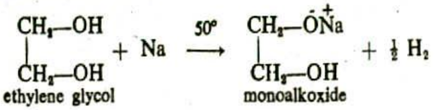
$$CH_2{=}CH_2 + HO{-}Cl \longrightarrow CH_2OH{-}CH_2Cl$$



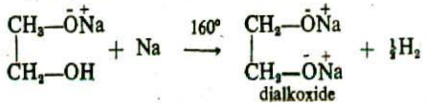
Properties (*Physical*). Glycol is a colourless viscous liquid, bp 197°, mp −11·5°, sp gr 1·111 at 20°. It has a sweet taste. It is miscible with water and ethyl alcohol in all proportions, but is insoluble in ether. It is as toxic as methyl alcohol when taken orally.

(*Chemical*). Ethylene glycol molecule is made of two primary alcohol groups joined together. Its chemical reactions are, therefore, those of primary alcohols twice over. Generally, one OH group is attacked completely before the other reacts. More vigorous conditions are sometimes needed for reaction of the second of the two OH groups.

(1) **Action with Sodium.** It reacts with sodium at 50° to form monoalkoxide and a dialkoxide when temperature is raised.

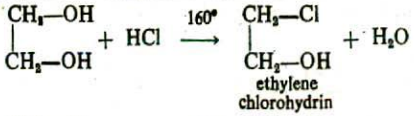


$$\underset{\text{ethylene glycol}}{\begin{array}{l}CH_2{-}OH\\ |\\ CH_2{-}OH\end{array}} + Na \xrightarrow{50^\circ} \underset{\text{monoalkoxide}}{\begin{array}{l}CH_2{-}\overset{-}{O}\overset{+}{Na}\\ |\\ CH_2{-}OH\end{array}} + \tfrac{1}{2}H_2$$

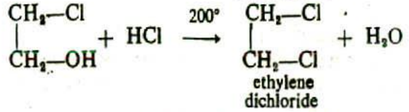


$$\begin{array}{l}CH_2{-}\overset{-}{O}\overset{+}{Na}\\ |\\ CH_2{-}OH\end{array} + Na \xrightarrow{160^\circ} \underset{\text{dialkoxide}}{\begin{array}{l}CH_2{-}\overset{-}{O}\overset{+}{Na}\\ |\\ CH_2{-}\overset{-}{O}\overset{+}{Na}\end{array}} + \tfrac{1}{2}H_2$$

(2) *Action with Hydrogen Chloride.* Hydrogen chloride reacts with ethylene glycol in two steps first forming ethylene chlorohydrin at 160° and then at 200° to yield ethylene dichloride.

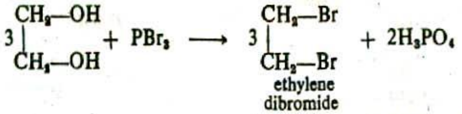


$$\begin{array}{l}CH_2{-}OH\\ |\\ CH_2{-}OH\end{array} + HCl \xrightarrow{160^\circ} \underset{\substack{\text{ethylene}\\ \text{chlorohydrin}}}{\begin{array}{l}CH_2{-}Cl\\ |\\ CH_2{-}OH\end{array}} + H_2O$$



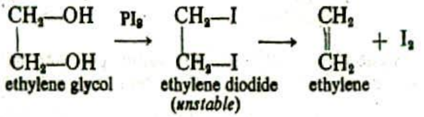
$$\begin{array}{l}CH_2{-}Cl\\ |\\ CH_2{-}OH\end{array} + HCl \xrightarrow{200^\circ} \underset{\substack{\text{ethylene}\\ \text{dichloride}}}{\begin{array}{l}CH_2{-}Cl\\ |\\ CH_2{-}Cl\end{array}} + H_2O$$

(3) *Action with Phosphorus Halides.* It reacts with phosphorus trichloride and phosphorus tribromide to form the corresponding dihalides when both the OH groups are replaced by halogen atom.



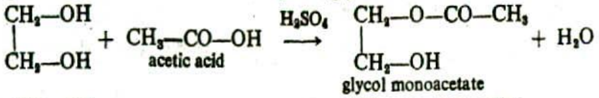
$$3\begin{array}{l}CH_2{-}OH\\ |\\ CH_2{-}OH\end{array} + PBr_3 \longrightarrow 3\underset{\substack{\text{ethylene}\\ \text{dibromide}}}{\begin{array}{l}CH_2{-}Br\\ |\\ CH_2{-}Br\end{array}} + 2H_3PO_4$$

Phosphorus triiodide, however, produces ethylene diodide which being unstable at once splits out iodine to yield ethylene.

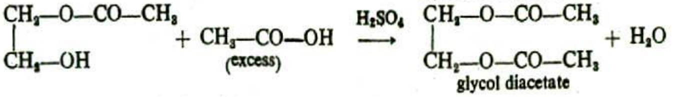


$$\underset{\text{ethylene glycol}}{\begin{array}{l}CH_2{-}OH\\ |\\ CH_2{-}OH\end{array}} \xrightarrow{PI_3} \underset{\substack{\text{ethylene diodide}\\ (\textit{unstable})}}{\begin{array}{l}CH_2{-}I\\ |\\ CH_2{-}I\end{array}} \longrightarrow \underset{\text{ethylene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}} + I_2$$

(4) *Action with Carboxylic Acids.* It reacts with carboxylic acids to give mono- or diesters, depending upon the relative amounts of ethylene glycol and acid taken.

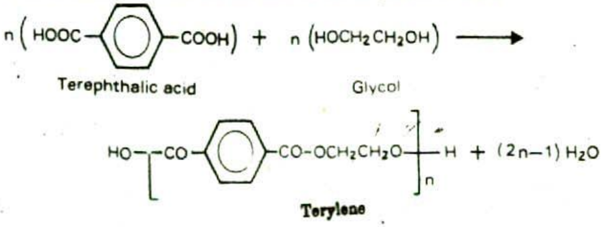


$$\begin{array}{l}CH_2{-}OH\\ |\\ CH_2{-}OH\end{array} + \underset{\text{acetic acid}}{CH_3{-}CO{-}OH} \xrightarrow{H_2SO_4} \underset{\text{glycol monoacetate}}{\begin{array}{l}CH_2{-}O{-}CO{-}CH_3\\ |\\ CH_2{-}OH\end{array}} + H_2O$$

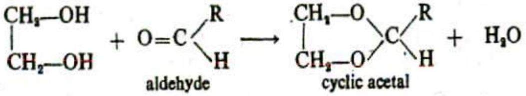


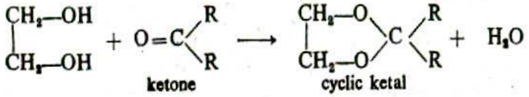
$$\begin{array}{l}CH_2{-}O{-}CO{-}CH_3\\ |\\ CH_2{-}OH\end{array} + \underset{\text{(excess)}}{CH_3{-}CO{-}OH} \xrightarrow{H_2SO_4} \underset{\text{glycol diacetate}}{\begin{array}{l}CH_2{-}O{-}CO{-}CH_3\\ |\\ CH_2{-}O{-}CO{-}CH_3\end{array}} + H_2O$$

When esterified with a dibasic acid it forms polymers *e.g.*,

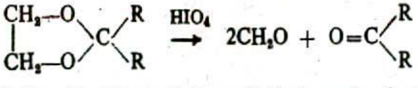


(5) *Action with Aldehydes or Ketones.* Ethylene glycol condenses with aldehydes or ketones in the presence of *p*-toluene sulphonic acid to yield respectively cyclic acetals or ketals.

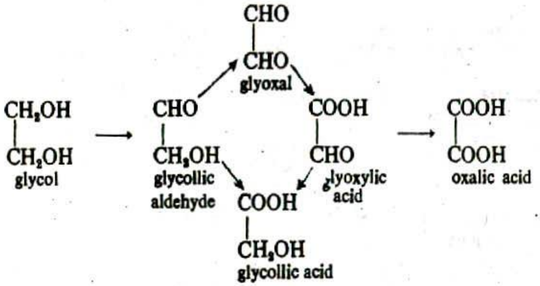




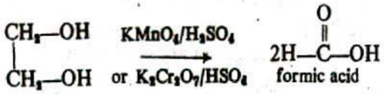
The formation of cyclic ketal can be used as a means of protecting carbonyl groups in reactions carried in alkaline solutions. The carbonyl group can be regenerated by the action of periodic acid on the ester.



(6) *Oxidation.* (*i*) The oxidation of ethylene glycol with nitric acid yields a number of substances as one or both the primary alcohol groups may be oxidised first to aldehyde and then carboxylic groups. The oxalic acid is obtained as the final product of oxidation.

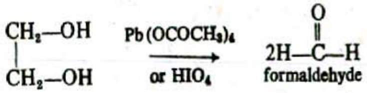


(*ii*) Oxidation of ethylene glycol with acid potassium permanganate or acid dichromate results in the formation of formic acid by cleavage of carbon-carbon bond.



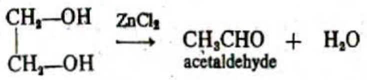
$$\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix} \xrightarrow[\text{or } K_2Cr_2O_7/HSO_4]{KMnO_4/H_2SO_4} 2H-\overset{\overset{O}{\|}}{C}-OH$$

(*iii*) When oxidised with lead tetra-acetate or periodic acid, ethylene glycol produces formaldehyde.



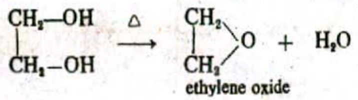
$$\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix} \xrightarrow[\text{or } HIO_4]{Pb(OCOCH_3)_4} 2H-\overset{\overset{O}{\|}}{C}-H$$

(7) *Dehydration.* (*i*) When heated with zinc chloride, ethylene glycol gives acetaldehyde.

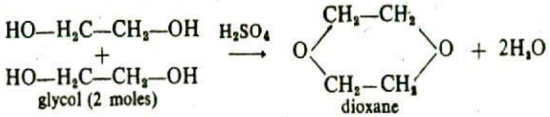


$$\begin{matrix}CH_2-OH\\|\\CH_2-OH\end{matrix} \xrightarrow{ZnCl_2} CH_3CHO + H_2O$$

(*ii*) When heated alone at 500°, it gives ethylene oxide.



(*iii*) Upon heating with concentrated sulphuric acid, it is converted to *dioxane* which is used as an industrial solvent.



Uses. Since glycol forms freezing mixtures with water (60 per cent solution freezing at —49°), it is sold under the name *Prestone* for use as anti-freeze for motor car radiators and as a cooling liquid in aeroplane motors. It is also used : (*i*) for preventing ice formation on aeroplane wings, (*ii*) in making low-freezing dynamite, (*iii*) as a preservative, (*iv*) as a dielectric in electrical condensers, and (*v*) as a starting material for numerous valuable compounds : nitroglycol, an explosive ; diglycol oleate, a rubber ; glycol stearate, a lubricant for watch springs ; monomethyl ether, a solvent for cellulose, terylene etc.

Ethylene Chlorohydrin, 2-*Chloroethanol*, $CH_2Cl{-}CH_2OH$.

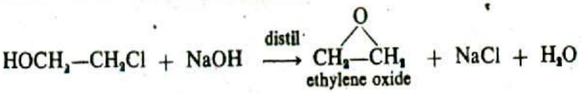
It is made on a large scale by bubbling ethylene into aqueous solution of hypochlorous acid (chlorine water)

$$H_2C{=}CH_2 + HOCl \longrightarrow \underset{\text{ethylene chlorohydrin}}{HOCH_2{-}CH_2Cl}$$

It is also obtained by the action of hydrogen chloride on glycol at 100°.

$$HOCH_2{-}CH_2OH + HCl \xrightarrow{100^\circ} HOCH_2{-}CH_2Cl$$

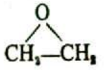
Properties. Ethylene chlorohydrin is a colourless liquid, bp 128·8°. It is miscible in water in all proportions. When distilled with concentrated alkali solution it yields ethylene oxide.



Ethylene chlorohydrin possesses two different functional groups and is useful in organic synthesis. For example, by heating with aqueous sodium cyanide it may be converted to ethylene cyanohydrin which upon hydrolysis with hydrochloric acid gives β-hydroxypropionic acid.

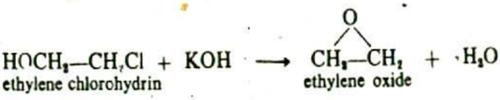
$$HOCH_2{-}CH_2Cl + NaCl \longrightarrow \underset{\text{ethylene cyanohydrin}}{HOCH_2{-}CH_2CN} + NaCl$$

$$HOCH_2{-}CH_2CN + 2H_2O \longrightarrow HOCH_2{-}CH_2COONH_4 \xrightarrow{HCl} \underset{\beta\text{-hydroxypropionic acid}}{HOCH_2{-}CH_2COOH} + NH_4Cl$$

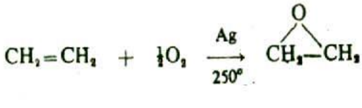
Ethylene Oxide, *Epoxyethane*, 

It is a cyclic ether and is isomeric with acetaldehyde.

Preparation. Ethylene oxide may be prepared by distilling ethylene chlorohydrin with concentrated potassium hydroxide solution.

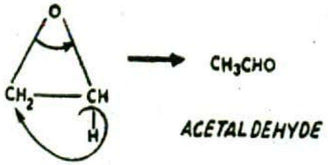


It is manufactured by passing ethylene and oxygen under pressure over a silver catalyst at 250°.

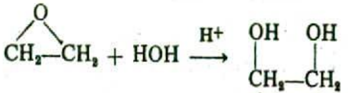


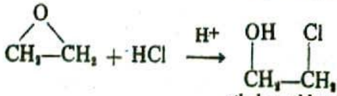
Properties. Ethylene oxide is a gas at ordinary temperature and pressure. Liquid substance boils at 13° and has ethereal smell. It is soluble in water, alcohol and ether.

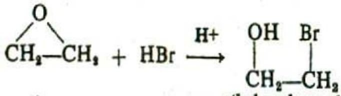
(1) Ethylene oxide upon heating undergoes molecular rearrangement to form acetaldehyde.

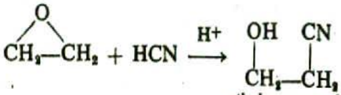


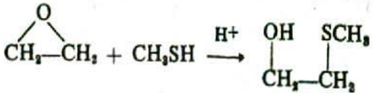
(2) *Ring-opening reactions in acid medium.* Ethylene oxide reacts with several reagents in acid medium when the oxide ring cleaves to form addition products. Thus it reacts with H_2O, HCl, HBr, HCN, CH_3SH to form ethylene glycol, ethylene chlorohydrin, ethylene bromohydrin, ethylene cyanohydrin and monothioethylene glycol respectively.


ethylene glycol

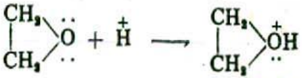

ethylene chlorohydrin

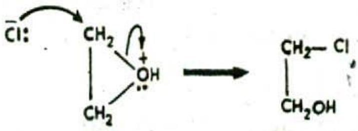

ethylene bromohydrin


ethylene cyanohydrin


monothioethylene glycol

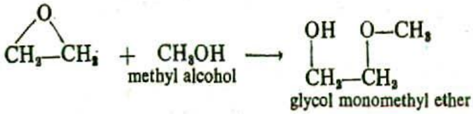
MECHANISM. In all the above reactions, ethylene oxide reacts with a proton to produce oxonium ion which is attacked by a nucleophile.

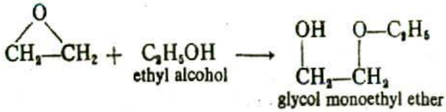

oxonium ion


ETHYLENE CHLOROHYDRIN

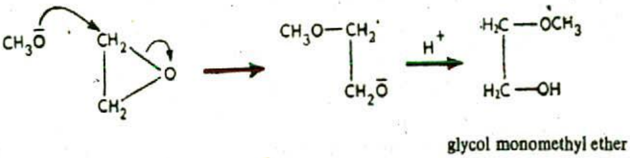
(3) *Ring-opening reactions in basic medium.* Ethylene oxide reacts with alcohols and ammonia under the influence of basic catalysts to form addition products—alcohol ethers or alcohol amines, by a rupture of the oxide ring.

(*i*) It reacts with alcohols upon heating under pressure to form monoalkyl ethers.



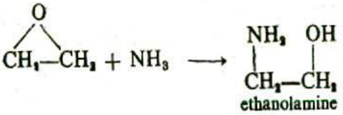


MECHANISM. In basic medium alcohols furnish alkoxy ions ($CH_3\bar{O}$, $C_2H_5\bar{O}$), and the reaction follows the following pathway.

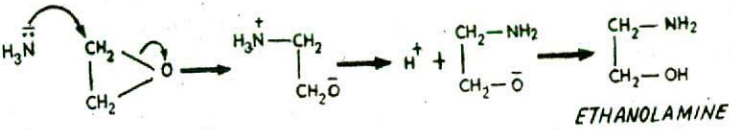


The glycol monomethyl ether is used as a solvent for cellulose acetate under the name 'cellosolve'. Ethyl and butyl alcohols give 'ethyl cellosolve' and 'butyl cellosolve'. The cellosolves contain both the alcohol and ether groups and are, therefore, excellent solvents for making lacquers.

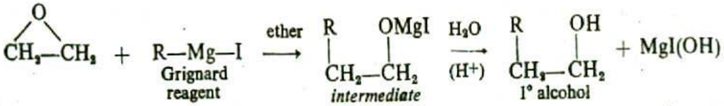
(*ii*) Ethylene glycol reacts with ammonia to give *ethanolamine*.



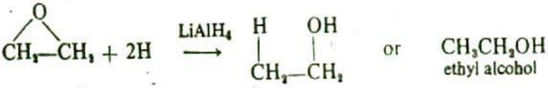
MECHANISM :



(*iii*) It reacts with Grignard reagents (RMgX) to form addition compounds as intermediates which upon acid hydrolysis yield 1° alcohols.



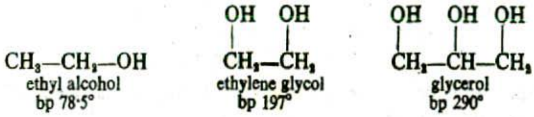
(4) Ethylene oxide when reduced with lithium aluminium hydride gives ethyl alcohol.



Uses. Ethylene oxide is an excellent fumigant and insecticide for grain, dried fruits and tobacco. It is used as starting material for manufacturing *cellosolves* required as solvents for cellulose acetate ; and for the synthesis of ethylene glycol.

TRIHYDRIC ALCOHOLS OR TRIOLS

Alcohols containing three OH groups are called the trihydric alcohols or **Triols**. The introduction of the third OH group in a diol molecule raises the boiling point by about 100°, increasing the viscosity, and makes the alcohol more sweet. An increase in the number of OH groups also enhances the hydrogen bonding ability and association, thereby raising the boiling points. Thus,



$$\underset{\text{ethyl alcohol, bp }78{\cdot}5^\circ}{CH_3{-}CH_2{-}OH} \qquad \underset{\text{ethylene glycol, bp }197^\circ}{\overset{OH}{\overset{|}{CH_2}}{-}\overset{OH}{\overset{|}{CH_2}}} \qquad \underset{\text{glycerol, bp }290^\circ}{\overset{OH}{\overset{|}{CH_2}}{-}\overset{OH}{\overset{|}{CH}}{-}\overset{OH}{\overset{|}{CH_2}}}$$

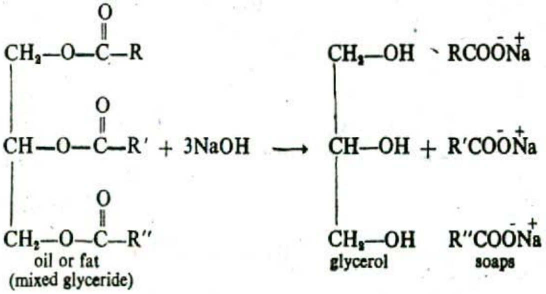
Chemically, triols give many reactions of the primary and secondary alcoholic groups which they may contain. They give the simple reactions of OH groups in triplicate. The only important member of the class is glycerol or 1, 2, 3-propanetriol.

GLYCEROL, *Glycerine, 1, 2, 3-Propanetriol*, $CH_2OH{-}CHOH{-}CH_2OH$

Glycerol is the simplest trihydric alcohol (triol). The name glycerol or glycerine was originally derived from the word *glyceros*, meaning sweet. Its IUPAC name is 1,2,3,-propanetriol since glycerol could be considered as trihydroxy derivative of propane. It occurs in almost all natural animal fats and vegetable oils as the glyceryl esters of higher organic acids.

Manufacture. Glycerol can be prepared industrially by the following methods.

(*i*) *By the Hydrolysis of Oils and Fats.* Natural oils and fats are the triesters of glycerol with higher organic acids, mainly palmitic acid, $CH_3(CH_2)_{14}COOH$, stearic acid, $CH_3(CH_2)_{16}COOH$, and oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$. Upon hydrolysis with alkali, the fats and oils produce glycerol and the salt of the above acids which are called soaps.



$$\underset{\substack{\text{oil or fat}\\\text{(mixed glyceride)}}}{\begin{array}{l} CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}R \\ | \\ CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}R' \\ | \\ CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}R'' \end{array}} + 3NaOH \longrightarrow \underset{\text{glycerol}}{\begin{array}{l} CH_2{-}OH \\ | \\ CH{-}OH \\ | \\ CH_2{-}OH \end{array}} \begin{array}{l} RCO\overset{-}{O}\overset{+}{Na} \\ \\ +\ R'CO\overset{-}{O}\overset{+}{Na} \\ \\ R''CO\overset{-}{O}\overset{+}{Na} \\ \text{soaps} \end{array}$$

The hydrolysis of fats is carried originally either for soap manufacture or for the production of stearic acid needed in the candle industry, and glycerol is obtained as a by-product. This is still a commercial source of glycerol.

Glycerol from Soap Manufacture. In soap manufacture, the fat is hydrolysed by boiling with alkali solution. The free fatty acids produced by hydrolysis react with the alkali to form solid soap while the glycerol is left in solution (*Spent lye*).

$$\text{Fat} + \text{alkali solution } (\textit{lye}) \longrightarrow \underbrace{\text{Glycerol} + \text{alkali left} + \text{Soap}}_{\textit{Spent lye}}$$

After the removal of soap, the spent lye containing 3 to 5 per cent glycerol is treated for its recovery. The impurities present in it are precipitated by adding alum and the filtrate concentrated by evaporation. Since glycerol decomposes much below its boiling point, the evaporation is carried under vacuum. The concentrated solution which now contains about 80 per cent glycerol is treated with animal charcoal and purified by distillation with super-heated steam under reduced pressure. The distillate is then evaporated *in vacuo* until the glycerol has specific gravity of 1·26.

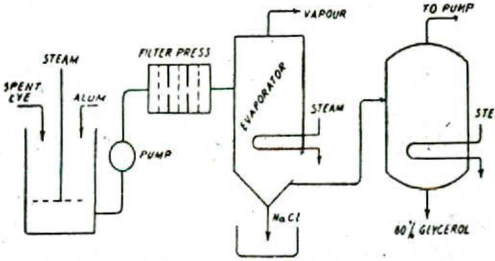


Fig. 17·1. Recovery of Glycerol from Spent Lye.

Glycerol from Candle Industry. In making candles from wax, the latter is mixed with a little stearic acid so that it may not soften on heating The stearic acid needed for the purpose is obtained by the hydrolysis of solid fats carried by heating with water (or steam) under pressure using sulphuric acid as a catalyst. The solid stearic acid is removed and the remaining solution (*Sweet Water*) after neutralisation is treated for the recovery of glycerol as described before.

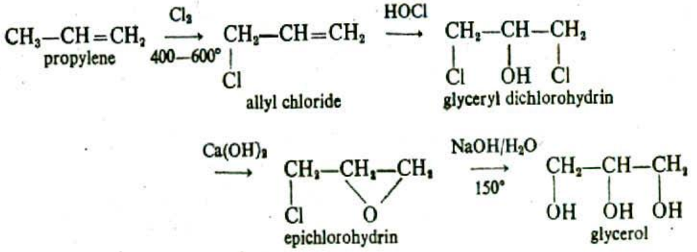
(2) *By the Fermentation of Sugar.* Glycerol is also obtained by the fermentation of molasses or sugar in the presence of sodium sulphite.

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{Na_2SO_3} \underset{\text{glycerol}}{C_3H_5(OH)_3} + \underset{\text{acetaldehyde}}{CH_3CHO} + CO_2$$

Sodium sulphite upon hydrolysis yields an alkaline medium which favours the above course of fermentation. The yield of glycerol is as high as 20—25 per cent. This method was used by Germany during war when there was acute shortage of fats.

(3) *Synthetic Methods.* In USA over half the annual production of glycerol is now made by synthetic methods. In the following two methods propylene obtained from petroleum is the starting material.

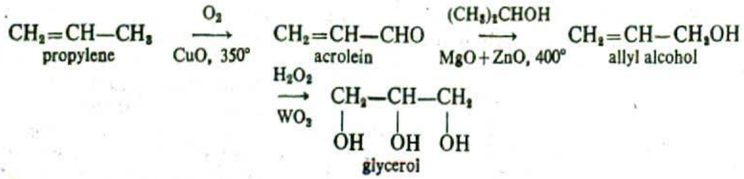
(*a*) *via* ALLYL CHLORIDE. Propylene is chlorinated at 400—600° to give allyl chloride which upon treatment with hypochlorous acid gives glyceryl dichlorohydrin. The dichlorohydrin when reacted with lime forms epichlorohydrin which when hydrolysed with sodium hydroxide yields glycerol.



$$\underset{\text{propylene}}{CH_3-CH=CH_2} \xrightarrow[400-600^\circ]{Cl_2} \underset{\text{allyl chloride}}{\underset{Cl}{CH_2}-CH=CH_2} \xrightarrow{HOCl} \underset{\text{glyceryl dichlorohydrin}}{\underset{Cl}{CH_2}-\underset{OH}{CH}-\underset{Cl}{CH_2}}$$

$$\xrightarrow{Ca(OH)_2} \underset{\text{epichlorohydrin}}{\underset{Cl}{CH_2}-CH_2-CH_2 \text{ (O bridge)}} \xrightarrow[150^\circ]{NaOH/H_2O} \underset{\text{glycerol}}{\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}}$$

(*b*) *via* ACROLEIN. Propylene is oxidised with oxygen in the presence of CuO catalyst at 350° to produce acrolein. This is then reduced to allyl alcohol by isopropyl alcohol in the presence of MgO + ZnO catalyst at 400°. The allyl alcohol upon addition of hydrogen peroxide in the presence of tungsten oxide (WO_3) as catalyst yields glycerol.



$$\underset{\text{propylene}}{CH_2{=}CH{-}CH_3} \xrightarrow[CuO,\ 350°]{O_2} \underset{\text{acrolein}}{CH_2{=}CH{-}CHO} \xrightarrow[MgO+ZnO,\ 400°]{(CH_3)_2CHOH} \underset{\text{allyl alcohol}}{CH_2{=}CH{-}CH_2OH}$$

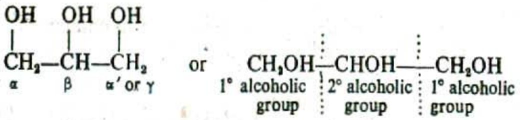
$$\xrightarrow[WO_3]{H_2O_2} \underset{\text{glycerol}}{\begin{array}{ccc} CH_2 & {-}CH{-} & CH_2 \\ | & | & | \\ OH & OH & OH \end{array}}$$

In a country like India where petroleum is not found in abundance, propylene required for the above syntheses may also be obtained from acetone of the wood distillation industry.

$$\underset{\text{acetone}}{CH_3{-}CO{-}CH_3} \xrightarrow{+2H} \underset{\text{isopropyl alcohol}}{CH_3{-}CHOH{-}CH_3} \xrightarrow{-H_2O} \underset{\text{propylene}}{CH_3{-}CH{=}CH_2}$$

Properties (*Physical*). Glycerol is a colourless and odourless thick syrupy liquid having a sweet taste. It boils at 290° with slight decomposition. On cooling glycerol forms transparent solid crystals, mp 17°. It is hygroscopic and water soluble, but it is insoluble in ether. It is nontoxic.

(*Chemical*). Glycerol molecule is made of two primary alcoholic groups and one secondary alcoholic group, and it undergoes many of the reactions to be expected of these types of alcohols.

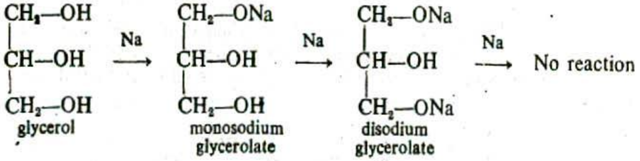


$$\begin{array}{ccc} OH & OH & OH \\ | & | & | \\ CH_2 & {-}CH{-} & CH_2 \\ \alpha & \beta & \alpha' \text{ or } \gamma \end{array} \quad \text{or} \quad \begin{array}{c|c|c} CH_2OH{-} & CHOH{-} & {-}CH_2OH \\ 1° \text{ alcoholic group} & 2° \text{ alcoholic group} & 1° \text{ alcoholic group} \end{array}$$

The carbon atoms in glycerol are indicated as α, β, α′, or γ as shown above.

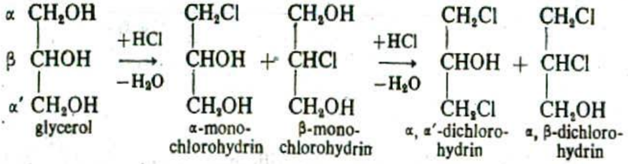
In general, the two primary alcoholic groups are more reactive than the secondary alcoholic group. Some of the reactions that are characteristic of monohydric compounds are modified to a certain extent by the presence of three OH groups in the same molecule.

(1) *Reaction with Sodium*. When glycerol is treated with sodium at room temperature, one α-hydroxyl group is attacked to form monosodium glycerolate. At higher temperatures the second α-hydroxyl is also attacked to give disodium glycerolate. β-hydroxyl group, however, does not react at all.



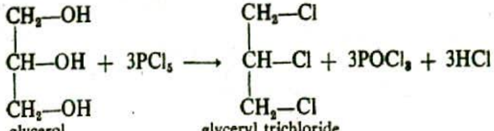
$$\underset{\text{glycerol}}{\begin{array}{l} CH_2{-}OH \\ | \\ CH{-}OH \\ | \\ CH_2{-}OH \end{array}} \xrightarrow{Na} \underset{\text{monosodium glycerolate}}{\begin{array}{l} CH_2{-}ONa \\ | \\ CH{-}OH \\ | \\ CH_2{-}OH \end{array}} \xrightarrow{Na} \underset{\text{disodium glycerolate}}{\begin{array}{l} CH_2{-}ONa \\ | \\ CH{-}OH \\ | \\ CH_2{-}ONa \end{array}} \xrightarrow{Na} \text{No reaction}$$

(2) *Reaction with Hydrogen Chloride*. When hydrogen chloride is passed into glycerol at 110°, both α- and β-glycerol monochlorohydrins are obtained. Upon continued action of hydrogen chloride at 110° glycerol α, α′-dichlorohydrin and glycerol α, β-dichlorohydrin are produced.



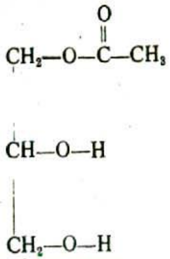
$$\underset{\text{glycerol}}{\begin{array}{ll} \alpha & CH_2OH \\ & | \\ \beta & CHOH \\ & | \\ \alpha' & CH_2OH \end{array}} \xrightarrow[-H_2O]{+HCl} \underset{\alpha\text{-monochlorohydrin}}{\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\beta\text{-monochlorohydrin}}{\begin{array}{l} CH_2OH \\ | \\ CHCl \\ | \\ CH_2OH \end{array}} \xrightarrow[-H_2O]{+HCl} \underset{\alpha,\alpha'\text{-dichlorohydrin}}{\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array}} + \underset{\alpha,\beta\text{-dichlorohydrin}}{\begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2OH \end{array}}$$

(3) *Reaction with Phosphorus Pentachloride*. Glycerol reacts with phosphorus pentachloride to form glyceryl trichloride, all the three OH groups in it being replaced by Cl atoms.



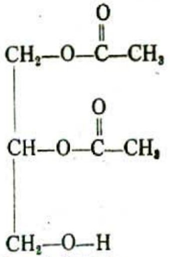
$$\begin{array}{l}CH_2-OH\\ |\\ CH-OH\\ |\\ CH_2-OH\\ \text{glycerol}\end{array} + 3PCl_5 \longrightarrow \begin{array}{l}CH_2-Cl\\ |\\ CH-Cl\\ |\\ CH_2-Cl\\ \text{glyceryl trichloride}\end{array} + 3POCl_3 + 3HCl$$

(4) *Reaction with Organic Acids.* When glycerol is treated with monocarboxylic acids, *mono-*, *di-* or *tri-esters* may be obtained depending on the amount of acid used. With acetic acid and acetic anhydride, glycerol forms three esters.



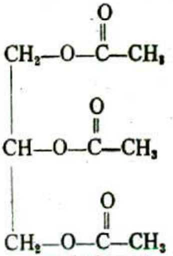
$$\begin{array}{l}CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3\\ |\\ CH-O-H\\ |\\ CH_2-O-H\end{array}$$

glyceryl monoacetate



$$\begin{array}{l}CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3\\ |\\ CH-O-\overset{\overset{O}{\|}}{C}-CH_3\\ |\\ CH_2-O-H\end{array}$$

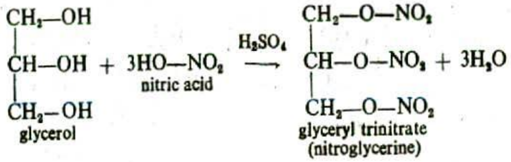
glyceryl diacetate



$$\begin{array}{l}CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3\\ |\\ CH-O-\overset{\overset{O}{\|}}{C}-CH_3\\ |\\ CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3\end{array}$$

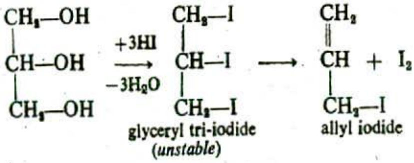
glyceryl triacetate

(5) *Reaction with Nitric Acid.* Glycerol reacts with nitric acid in the presence of sulphuric acid at temperatures below 25° to form glyceryl trinitrate, commonly known as *nitroglycerine*.



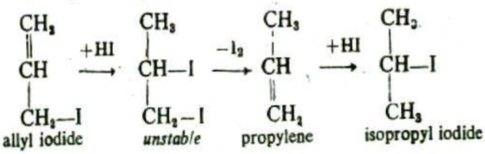
$$\begin{array}{l}CH_2-OH\\ |\\ CH-OH\\ |\\ CH_2-OH\\ \text{glycerol}\end{array} + \underset{\text{nitric acid}}{3HO-NO_2} \xrightarrow{H_2SO_4} \begin{array}{l}CH_2-O-NO_2\\ |\\ CH-O-NO_2\\ |\\ CH_2-O-NO_2\\ \text{glyceryl trinitrate}\\ \text{(nitroglycerine)}\end{array} + 3H_2O$$

(6) **Reaction with Hydrogen Iodide.** (*a*) When glycerol is warmed with a small amount of hydrogen iodide, it gives glyceryl tri-iodide. The tri-iodide being unstable at once splits out a molecule of iodine to form allyl iodide.



$$\begin{array}{l}CH_2-OH\\ |\\ CH-OH\\ |\\ CH_2-OH\end{array} \xrightarrow[-3H_2O]{+3HI} \begin{array}{l}CH_2-I\\ |\\ CH-I\\ |\\ CH_2-I\\ \text{glyceryl tri-iodide}\\ (\textit{unstable})\end{array} \longrightarrow \begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2-I\\ \text{allyl iodide}\end{array} + I_2$$

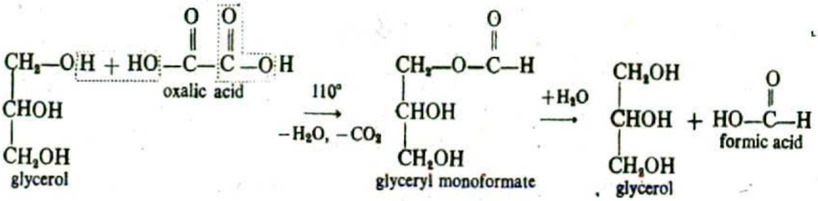
(*b*) When glycerol is heated with a large amount of hydrogen iodide, allyl iodide first produced as above is reduced to propylene. In the presence of excess of hydrogen iodide, propylene adds a molecule of hydrogen iodide giving isopropyl iodide.



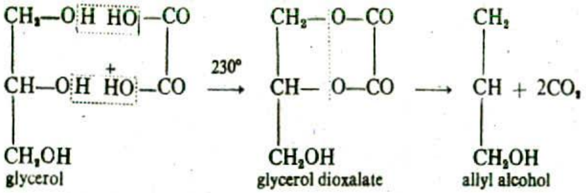
$$\begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2-I\\ \text{allyl iodide}\end{array} \xrightarrow{+HI} \begin{array}{l}CH_3\\ |\\ CH-I\\ |\\ CH_2-I\\ \textit{unstable}\end{array} \xrightarrow{-I_2} \begin{array}{l}CH_3\\ |\\ CH\\ \|\\ CH_2\\ \text{propylene}\end{array} \xrightarrow{+HI} \begin{array}{l}CH_3\\ |\\ CH-I\\ |\\ CH_3\\ \text{isopropyl iodide}\end{array}$$

(7) *Reaction with Oxalic acid.* Glycerol reacts with oxalic acid in two ways.

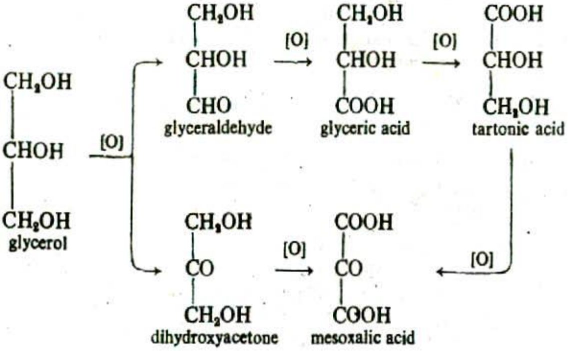
(*a*) **Formation of Formic acid.** When heated with crystalline oxalic acid to 110°, glycerol forms glycerol monoformate which upon hydrolysis gives formic acid and glycerol is regenerated.



(*b*) **Formation of Allyl alcohol.** When glycerol is heated with oxalic acid to 230°, glycerol dioxalate is produced. It at once splits out two molecules of carbon dioxide and forms allyl alcohol.

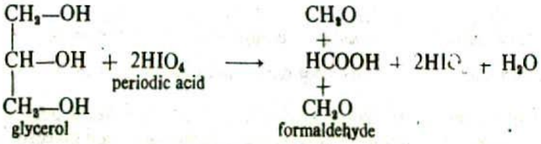


(8) *Oxidation.* The two primary alcohol groups in glycerol are capable of being oxidised to the aldehyde and then the carboxyl group, while the secondary alcohol group can be oxidised to the carbonyl group. Thus glycerol can give rise to a variety of oxidation products depending on the nature of the oxidising agent used.



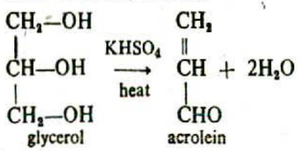
Thus dilute nitric acid converts glycerol into glyceric acid and tartonic acid, while concentrated nitric acid oxidises it to mainly glyceric acid. Bismuth nitrate produces mainly mesoxalic acid. Sodium hypobromite, or hydrogen peroxide and ferrous sulphate (Fenton's reagent) oxidises glycerol to a mixture of glyceraldehyde and dihydroxyacetone.

Glycerol undergoes oxidative cleavage by periodic acid giving formaldehyde and formic acid.



When glycerol is dropped on solid potassium permanganate, it is ignited by the heat of reaction and burns with a blue flame.

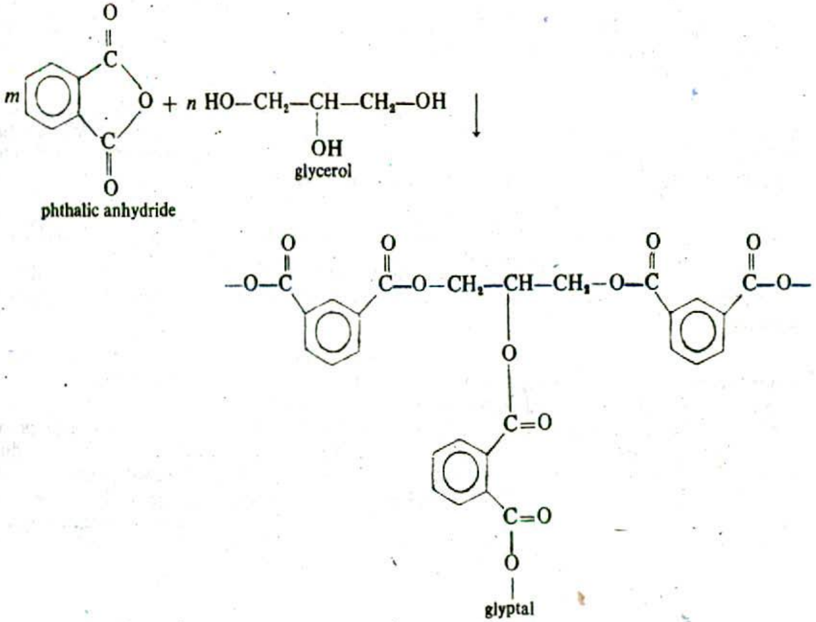
(9) *Dehydration.* When heated alone or with potassium hydrogensulphate, glycerol eliminates two molecules of water to form acrolein.



$$\begin{array}{l}CH_2-OH\\ |\\ CH-OH\\ |\\ CH_2-OH\end{array} \xrightarrow[heat]{KHSO_4} \begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CHO\end{array} + 2H_2O$$

This reaction is often used as a qualitative test for the presence of glycerol, since acrolein is easily detected on account of its peculiar odour.

(10) *Formation of Glyptal resins.* Glycerol reacts with phthalic anhydride forming polyesters known as glyptals. Each of the three OH groups in glycerol forms an ester linkage with the anhydride, giving a thermosetting polymer (*plastic*) used for making synthetic fibers.



Uses. Glycerol is used :

(*i*) as a sweetening agent in beverages and confectionary ;

(*ii*) in the preparation of high class toilet soaps and cosmetics;

(*iii*) in preserving tobacco from drying out ;

(*iv*) as *antifreeze* in automobile radiators ;

(*v*) for lubricating fine machinery such as watches and clocks;

(*vi*) as a preservative for fruits and other eatables which require to be kept moist;

(*vii*) in making printing inks and inks for stamp pads ;

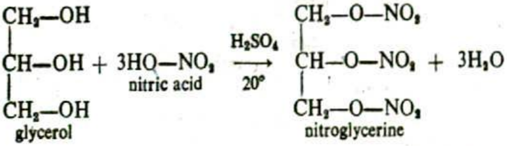
(*viii*) in the preparation of nitroglycerine ;

(*ix*) as a starting material for several allyl and propyl derivatives ; and

(*x*) for the manufacture of glyptal plastics used for artificial fibers.

Nitroglycerine, *Glyceryl trinitrate*, $C_3H_5(ONO_2)_3$. The name 'nitroglycerine' assigned to ubstance is incorrect. It is a triester of glycerol and nitric acid, and hence the proper name ld be *glyceryl trinitrate* or simply *glyceryl nitrate*.

Preparation. Nitroglycerine is manufactured by adding glycerol slowly to a mixture of nitric acid and sulphuric acid maintained at 20°.



$$\begin{array}{l}CH_2{-}OH\\ |\\ CH{-}OH\\ |\\ CH_2{-}OH\\ \text{glycerol}\end{array} + \underset{\text{nitric acid}}{3HO{-}NO_2} \xrightarrow[20^\circ]{H_2SO_4} \begin{array}{l}CH_2{-}O{-}NO_2\\ |\\ CH{-}O{-}NO_2\\ |\\ CH_2{-}O{-}NO_2\\ \text{nitroglycerine}\end{array} + 3H_2O$$

After the reaction is complete, the mixture is run into ice cold water. The oily layer of nitro glycerine that separates at the top is removed. It is washed with water and then with sodium carbonate solution to remove any acids. It is finally dried by passing through a mat of sponges.

Properties. Nitroglycerine is a colourless oily liquid (sp gr 1·6) with a sweet burning taste. Upon cooling it forms crystals, mp 13·2°. It is insoluble in water but dissolves readily in alcohol and ether. It is poisonous, its vapour causing violent headache and loss of consciousness.

The most important property of nitroglycerine is its explosive power. Its molecule having nitrogen fully loaded with oxygen is very susceptible to external shock. When struck a sharp blow, it explodes with great violence. The explosion reaction consists of internal combustion attended by splitting out of elemental nitrogen.

$$4C_3H_5(ONO_2)_3 \xrightarrow{\text{shock}} 6N_2(g) + 12CO_2(g) + 10H_2O(g) + O_2(g)$$

The sudden liberation of the large volumes of gases in a space initially occupied by the liquid substance causes an explosion wave of enormous pressure, accounting for the damaging effect of detonation.

Uses. As an Explosive. Nitroglycerine was first prepared in 1866 but its use as explosive proved to be dangerous as it exploded almost whimsically on receiving the slightest shock during transportation. In 1866 Alfred Nobel discovered that when absorbed in '*kieslguhr*', a porous earth, nitroglycerine could be transported without risk of explosion. The explosive so prepared was called **Dynamite**. Now-a-days the dynamite is made by using adsorbents such as dust or starch in place of kieslguhr and ammonium nitrate (or sodium nitrate) is added to ensure complete combustion of these materials. Modern explosives such as *blasting gelatin* and *cordite* contain nitroglycerine mixed with *gun cotton* (cellulose nitrate). Dynamite is used to shoot oil wells and in building roads, dams and tunnels where the removal of rock and earth is required.

(2) As a Medicine. Nitroglycerine is used as a medicine for treatment of heart disease *angina pictoris*, and also for asthma as it dilates the blood vessels and thus relieves blood pressure.

QUESTIONS

1. How is ethylene glycol prepared ? How does it react with : (*a*) PI_3 ; (*b*) HIO_4 ; and (*c*) CH_3CHO/H^+.

2. How can you obtain oxalic acid, succinic acid, ethylene, acetylene, and chlorohydrin from ethylene glycol ? Give reaction equations only.

3. How is ethylene oxide prepared ? How does it react with :
(*a*) H_2O/H^+ ; (*b*) CH_3OH ; (*c*) HCl ; (*d*) CH_3MgI, then H_2O/H^+ (*Jabalpur BSc, 1993*)

4. How is glycerol prepared from propene ? How does it react with :
(*a*) HI ; (*b*) Oxalic acid ; (*c*) HNO_3 ; (*d*) Fused $KHSO_4$ (*Aligarh BSc, 1993*)

5. How is glycerol manufactured from natural oils and fats ? What is the action of the following reagents on glycerol ?
(*a*) Nitric acid ; (*b*) Hydrogen iodide ; (*c*) Oxalic acid ; (*d*) Potassium hydrogen sulphate. (*Magadh BSc Hons, 1993*)

6. How is glycerol prepared from oils ? Explain with equations. Starting from glycerol how are the following compounds prepared : (*i*) Nitroglycerine ; and (*ii*) Isopropyl iodide. (*Banaras BSc, 1994*)

7. What happens when :

(*a*) Glycerol is heated with $KHSO_4$.

(*b*) Glycerol is heated with oxalic acid (*Meerut BSc, 1993; Madras BSc, 1994*)

8. How will you synthesise the following compounds from glycerol :

(*a*) Allyl alcohol (*Calicut BSc, 1994*)

(*b*) Acrolein (*Jabalpur BSc, 1993*)

(*c*) Nitroglycerine (*Karnataka BSc, 1994*)

9. Write a step-by-step mechanism for the Pinacol-Pinacalone rearrangement.

(*Saugar BSc, 1993 ; North Eastern Hill BSc, 1994*)

10. Explain : The boiling point of ethylene glycol (198°C) is so much higher than that of 1-propanol (97°C) even though their molecular weights are about the same.

11. A compound of formula $C_3H_8O_2$ undergoes acetylation with acetic anhydride to form a derivative of the formula $C_7H_{12}O_4$. Determine the number of hydroxyl groups present in the compound. What is its possible structure ?

Answer. There are *two* -OH groups. The compound could be 1,2-Propanediol *or* 1,3-Propanediol.

12. A compound of formula $C_3H_8O_3$ undergoes acetylation with acetic anhydride to form a derivative of the formula $C_9H_{14}O_6$. Determine the number of hydroxyl groups in the compound ? What is its possible structure ?

Answer. There are *three* -OH groups. The compound is 1,2,3-Propanetriol (Glycerol).

Chapter 18

Ethers

Ethers are a class of compounds which contain an oxygen linked to two alkyl or hydrocarbon groups by single bonds,

$$R{-}O{-}R$$

They are designated as **Symmetrical ethers** (simple ethers) or **Unsymmetrical ethers** (mixed ethers) according as the two alkyl groups bonded to oxygen atom are same or different.

$R{-}O{-}R$	$R{-}O{-}R'$
e.g. $CH_3{-}O{-}CH_3$	*e.g.* $CH_3{-}O{-}C_2H_5$
Symmetrical ether or simple ether	**Unsymmetrical ether or Mixed ether**

The functional group of ethers is C—O—C which is often referred to as *'ethereal group'*. The oxygen atom flanked by two carbons is called 'ethereal oxygen'.

Ethers may be considered as derivatives of alkanes obtained by replacing a $-CH_2-$ group by —O—.

$R{-}CH_2{-}R$	$R{-}O{-}R$
alkane	ether

These compounds are also looked upon as the monoalkyl derivatives of alcohols and dialkyl derivatives of water.

$R{-}O{-}H$	$R{-}O{-}R$	$H{-}O{-}H$
alcohol	ether	water

STRUCTURE

The oxygen atom in ethers forms a bridge between the two alkyl groups by forming two single bonds; one with each of the two groups. Thus, the electronic structure of ethers may be written as

$$R \overset{\times}{\cdot}\overset{..}{\underset{..}{O}}\overset{\times}{\cdot} R' \quad \text{or} \quad R{-}\overset{..}{\underset{..}{O}}{-}R' \quad \text{or} \quad R{-}O{-}R'$$

In orbital representation of ethers, it may be considered that the two single or σ bonds are produced as a result of overlap between two half-filled p orbitals on oxygen and two sp^3-hybridised orbitals on alkyl groups (one belonging to each group). Since these two p orbitals of oxygen are perpendicular to each other, the resultant $\angle$ R—O—R' must be 90°.

But experimental evidence suggests that ∠ROR′ is 110°.

This value of bond angle suggests the presence of sp^3-hybridised orbitals on oxygen of ethers similar to oxygen in water. The ∠ H—O—H in water is 105° and this divergence from the tetrahedral angle of 109° 28′ may be attributed to lone pair—lone pair repulsions which decrease the bond angle. On the other hand, in ethers the repulsions between the bulkier alkyl groups almost counterbalance the effect of lone pair—lone pair interactions and tetrahedral angle is almost retained. This justifies an R—O—R′ angle of 110° in ethers (Fig. 18·2).

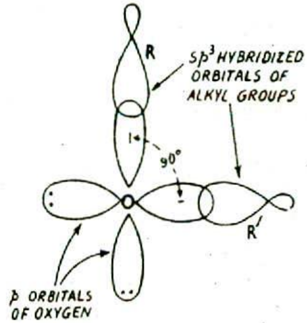


Fig. 18·1. Orbital representation of an Ether molecule

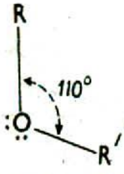


Fig. 18·2. Geometry of ether

NOMENCLATURE

(1) **The Common System.** Ethers are commonly named by giving the names of the two alkyl groups bonded to oxygen as separate words in alphabetical order and adding 'ether' as the third word. Thus,

$CH_3—O—C_2H_5$	$CH_3—O—CH_2CH_2CH_3$
ethyl methyl ether	methyl n-propyl ether

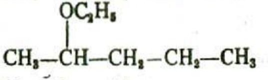
When the two alkyl groups linked to oxygen are same (R—O—R), the ether is named 'dialkyl ether'. But it is a common practice to out the prefix 'di'. Thus,

$CH_3—O—CH_3$	dimethyl ether or methyl ether
$C_2H_5—O—C_2H_5$	diethyl ether or ethyl ether

In everyday laboratory language, the name 'ether' unqualified means diethyl ether.

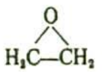
(2) **The IUPAC System.** This system allows symmetrical ethers to retain their common names because these have become too familiar. However, when an unsymmetrical ether which is made of a relatively small alkyl group and a much larger one, the small alkyl group plus the oxygen atom (alkoxy group RO—) is treated as a substituent on the large alkyl group. Thus the ether is named as alkoxy derivative of the parent hydrocarbon of the large alkyl chain. The position of the alkoxy substituent is indicated by the number of the carbon to which it is attached. Thus,

$CH_3—O—CH_2—CH_2—CH_3$ 1-methoxypropane

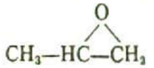


$CH_3—\overset{OC_2H_5}{\overset{|}{C}}H—CH_2—CH_2—CH_3$ 2-ethoxypentane

(3) **Cyclic Ethers** formed between oxygen and two adjacent carbon atoms are known as *oxides* or *epoxy compounds*. They are either named as the oxides of the corresponding alkenes or as epoxy derivatives of the alkanes. Thus,



epoxyethane, ethylene oxide

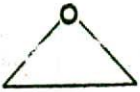


1, 2-epoxypropane, propylene oxide

In large cyclic ethers, the oxygen is treated as a substitute for a methylene group, its location given by a number and the prefix 'oxa'. Thus,

Oxacyclohexane

However, the lower molecular weight cyclic ethers have trivial names (given in brackets) which are ordinarily used.



OXIRANE (ETHYLENE OXIDE)

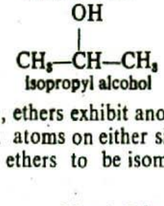
OXETANE (TRIMETHYLENE OXIDE)

1,4-DIOXANE

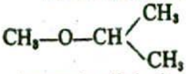
ISOMERISM

Ethers exhibit two types of isomerism :

(1) **Functional isomerism.** Ethers show functional isomerism with alcohols having the same carbon content. Thus each ether has one or more isomeric alcohols. The number of isomeric alcohols corresponding to an individual ether goes on increasing as we go higher in the series. Thus,

Molecular formula	*Ether*	*Isomeric alcohols*
C_2H_6O	$CH_3{-}O{-}CH_3$ dimethyl ether	CH_3CH_2OH ethyl alcohol
$C_4H_{10}O$	$CH_3{-}CH_2{-}O{-}CH_2{-}CH_3$ diethyl ether	$CH_3{-}CH_2{-}CH_2{-}OH$ *n*-popyl alcohol
		 $CH_3{-}\overset{\overset{\large OH}{\vert}}{C}H{-}CH_3$ Isopropyl alcohol

(2) **Metamerism.** In addition to the usual chain isomerism, ethers exhibit another type of isomerism due to the presence of unequal number of carbon atoms on either side of the ethereal oxygen. This is called *metamerism* and enables simple ethers to be isomeric with mixed ethers. For example,

Molecular formula	*Simple Ether*	*Mixed Ethers*
$C_4H_{10}O$	$CH_3{-}CH_2{-}O{-}CH_2{-}CH_3$ diethyl ether	$CH_3{-}O{-}CH_2{-}CH_2{-}CH_3$ methyl-*n*-propyl ether
		 $CH_3{-}O{-}CH\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_3\end{smallmatrix}$ isopropyl methyl ether

METHODS OF PREPARATION

Directly or indirectly, ethers are always prepared from alcohols. The general methods of synthesis of ethers are given below.

(1) **Dehydration of Alcohols.** Symmetrical ethers are prepared by heating an alcohol with concentrated sulphuric acid. Two molecules of the alcohol eliminate a molecule of water to form ether.

$$\underset{\text{alcohol}}{2ROH} \xrightarrow[140^\circ]{H_2SO_4} \underset{\text{ether}}{R{-}O{-}R} + H_2O$$

e.g.,
$$\underset{\text{ethyl alcohol}}{2CH_3CH_2OH} \xrightarrow[140^\circ]{H_2SO_4} \underset{\text{diethyl ether}}{CH_3CH_2{-}O{-}CH_2CH_3} + H_2O$$

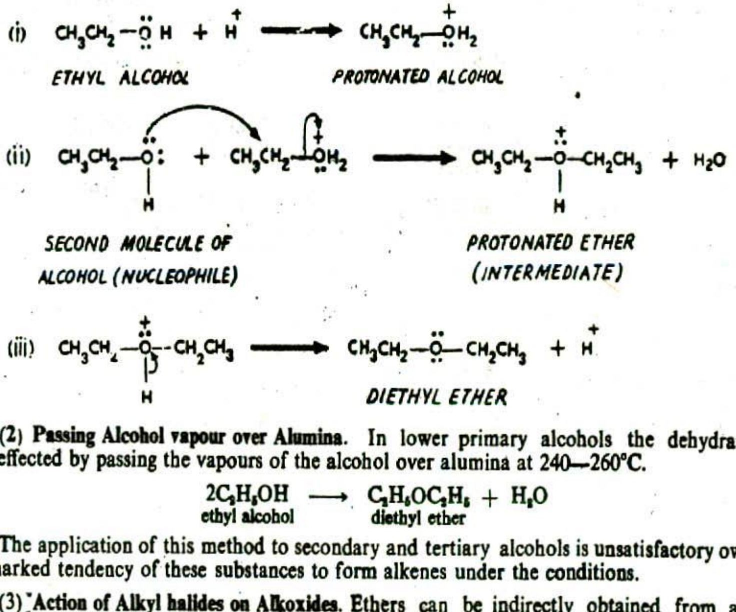
Diethyl ether boils at 35° and is removed from the reaction mixture as it is produced.

The success of this method depends upon the careful control of experimental conditions. The temperature is kept at 140° and alcohol used in excess. If the temperature increases to 150°, significant amounts of alkenes are obtained. Thus at 160°, the product from ethyl alcohol and sulphuric acid is mainly ethylene which is produced by intramolecular dehydration of alcohol.

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} \xrightarrow[160^\circ]{H_2SO_4} \underset{\text{ethylene}}{CH_2{=}CH_2} + H_2O$$

While primary alcohols, and to some extent secondary alcohols, react with sulphuric acid at 140° to form ethers, tertiary alcohols almost exclusively yield alkenes.

MECHANISM. The reaction of ethyl alcohol and conc sulphuric acid which furnishes H+ ions takes place by the following steps. The first step is the protonation of alcohol and this is followed by nucleophilic substitution by a second molecule of alcohol (S_N1 process). The resulting intermediate (protonated ether) then loses a proton to give ether.



(2) Passing Alcohol vapour over Alumina. In lower primary alcohols the dehydration may be effected by passing the vapours of the alcohol over alumina at 240—260°C.

$$\underset{\text{ethyl alcohol}}{2C_2H_5OH} \longrightarrow \underset{\text{diethyl ether}}{C_2H_5OC_2H_5} + H_2O$$

The application of this method to secondary and tertiary alcohols is unsatisfactory owing to the marked tendency of these substances to form alkenes under the conditions.

(3) **Action of Alkyl halides on Alkoxides.** Ethers can be indirectly obtained from alcohols by converting them to alkoxides and then reacting them with alkyl halides (**Williamson's Synthesis**).

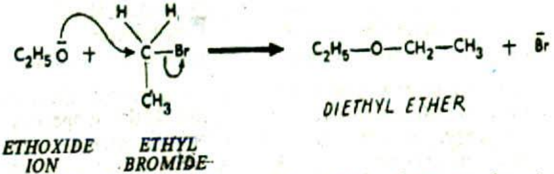
$$\underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{sod ethoxide}}{2C_2H_5O^-Na^+} + H_2$$

$$C_2H_5O^-Na^+ + \underset{\text{ethyl bromide}}{BrC_2H_5} \longrightarrow \underset{\text{diethyl ether}}{C_2H_5{-}O{-}C_2H_5} + Na^+Br^-$$

By taking a different alkyl halide, we can get mixed ether by this method.

$$C_2H_5O^-Na^+ + \underset{\text{methyl iodide}}{ICH_3} \longrightarrow \underset{\text{ethyl methyl ether}}{C_2H_5{-}O{-}CH_3} + Na^+I^-$$

This method is not applicable to tertiary alkyl halides because the alkoxide ions being both powerful nucleophiles and bases would bring dehydrohalogenation of the tertiary alkyl halides to form alkenes preferentially. However, Williamson's synthesis is very successful with primary alkyl halides and then the mechanism is usually S_N2. Thus,



(4) **Heating Alkyl halides with Silver oxide.** Simple ethers can be obtained by boiling alkyl halides with *dry* silver oxide (Ag_2O). Thus,

$$\begin{array}{c} C_2H_5I \\ C_2H_5I \\ \text{ethyl iodide} \end{array} + Ag_2O \longrightarrow \begin{array}{c} C_2H_5 \\ C_2H_5 \\ \text{diethyl ether} \end{array}\!\!> O + 2AgI$$

It may be considered a sort of double decomposition taking place between the alkyl halide and silver oxide.

By taking a mixture of two different alkyl halides the method can be used for the formation of *mixed ethers.*

(5) **Action of a lower Halogenated ether with a Grignard reagent.** This is a good method for preparing higher ethers from lower members. Thus,

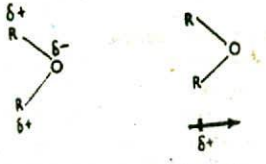
$$\underset{\text{monochlorodimethyl ether}}{CH_3OCH_2Cl} + \underset{\text{ethylmagnesium bromide}}{BrMgC_2H_5} \longrightarrow \underset{\text{methyl propyl ether}}{CH_3OCH_2C_2H_5} + Mg(Br)Cl$$

$$\underset{\text{monochlorodimetyl ether}}{CH_3OCH_2Cl} + BrMgC_2H_5 \longrightarrow \underset{\text{methyl propyl ether}}{CH_3OCH_2C_2H_5} + Mg\begin{array}{l} Br \\ Cl \end{array}$$

PHYSICAL PROPERTIES

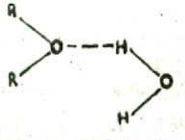
(1) Excepting dimethyl ether and ethyl methyl ether both of which are gases, all ethers are colourless liquids with pleasant odours.

(2) Ether molecules are slightly polar (1·18 D for dimethyl ether).



The small polarity, however, does not affect their boiling points appreciably which are much the same as that of alkanes of comparable molecular weights. Unlike alcohols, ethers cannot form hydrogen bonds since they themselves have no –OH groups and hence they have lower boiling points than the isomeric alcohols.

(3) Ethers are slightly soluble in water. This is attributed to formation of hydrogen bonds between water and the ether oxygen.



(4) Their specific gravities and boiling points show a gradual increase with increase in molecular weights.

(5) Lower ethers act as anaesthetics.

Table. Physical Proporties of some Ethers

Name of Ether	*Boiling Point*	*Specific Gravity*
Dimethyl ether, $CH_3—O—CH_3$	−24°	
Ethyl methyl ether, $CH_3—O—C_2H_5$	7·9°	0·7260 (0°)
Diethyl ether, $C_2H_5—O—C_2H_5$	35°	0·7135 (20°)
Methyl propyl ether, $CH_3—O—C_3H_7$	39°	0·7460
Ethyl propyl ether, $C_2H_5—O—C_3H_7$	61°	0·7546 (0°)
Dipropyl ether, $C_3H_7—O—C_3H_7$	91°	0·7360 (20°)

CHEMICAL PROPERTIES

The chemical behaviour of ethers follows from their structure. They consist of two alkyl groups linked to an oxygen atom.

R	—O—	R′
Alkyl group	Ethereal oxygen	Alkyl group

(*i*) At the hydrocarbon group ethers behave exactly like alkanes, undergoing halogenation.

(*ii*) The *ethereal* oxygen (linked to two carbons) is inert. However by virtue of lone pairs at the oxygen atom, ethers are capable of forming co-ordination complexes with electron deficient compounds.

(*iii*) Unlike carbon-to-carbon linkage, carbon-to-oxygen linkage is not very stable. Although unaffected under ordinary conditions, ethers can be made to react with water, acids, phosphorus pentachloride etc., when one or both the oxygen bonds are ruptured.

The general reactions of ethers are given below.

(1) **Inertness.** Owing to the absence of active groups and multiple bonds from their molecules, ethers are comparatively inert substances. The reagents like ammonia, alkalis, dilute acids and metallic sodium have no action upon them in cold. They are not readily oxidised or reduced.

SUBSTITUTION REACTIONS OF THE ALKYL GROUPS

(2) **Halogenation**. Ethers when heated with chlorine or bromine undergo halogenation, the extent of which depends upon the reaction conditions. Halogenation preferentially takes place at α carbon atoms. Thus,

$$\underset{\text{diethyl ether}}{CH_3CH_2OCH_2CH_3} \xrightarrow[\textit{dark}]{Cl_2} CH_3CHClOCH_2CH_3 \xrightarrow[\textit{dark}]{Cl_2} \underset{\alpha,\,\alpha'\text{-dichloro-diethyl ether}}{CH_3CHClOCHClCH_3}$$

In presence of light perchlorodiethyl ether is obtained.

$$\underset{\text{diethyl ether}}{(C_2H_5)_2O} \xrightarrow[\textit{light}]{Cl_2} \underset{\text{perchlorodiethyl ether}}{(C_2Cl_5)_2O}$$

ADDITION REACTIONS OF THE O ATOM

(3) **Formation of Peroxides.** In contact with air or ozone, ethers form peroxides.

$$\underset{\text{diethyl ether}}{(C_2H_5)_2O} + O \longrightarrow \underset{\text{peroxide}}{(C_2H_5)_2O{\rightarrow}O}$$

The formation of peroxides is accelerated by ultraviolet light and by the absence of moisture.

(4) **Formation of Oxonium salts.** Ethers like alcohols are weakly basic and react with strong acids (*e.g.*, H_2SO_4, $HClO_4$, HBr) to form oxonium salts. Thus,

$$H_5C_2-\ddot{\underset{..}{O}}-C_2H_5 + H_2SO_4 \xrightarrow{\text{ice cold}} \left[C_2H_5-\overset{+}{\ddot{\underset{|\atop H}{O}}}-C_2H_5\right]H\bar{S}O_4$$

diethyl ether

diethyloxonium hydrogen sulphate

Oxonium salts are stable in high concentration of acids. When their acid solution is diluted with water, the oxonium salts are dissociated into original ether and the acid, because water is a stronger base than ethers.

Ethers form relatively stable complexes with lewis acids (*e.g.*, BF_3 and RMgX) by coordination.

$$H_5C_2-\ddot{\underset{..}{O}}-C_2H_5 + BF_3 \longrightarrow H_5C_2-\underset{..}{\overset{F_3B\leftarrow}{O}}-C_2H_5$$

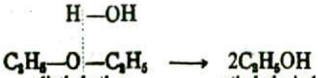
diethyl ether

boron trifluoride

boron trifluoride etherate

DECOMPOSTION REACTIONS INVOLVING RUPTURE OF C—O LINKAGES

(5) **Hydrolysis.** When boiled with water or treated with steam, ethers are decomposed at one of the oxygen bonds to form alcohols.



$$\begin{matrix} & H-OH & \\ C_2H_5-O & -C_2H_5 & \end{matrix} \longrightarrow 2C_2H_5OH$$

diethyl ether

ethyl alcohol

The rate of hydrolysis of ethers is accelerated considerably by the presence of acids.

(6) **Action of Phosphorus Pentachloride.** With hot phosphorus pentachloride, ethers react with cleavage at both the oxygen bonds forming alkyl chlorides.

$$\begin{matrix} Cl & -PCl_3- & Cl \\ C_2H_5 & -O- & C_2H_5 \end{matrix} \longrightarrow 2C_2H_5Cl + POCl_3$$

ethyl chloride

(7) **Action of Halogen Acids.** Ethers are readily cleaved by hydriodic acid or hydrobromic acid. The final products of reaction are governed by the reaction conditions.

(*a*) In cold ethers split to form a molecule of alkyl halide and alcohol. Thus,

$$C_2H_5-O-C_2H_5 + HI \longrightarrow C_2H_5I + C_2H_5OH$$

diethyl ether

In mixed ethers, the iodine goes with the smaller alkyl group.

$$CH_3-O-C_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$$

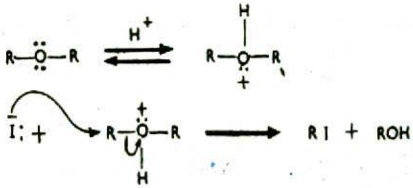
ethyl methyl ether

(*b*) In hot and with excess of hydriodic acid, both alkyl groups appear as alkyl iodides.

$$C_2H_5-O-C_2H_5 + 2HI \longrightarrow 2C_2H_5I + H_2O$$

$$CH_3-O-C_2H_5 + 2HI \longrightarrow CH_3I + C_2H_5I + H_2O$$

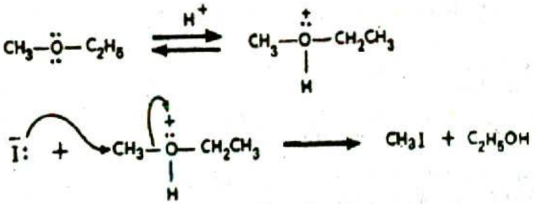
MECHANISM : The mechanism of fission of ethers in the above reactions is an S_N1 eaction on the oxonium salt.



The alcohol thus formed reacts with excess of HI to form ethyl iodide.

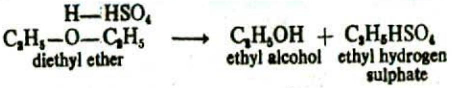
$$C_2H_5OH + HI \longrightarrow C_2H_5I + H_2O$$

In the case of a mixed ether like ethyl methyl ether ($CH_3—O—CH_2CH_3$), the iodide ion attacks methyl group preferentially because the transition state here would be less sterically hindered. Also the inductive effect of the methyl in ethyl group makes the carbon atom of CH_2 less positive than the other methyl group when no such factor operates.



Ethyl alcohol reacts with excess of HI to form ethyl iodide.

(8) **Action of Sulphuric Acid**. Cold concentrated sulphuric acid has no action on ethers except that it dissolves them forming oxonium salts. However, if the solution is heated, the ether is decomposed to yield a molecule of the alcohol and alkyl hydrogen sulphate.



$$\underset{\text{diethyl ether}}{\overset{H—HSO_4}{C_2H_5—O—C_2H_5}} \longrightarrow \underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\text{ethyl hydrogen sulphate}}{C_2H_5HSO_4}$$

With excess of sulphuric acid, the molecule of alcohol produced also reacts to form alkyl hydrogen sulphate.

USES OF ETHERS

(1) Being characterised by their general inertness, ethers are extensively used as **indifferent solvents** both in the laboratory and commerce.

(2) Lower ethers are employed as **general anaesthetics**. Since they produce intense local cooling when sprayed on skin, ethers are also used as **local anaesthetics** for minor surgical operations.

(3) Lower ethers are volatile liquids which on evaporation produce low temperatures. They are, therefore, used as **refrigerants.**

DIMETHYL ETHER, $(CH_3)_2O$

It is the simplest member of the series and may be obtained by any of the general methods of preparation. Industrially it is prepared by passing methyl alcohol vapours maintained at 15 atmos pressure and 350—400° temperature over $AlPO_4$ catalyst.

It is a gas (bp -24°), extremely soluble in water and gives all the general characteristics of ethers. Dimethyl ether is largely employed as a refrigerant and a low-temperature solvent.

DIETHYL ETHER, ETHER, $(C_2H_5)_2O$

This is the most important representative of this class and is often referred to as simply **ether**. From its method of formation by heating alcohol with sulphuric acid, diethyl ether was at one time named **Ether Sulphuric.**

Preparation. Diethyl ether may be prepared by Williamson's synthesis.

$$\underset{\text{sod ethoxide}}{C_2H_5\bar{O}\overset{+}{Na}} + C_2H_5Br \longrightarrow \underset{\text{diethyl ether}}{C_2H_5-O-C_2H_5} + \overset{+}{Na}\bar{Br}$$

But it is generally prepared in the laboratory and on a large scale by heating ethyl alcohol with concentrated H_2SO_4 at 140°. This reaction is often referred to as ***Williamson's*** *continuous etherification process.*

$$\underset{\text{ethyl alcohol}}{2C_2H_5OH} \xrightarrow[140^\circ]{H_2SO_4} \underset{\text{diethyl ether}}{C_2H_5-O-C_2H_5} + H_2O$$

LABORATORY PREPARATION. Equal volumes of alcohol and conc H_2SO_4 are heated in a flask fitted with a dropping funnel and a water condenser which in turn is connected to a receiver immersed in ice. When the temperature of the contents in the flask reaches 140°, ether begins to distil over. Alcohol is now run in from the dropping funnel at the same rate at which ether distils over. The process is continuous and hence the name *Continuous Etherification Process.*

Ether thus obtained is contaminated with water, alcohol and sulphurous acid. It is first shaken with dil. NaOH which removes H_2SO_3. The organic layer is then separated and treated with a 5 per cent $CaCl_2$ solution which removes alcohol. The ethereal layer is separated again, dried over anhydrous $CaCl_2$ and distilled.

COMMERCIAL METHOD. It employs the same reaction as given above. The essential details of the plant used for the purpose are depicted in Fig. 18·2

Now-a-days most of the ether of commerce is obtained by the reaction of ethylene with sulphuric acid. The ethylene is produced by the cracking of petroleum.

$$\underset{\text{ethylene}}{CH_2=CH_2} + \underset{\text{conc sulphuric acid}}{HOSO_2OH} \longrightarrow \underset{\text{ethyl hydrogen sulphate}}{CH_3-CH_2OSO_3H}$$

A part of the ethyl hydrogen sulphate thus obtained is hydrolysed to alcohol by adding water to the reaction mixture. The alcohol then reacts with conc sulphuric acid to give ether.

$$CH_3CH_2OSO_3H + HOH \longrightarrow \underset{\text{ethyl alcohol}}{CH_3CH_2OH} + H_2SO_4$$

$$CH_3CH_2OSO_3H + CH_3CH_2OH \longrightarrow \underset{\text{diethyl ether}}{CH_3CH_2OCH_2CH_3} + CH_3CH_2CH_2OSO_3H$$

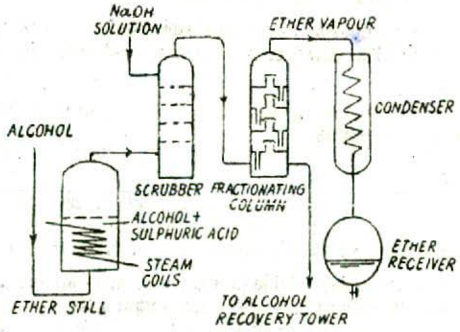


Fig. 18·2. Manufacture of Diethyl ether.

Properties. It is a colourless highly volatile liquid having a rather pleasant odour and a sweetish burning taste. It boils at 34·6° and has a specific gravity 0·720 at 15°. The vapour of diethyl ether is about two and a half times heavier than air. At 20° it is soluble in water to the extent of 7 per cent while water dissolves in ether to the extent of 3 per cent at the same temperature. On inhalation its vapours produce general anaesthesia.

The chemical reactions of diethyl ether have already been discussed under the general treatment.

It is highly inflammable and its vapours form explosive mixtures with air. Ether burns with a clear flame.

$$\underset{\text{diethyl ether}}{C_2H_5OC_2H_5} + 6O_2 \longrightarrow 4CO_2 + 5H_2O$$

Ether dissolves readily in aqueous solution of hydrogen chloride forming oxonium salt.

In contact with air, ether forms the peroxide which is highly explosive. Hence, old ether that has been exposed to air for long should never be distilled without the previous removal of peroxide.

Uses. (1) Ether is an excellent solvent and is used for extracting organic sebstances from aqueous solutions. Being immiscible with water the ethereal layer can be easily separated and evaporated to give back the organic substance.

(2) It is an excellent inert medium for many organic reactions such as the Wurtz-Fittig and the Grignard reactions.

(3) Ether is one of the best known anaesthetics. It is superior to chloroform in that it produces loss of consciousness without interfering much with the functions of heart and lungs.

ESTIMATION OF METHOXY OR ETHOXY GROUPS

The *methoxy* or *ethoxy* groups are estimated by **Zeisel's method**. A known weight of the sample is heated with concentrated HI to form methyl iodide (or ethyl iodide). The iodide is then treated with alcoholic silver nitrate to give precipitate of silver iodide.

Reactions for Methoxy Group

$$ROCH_3 + HI \longrightarrow ROH + CH_3I$$

$$CH_3I + AgNO_3 \longrightarrow CH_3NO_3 + AgI \text{ (precipitate)}$$

Reactions for Ethoxy Group

$$ROC_2H_5 + HI \longrightarrow ROH + C_2H_5I$$

$$C_2H_5I + AgNO_3 \longrightarrow C_2H_5NO_3 + AgI \text{ (precipitate)}$$

Calculations :

Weight of the sample taken = w_1 g
Weight of AgI formed = w_2 g
From the above reaction equations :
1 mole of AgI ≡ one OCH_3 group
or 234 g of AgI ≡ 31 g of OCH_3 group

Percentage of methoxy group

$$= \frac{31}{234} \times \frac{w_2}{w_1} \times 100$$

Similarly,

1 mole of AgI ≡ one OC_2H_5 group
or 234 g of AgI ≡ 45 g of OC_2H_5 group

Percentage of ethoxy group

$$= \frac{45}{234} \times \frac{w_2}{w_1} \times 100$$

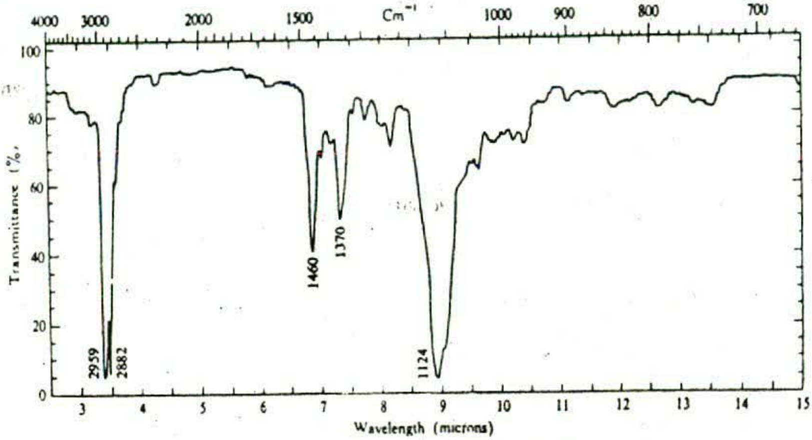


Fig. 18·3. Infrared spectrum of Dibutyl ether.

Infrared spectra of Ethers. Ethers containing CH_2-O-CH_2 group in their molecule absorb radiations in the region $1060-1150 \text{ cm}^{-1}$ as is indicated in the Infrared spectrum of dibutyl ether given above.

COMPARISON OF ETHERS AND ALCOHOLS.

Ethers have the general formula $R-O-R'$ while alcohols are represented by $R-O-H$. Since in ether the reactive H-atom of alcohols is replaced by relatively less reactive alkyl group, the ethers are chemically inert. Nevertheless, ethers and alcohols have many similar physical properties and chemical reactions, the former doing so under more drastic conditions. This may be illustrated by taking example of ethyl alcohol and diethyl ether.

Ethyl alcohol, C_2H_5OH	*Diethyl ether, $(C_2H_5)_2O$*
Physical Properties :	
(1) Sweet alcoholic odour.	(1) Pleasant ethereal odour.
(2) Volatile liquid, bp 78°.	(2) Volatile liquid, bp 35°.
(3 Miscible with water.	(3) Immiscible with water.
Chemical Reactions :	
(1) Forms alkonium salts with strong acids.	(1) Forms oxonium salts.
(2) Question of hydrolysis does not arise.	(2) Hydrolysed to ethanol.
(3) Reacts with cold HI to form C_2H_5I, and when heated reduced to ethane.	(3) Forms ethyl iodide and ethanol. When heated gives two molecules of ethyl iodide.
(4) With hot conc H_2SO_4, gives $C_2H_5HSO_4$ H_2O.	(4) Gives $C_2H_5HSO_4$ and C_2H_5OH.
(5) With PCl_5 it forms ethyl chloride and HCl.	(5) Forms ethyl chloride (2 molecules).
(6) Reacts with sodium to form C_2H_5ONa and H_2.	(6) No action.
(7) Reacts with acetyl chloride to form ethyl acetate.	(7) No action.
(8) On oxidation yields acetaldehyde.	(8) Not easily oxidised.
(9) Reacts with chlorine by oxidation and by substitution to form chloral.	(9) Undergoes chlorination to give polyhalogen derivatives.

QUESTIONS

1. Outline the methods of preparation and properties of ethers. *(Udaipur BSc, 1993)*
2. How is diethyl ether prepared in the laboratory ? *(Madras BSc, 1993)*
3. How is diisopropyl ether prepared ? *(Rajasthan BSc, 1994)*
4. How does diethyl ether react with :
   (*a*) cold conc. H_2SO_4 ; (*b*) PCl_5 ; (*c*) hot conc. HI ; (*d*) O_2
5. Ethers react with concentrated H_2SO_4 to form :
   (*a*) Alkyl free radical ; (*b*) Zwitterion ; (*c*) Oxyanion ; (*d*) Oxonium ion *(Kakatyia BSc, 1994)*

Answer. (*d*)

6. How will you distinguish between :
   (*a*) Diethyl ether and ethanol
   (*b*) Diethyl ether and *n*-pentane
   (*c*) Allyl propyl ether and diisopropyl ether *(Nehu BSc Hons, 1994)*

Hint. (*a*) Ethanol reacts with sodium metal to produce hydrogen gas (seen as bubbles). Diethyl ether does not react ; (*b*) Diethyl ether reacts with conc. H_2SO_4 to give a homogeneous solution containing the oxonium ion. *n*-Pentane does not react with sulphuric acid ; and (*c*) Allyl propyl ether decolourises Br_2/CCl_4 solution. Diisopropyl ether does not.

7. How will you synthesise :
   (*a*) Ethyl *n*-propyl ether from ethylene
   (*b*) Ethylene glycol from diethyl ether
   (*c*) *n*-Butyl *t*-butyl ether from 1-butene
   (*d*) Divinyl ether from ethylene.

Hint. (*c*) (*i*) HBr/R_2O_2 , (ii) H_2O/H^+, (*iii*) Na/ether, and (*iv*) $CH_3CH_2CH_2CH_2Br$ (from step *i*) ; (*d*) (*i*) HOCl, (*ii*) H_2SO_4/heat, and (*iii*) alcoholic KOH.

8. Explain : *n*-Butyl alcohol (bp 118°C) has a much higher boiling point than its isomer diethyl ether (bp 35°C).
9. Arrange the following compounds in order of increasing solubility in water.
   (*a*) $CH_3CH_2OCH_2CH_3$
   (*b*) CH_3CH_2OH
   (*c*) $CH_3CH_2CH_2CH_2CH_3$

Answer. (*c*) < (*a*) < (*b*)

10. Write a note on : Williamson's ether synthesis. *(Delhi BSc, 1994 ; Bangalore BSc, 1994)*
11. What are the limitations of Williamson's ether synthesis ? *(Calicut BSc, 1994)*
12. Discuss the mechanism of Williamson's ether synthesis. *(Panjab BSc, 1994)*
13. Give a step-by-step mechanism for the reaction of ethanol with conc. H_2SO_4 at 140°C to form diethyl ether. *(Sambalpur BSc Hons, 1994)*
14. Why can ethers be cleaved by hot, concentrated HI or HBr, but not by concentrated HCl ?

Answer. The Cl^- ion is a weak nucleophilic reagent, whereas Br^- and I^- ions are good nucleophiles.

15. (a) Describe the Zeisel method for the estimation of methoxy groups.

(*b*) In an experiment 4.24 mg of a compound of molecular formula $C_{20}H_{21}O_4N$, when heated with concentrated HI, yields CH_3I which after passing through alcoholic $AgNO_3$ gave 11.62 mg of AgI. Calculate the number of methoxy groups in it.

Answer. (*b*) 4

16. Compound (A), $C_4H_{10}O$, is found to be soluble in sulphuric acid. (A) does not react with sodium or potassium permanganate. When (A) is heated with excess of hydroiodic acid, it is converted into a single alkyl iodide. What is the structural formula of (A) ?

Answer. $CH_3CH_2OCH_2CH_3$

17. An organic compound with the formula $C_4H_{10}O_3$ shows properties of both an alcohol and an ether. When treated with an excess of hydrogen bromide, it yields only one organic compound, 1,2-dibromoethane. Give the structural formula for the original compound.

Answer. $HOCH_2CH_2OCH_2CH_2OH$

Chapter 19

Organosulphur Compounds— Thioalcohols and Thioethers

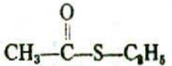
Sulphur lies directly below oxygen in Group VI of the Periodic Table. Therefore, these two elements have similar outer shell configuration.

O (at no=8) $1s^2\ 2s^2\ 2p^4$
S (at no=16) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4\ 3d^0$

Hence sulphur is capable of forming several classes of organic compounds parallel to those containing oxygen, such as alcohols, ethers and esters. Thus we have thioalcohols, thioethers and thioesters. For example,

$CH_3{-}S{-}H$
methyl thioalcohol

$CH_3CH_2{-}S{-}CH_2CH_3$
diethyl thioether

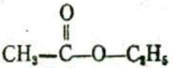


$$CH_3{-}\overset{\overset{O}{\|}}{C}{-}S{-}C_2H_5$$

ethyl thioacetate

$CH_3{-}O{-}H$
methyl alcohol

$CH_3CH_2{-}O{-}CH_2CH_3$
diethyl ether



$$CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}C_2H_5$$

ethyl acetate

The derivatives as above which contain C—S bonds are termed **Organosulphur Compounds**. In several respects the chemistry of analogous oxygen and sulphur compounds is similar. But their behaviour also displays several differences which are attributed to the facts that sulphur atom is larger, less electronegative and has unoccupied *d* orbitals which are only slightly higher in energy than the occupied 2*p* orbitals.

Interest in the chemistry of Organosulphur compounds has greatly increased in recent years. These compounds are of prime importance in many industrial operations, in the pharmaceutical chemistry, and are important participants in every metabolic process.

Of all organosulphur derivatives, thioalcohols and thioethers being the most important will be discussed in detail.

THIOALCOHOLS OR THIOLS

Thioalcohols are alcohols in which the oxygen atom of the OH group has been replaced by a sulphur atom.

$$\underset{\text{alcohol}}{R{-}O{-}H} \xrightarrow[+S]{-O} \underset{\text{thioalcohol}}{R{-}S{-}H} \text{ or } RSH$$

Thus they have the general formula R—S—H where R is an alkyl group. The IUPAC name of this class of compounds which is in common use in modern practice, is **Thiols**. Since thioalcohols react with mercury(II) ions to form insoluble mercury salts $(RS)_2Hg$, they were given the common name (now out of favour) **Mercaptans** (*mercurium*=mercury ; *captans*=catching).

The reactive $-SH$ group in thiols is the functional group. This is called **Sulphohydryl, Thiol or Mercapto group.**

Thiols occur as a small, though significant fraction of crude petroleum. They also have animal and vegetable origins. Thus butanethiol (C_4H_9SH) is a component of shunk secretion, where it serves as a defensive weapon. Propanethiol (C_3H_7SH) is evolved from freshly chopped onions. Allyl mercaptan ($CH_2{=}CH{-}CH_2SH$) is partly responsible for the odour of garlic. Thiols play key roles in biological processes.

STRUCTURE

As already stated, the electronic configuration of sulphur can be written as

Valency shell of S

$$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ \boxed{3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1}$$

$3s$, $3p_x$, $3p_y$, $3p_z$ atomic orbitals of the valency shell of sulphur combine to form four sp^3 hybridized orbitals. Two of these hybridized orbitals contain two electrons each (the lone pair electrons), while the other two are singly occupied (Fig. 19·1). In the formation of a thiol molecule RSH, one singly occupied sp^3 orbital of S atom overlaps with the sp^3 orbital of R group to form a σ bond. The second singly occupied sp^3 orbital of S overlaps with $1s$ orbital of H atom to form another σ bond. Thus the orbital structure of thiol may be represented as in Fig. 19·1.

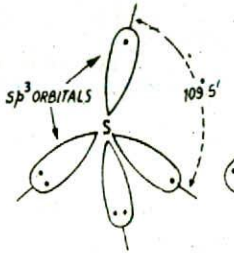


Fig. 19·1. Hybridized S atom with two lone pairs.

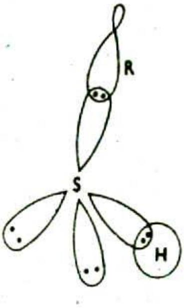


Fig. 19·2. Orbital structure of RSH.

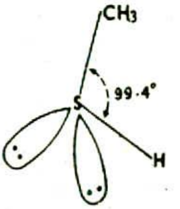


Fig. 19·3. ∠R—S—H in methanethiol shrink to 99·4°.

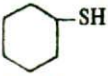
Since in thiols sulphur is hybridized, the ∠R—S—H should have been normally 109·5°. But the actual ∠R—S—H is shrunk to a much less value ; 99·4° in case of CH_3SH. This is attributed to the fact that the lone pair-lone pair interactions overshadow to some extent the bond pair-bond pair repulsions of S—R and S—H bonds. As a result ∠R—S—H is reduced considerably.

NOMENCLATURE

(1) **The Common Names.** Thioalcohols bear the common name *Alkyl mercaptans.* Thus the common name of an individual member of this class is obtained by writing the name of the alkyl group followed by the word 'mercaptan'. This system of naming thioalcohol is going out of favour.

(2) **The IUPAC Names.** According to this system thioalcohols are named as *Alkanethiols.* The name of an individual compound is derived by adding the suffix *-thiols* to the name of the parent hydrocarbon.

The common names and IUPAC names of some typical thiols are given below for illustration.

Compound	*Common Name*	*IUPAC Name*
$CH_3—SH$	methyl mercaptan	methanethiol
$CH_3CH_2—SH$	ethyl mercaptan	ethanethiol
$CH_3CH_2CH_2—SH$	propyl mercaptan	*n*-propanethiol 1-propanethiol
$CH_3CH_2CH_2CH_2—SH$	*n*-butyl mercaptan	*n*-butanethiol 1-butanethiol.
	cyclohexyl mercaptan	cyclohexanethiol

The IUPAC names are now generally used. When other functional groups are also present, the thiol function (—SH) is sometimes denoted by the prefix *mercapto*. For example,

$$HS—\overset{2}{C}H_2—\overset{1}{C}H_2-OH \qquad \text{2-mercaptoethanol}$$

$$HS—\overset{3}{C}H_2—\overset{2}{C}H_2—\overset{1}{C}H_2—OH \qquad \text{3-mercapto-1-propanol}$$

METHODS OF PREPARATION

Thiols can be prepared by the following general methods.

(1) *By the reaction of sodium hydrosulphide* ($\overset{+-}{NaSH}$) *with* (*a*) *alkyl halides* ; (*b*) *sodium alkyl sulphates.*

$$\underset{\text{ethyl bromide}}{CH_3CH_2\overset{\curvearrowright}{—}Br} + \underset{\text{(excess)}}{\overset{+-}{NaSH}} \longrightarrow \underset{\text{ethanethiol}}{CH_3CH_2—SH} + \overset{+-}{NaBr}$$

$$\underset{\text{sodium methyl sulphate}}{CH_3\overset{\curvearrowright}{—}O—SO_2—ONa} + \underset{\text{(excess)}}{\overset{+-}{NaSH}} \longrightarrow \underset{\text{methanethiol}}{CH_3—SH} + \overset{+}{Na_2}\overset{2-}{SO_4}$$

However, unless a large excess of the hydrosulphide is used or hydrogen sulphide is passed into the reaction mixture, significant amounts of sulphide (R_2S) may also be produced.

$$RSH + \overset{+-}{NaSH} \rightleftharpoons R\overset{-}{S}\overset{+}{Na} + H_2S$$

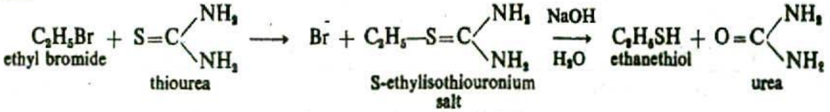
$$R\overset{-}{S}\overset{+}{Na} + RX \rightleftharpoons RSH + NaX$$

(2) *By passing a mixture of alcohol vapours and hydrogen sulphide* (*H—SH*) *gas over thorium catalyst at 400°.*

$$\underset{\text{ethyl alcohol}}{CH_3CH_2—OH} + H—SH \xrightarrow[400°]{ThO_2} \underset{\text{ethanethiol}}{CH_3CH_2—SH} + H_2O$$

This method forms thiol in good yield and is used commercially.

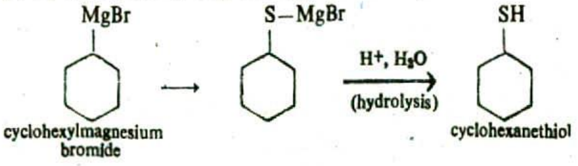
(3) *By the action of alkyl halides on thiourea and subsequent hydrolysis.* Thiourea is alkylated by the action of alkyl halides when S-alkylisothiouronium salt is produced which is a crystalline substance and can be isolated in pure form. This is then hydrolysed with aqueous alkali.



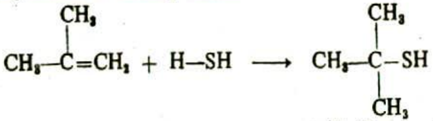
$$\underset{\text{ethyl bromide}}{C_2H_5Br} + \underset{\text{thiourea}}{S=C\begin{matrix}NH_2\\NH_2\end{matrix}} \longrightarrow \overset{-}{Br} + \underset{\text{S-ethylisothiouronium salt}}{C_2H_5—S=C\begin{matrix}NH_2\\NH_2\end{matrix}} \xrightarrow[H_2O]{NaOH} \underset{\text{ethanethiol}}{C_2H_5SH} + \underset{\text{urea}}{O=C\begin{matrix}NH_2\\NH_2\end{matrix}}$$

This eliminates the possibility of formation of sulphide as in method (1).

(4) *By the reaction of Grignard reagents with sulphur.*



(5) *By the addition of hydrogen sulphide (H—SH) to alkenes in presence of acid catalyst.* The addition takes place in accordance with Markovnikov Rule and this method is particularly used for the preparation of tertiary thiols.



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + H-SH \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-SH$$

tert-butyl mercaplan

PHYSICAL PROPERTIES

(1) Excepting methanethiol which is a gas, thiols are colourless volatile liquids at room temperature.

(2) Lower members have extremely powerful and disagreeable odours. About 1 part of ethanethiol in 50,000,000 parts of air can be detected by its odour. Thus thiols are mixed with commercial gases and refrigerating fluids to warn the user of leaks.

(3) The boiling points of the lower thiols are much lower than those of alcohols with the same number of carbons.

Thiol	*bp*	*alcohol*	*bp*	*Difference*
CH_3SH	6°	CH_3OH	56°	60°
CH_3CH_2SH	34·7°	CH_3CH_2OH	78°	43·3°
$CH_3CH_2CH_2SH$	67·5°	$CH_3CH_2CH_2OH$	98°	30·5°

This is so because sulphur is less electronegative than oxygen and hence there is less hydrogen bonding between thiol molecules. It is noticed that the difference in boiling points of thiols and alcohols diminishes with increasing carbon chain. The reason is that in higher alcohols association decreases because of the greater repelling tendency of higher alkyl groups.

(4) Unlike alcohols, thiols are insoluble in water. This is also attributed to the fact that thiol molecules do not form hydrogen bonds to an appreciable extent with water molecules. Thiols are, however, soluble in organic solvents like ethanol, ether, etc.

Table. Physical constants of some Thiols

Compound	*Formula*	*mp°C*	*bp°C*
methanethiol	CH_3SH	−123·0	6·0
ethanethiol	CH_3CH_2SH	−147·3	34·7
1-propanethiol	$CH_3CH_2CH_2SH$	−113·3	67·5
2-propanethiol	$CH_3CH(SH)CH_3$	−130·7	52·9
1-butanethiol	$CH_3CH_2CH_2CH_2SH$	−115·9	98·0
2-butanethiol	$CH_3CH_2CH(SH)CH_3$	−165·0	84·5
1-pentanethiol	$CH_3CH_2CH_2CH_2CH_2SH$	−75·7	126·5

CHEMICAL PROPERTIES

In their chemical behaviour, thiols resemble with alcohols in many ways. They, however, show marked difference from alcohols in respect of acidity and oxidation reactions.

(1) **Acidity ; Formation of mercaptides.** A sulphide ion RS^- in more stable than an oxide ion RO^-, since in the former the charge is dispersed throughout a larger volume. In other words protons bound to sulphur are less tightly held than those bound to oxygen. Thus one of the main differences between the thiols and alcohols is the greater acidity of thiols. The K_{HA} of ethanethiol is about 10^{-11}, compared to 10^{-17} for ethanol. The acidity of thiols enables them to react with aqueous alkali to give water-soluble salts known as **Mercaptides**.

$$\underset{\text{ethanethiol}}{CH_3CH_2SH} + NaOH \longrightarrow \underset{\text{sodium ethyl mercaptide}}{CH_3CH_2SNa} + H_2O$$

The thiol can be regenerated by treatment of the mercaptide with acids. Mercaptans present in petroleum are removed by scrubbing with an aqueous alkali.

Like hydrogen sulphide, thiols react with the ions of a number of heavy metals, such as mercury, gold and lead, to form water-insoluble mercaptides.

$$\underset{\text{ethanethiol}}{2CH_3CH_2SH} + HgCl_2 \longrightarrow \underset{\text{diethyl mercaptide}}{(CH_3CH_2)_2Hg} + 2HCl$$

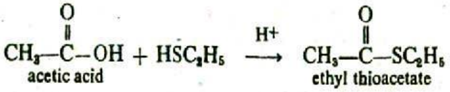
The mercury mercaptides can be crystallised from organic solvents and have low melting points. They are used in the identification of thiols.

The dithiol HS—CH$_2$—CHSH—CH$_2$OH, known as BAL (British anti-Lewisite) was employed to destroy arsenical war gases (Lewisite). It is also used as antidote for poisoning by arsenic, mercury, lead etc.

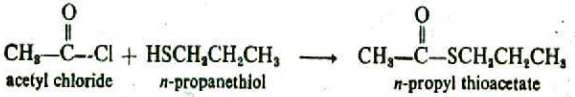
(2) **Reaction with Sodium**. Like alcohols, thiols react with metallic sodium with the evolution of hydrogen.

$$2C_2H_5SH + 2Na \longrightarrow \underset{\text{sodium mercaptide}}{2C_2H_5SNa} + H_2$$

(3) **Reaction with Carboxylic acids and Acid chlorides**. Thiols resemble alcohols in their reactions with carboxylic acids (preferably in the presence of inorganic acids) and acid chlorides to form **Thioesters.**

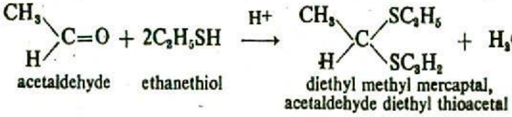


$$\underset{\text{acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + HSC_2H_5 \xrightarrow{H+} \underset{\text{ethyl thioacetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-SC_2H_5}$$

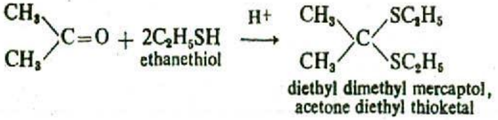


$$\underset{\text{acetyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + \underset{n\text{-propanethiol}}{HSCH_2CH_2CH_3} \longrightarrow \underset{n\text{-propyl thioacetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-SCH_2CH_2CH_3}$$

(4) **Reaction with Aldehydes and Ketones**. Thiols react with aldehydes and ketones in the presence of HCl to form **Mercaptals** (thioacetals) and **Mercaptols** (thioketals) respectively.



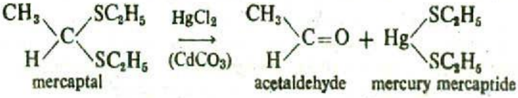
acetaldehyde ethanethiol diethyl methyl mercaptal, acetaldehyde diethyl thioacetal



ethanethiol diethyl dimethyl mercaptol, acetone diethyl thioketal

Alcohols similarly react with aldehydes and ketones to form *acetals* and *ketals*.

Mercaptals and mercaptols are more stable in acid solution than acetats and ketals. Thus aldehydes and ketones are protected in acid solution by converting them into mercaptals and mercaptols respectively. The orginal aldehydes and ketones can then be generated from these derivatives by treatment with HgCl$_2$ in presence of CdCO$_3$. For example,

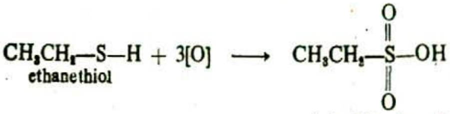


mercaptal acetaldehyde mercury mercaptide

(3) **Oxidation Reactions.** The most significant difference in the chemical behaviour of alcohols and thiols is the ease with which thiols are oxidised. Thus we find that thiols upon oxidation with a variety of mild oxidising agents such as I_2, HOCl, O_2 (in presence of Fe or Cu catalyst) or H_2O_2 yeld disulphides (R—S—S—R).

$$\underset{\text{ethanethiol}}{2CH_3CH_2{-}SH} + [O] \longrightarrow \underset{\text{diethyl disulphide}}{CH_3CH_2{-}S{-}S{-}CH_2CH_3}$$

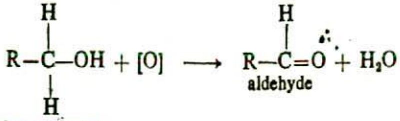
vigorous oxidation with nitric acid forms sulphonic acids, RSO_3H.



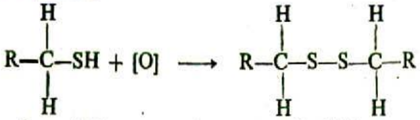
$$\underset{\text{ethanethiol}}{CH_3CH_2{-}S{-}H} + 3[O] \longrightarrow CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}OH$$

ethyl sulphonic acid

The difference between the oxidation of alcohols and thiols is that the oxidation of alcohols increases the oxidation level of carbon whereas the oxidation of thiols occurs at the sulphur atom.



$$\underset{\text{primary alcohol}}{R{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}OH} + [O] \longrightarrow \underset{\text{aldehyde}}{R{-}\overset{\overset{\displaystyle H}{|}}{C}{=}\ddot{O}} + H_2O$$

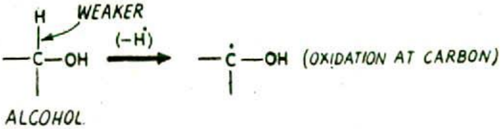


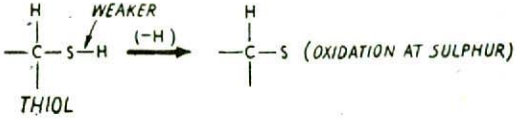
$$\underset{\text{primary thiol}}{R{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}SH} + [O] \longrightarrow \underset{\text{disulphide}}{R{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}S{-}S{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}R}$$

The difference in the oxidation reactions as described above may be interpreted in terms of the bond strengths :

C—H bond	O—H bond	S—H bond
85 Kcal	110 Kcal	80 Kcal

In the case of an alcohol, the oxidation proceeds by homolysis of the weaker C—H bond, while in thiols oxidation effects homolysis of the weaker S—H bond.



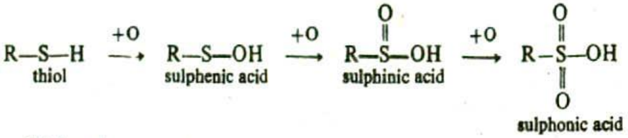


Thus the formation of free radicals R—S· from thiols is easy which combine to form the disulphide.

$$\underset{\text{thiol}}{2\ R{-}S{-}H} + [O] \longrightarrow \underset{\text{thinyl free radical}}{R{-}S\cdot} + H_2O$$

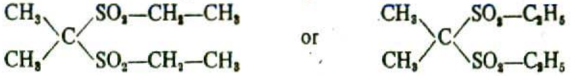
$$2R{-}S\cdot \longrightarrow R{-}S{-}S{-}R$$

The oxidation of thiols by treatment with nitric acid possibly takes place through the formation of sulphenic acid and sulphinic acid.

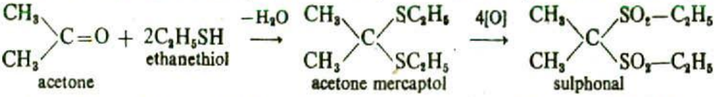


$$\underset{\text{thiol}}{R{-}S{-}H} \xrightarrow{+O} \underset{\text{sulphenic acid}}{R{-}S{-}OH} \xrightarrow{+O} \underset{\text{sulphinic acid}}{R{-}\overset{O}{\overset{\|}{S}}{-}OH} \xrightarrow{+O} \underset{\text{sulphonic acid}}{R{-}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}{-}OH}$$

Sulphonal,

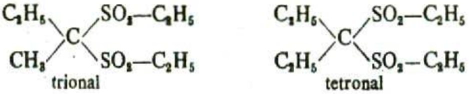


Preparation. It is prepared by the condensation of acetone with ethanethiol and subsequent oxidation of acetone mercaptol obtained by treatment with potassium permanganate.



Properties and Uses. Sulphonal forms colourless crystals, mp 126°. It is sparingly soluble in cold water but completely soluble in hot water.

Sulphonal respresents an important class of hypnotics. It is used as a sleep producing drug. Homologues of sulphonal, namely **Trional and Tetronal**, have been shown to be even more effective hypnotics.



Trional and tetronal are prepared by reaction of ethyl methyl ketone and diethyl ketone respectively with ethanethiol followed by oxidation.

THIOETHERS OR ALKYL SULPHIDES

Sulphur analogues of ethers are called *thioethers* or *alkyl sulphides*. The functional group of this class of compounds is the **Sulphide group** (—S—).

$$\underset{\text{thioether or alkyl sulphide}}{R{-}S{-}R} \qquad \underset{\text{sulphide group (functional group)}}{{-}S{-}}$$

The function sulphide thus consists of a sulphur atom bonded directly to two carbons, one on either side.

STRUCTURE

We have already discussed the orbital structure of alkanethiols in the begining of this chapter. The structure of alkyl sulphides can be derived similarly. Here both the singly occupied sp^3 hybrid orbitals of sulphur overlap with sp^3 orbitals of alkyl groups to form two (S—R) sigma bonds.

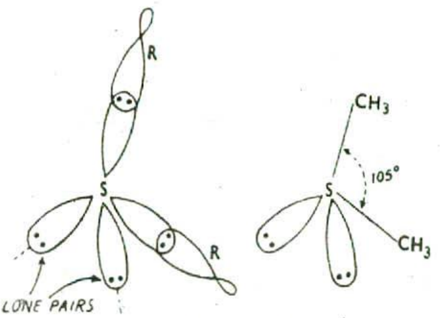


Fig. 19·4. Orbital structure of alkyl sulphides

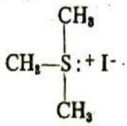
It may be noted that the bond-pair bond-pair repulsions of the two S—R bonds in alkyl sulphide would be greater than the bond-pair bond-pair repulsions of S—R and S—H bonds in thiol. Therefore, ∠C—S—C in sulphide is greater than ∠C—S—H in thiol. Thus methyl sulphide ($CH_3—S—CH_3$) has ∠C—S—C of 105° compared to ∠C—S—H of 99·4° in methanethiol.

NOMENCLATURE

The IUPAC names of thioethers are formed by prefixing the names of the two alkyl groups (bonded with S) in alphabetic order to the word sulphide. Their **Common Names** are obtained by writing the names of alkyl groups followed by the word 'thioether' or 'sulphide'.

$CH_3—S—CH_3$	$CH_3—CH_2—S—CH_2—CH_3$	$CH_3—S—CH_2—CH_3$
dimethyl sulphide (dimethyl thioether)	diethyl sulphide (diethyl thioether)	ethyl methyl sulphide (ethyl methyl thioether)

The sulphonium salts ($R_3\overset{+}{S}\overset{-}{X}$) are named like ammonium salts. Thus,



$$CH_3—\overset{CH_3}{\underset{CH_3}{S}}:^{+}I^{-}$$

trimethylsulphonium iodide

According to the **IUPAC System** sulphides are named as *alkyl thioalkanes*. The group —SR *i.e., alkylthio* forms the prefix to the name of the alkane pertaining to the larger alkyl group linked to sulphur. Thus,

$$CH_3S—\overset{1}{C}H_2—\overset{2}{C}H_2—\overset{3}{C}H_3$$

1-methylthiopropane

$$C_2H_5S—\overset{1}{C}H_2—\overset{2}{C}H_2—\overset{3}{C}H_2—\overset{4}{C}H_3$$

1-ethylthiobutane

PREPARATION

(1) *By heating potassium sulphide with an appropriate alkyl halide or potassium alkyl sulphate.*

$$\underset{\text{ethyl bromide}}{C_2H_5—Br} + \overset{+}{K}_2\overset{2-}{S} \longrightarrow \underset{\text{diethyl sulphide}}{C_2H_5—S—C_2H_5} + 2\overset{+}{K}\overset{-}{Br}$$

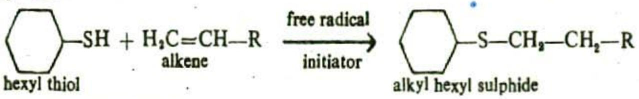
$$\underset{\text{pot methyl sulphate}}{2CH_3—O—SO_2—\overset{-}{O}\overset{+}{K}} + \overset{+}{K}_2\overset{2-}{S} \longrightarrow \underset{\text{dimethyl sulphide}}{CH_3—S—CH_3} + 2\overset{+}{K}_2\overset{2-}{SO_4}$$

(2) *By the action of salts of thiols and appropriate alkyl halides.*

$$\underset{\text{sodium ethyl mercaptide}}{CH_3CH_2—\overset{-}{S}\overset{+}{Na}} + CH_3—I \longrightarrow \underset{\text{ethyl methyl sulphide}}{CH_3CH_2—S—CH_3} + \overset{+}{Na}\overset{-}{I}$$

This method for the synthesis of organic sulphides is akin to Williamson Synthesis for ethers. Here the reaction is very rapid and gives excellent yields.

(3) *Free radical addition of thiols to alkenes is a smooth reaction for the preparation of alkyl sulphides.*



PHYSICAL PROPERTIES

(1) Alkyl sulphides are colourless, volatile liquids at room temperature.

(2) Unlike thiols, they have an ethereal odour which is not unpleasant.

(3) They are insoluble in water but soluble in ethanol, ether and other organic solvents.

(4) Their boiling points are only slightly above the boiling points of ethers of similar molecular weight. Their relatively low boiling points indicate small intermolecular attractions.

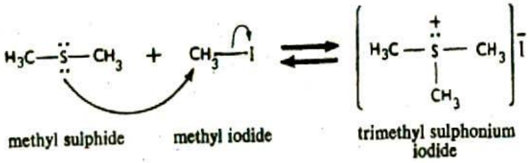
Table. Physical Constants of some Alkyl Sulphides

Compound	*Formula*	*mp °C*	*bp °C*
Dimethyl sulphide	$CH_3–S–CH_3$	− 98	37
Ethyl methyl sulphide	$CH_3–S–CH_2CH_3$	−106	67
Methyl propyl sulphide	$CH_3–S–CH_2CH_2CH_3$	−113	96
Diethyl sulphide	$CH_3CH_2–S–CH_2CH_3$	−103	92
Dipropyl sulphide	$CH_3CH_2CH_2–S–CH_2CH_2CH_3$	−103	143
Dibutyl sulphide	$(CH_3CH_2CH_2CH_2)_2S$	− 80	187

CHEMICAL PROPERTIES

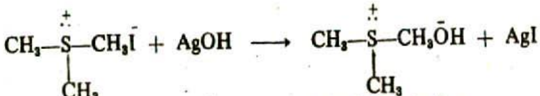
While ethers are relatively unreactive, the alkyl sulphides react readily with many reagents. They undergo two important reactions involving electron pairs on sulphur.

(1) **Reaction with Alkyl Halides.** Alkyl sulphides are highly nucleophilic reagents. They react with alkyl halides which undergo nucleophilic displacement readily to form **Sulphonium salts**. Thus,



The above reaction is reversible so that the sulphonium salt upon heating gives the parent sulphide and alkyl halide.

The sulphonium salts are crystalline substances, soluble in water and highly ionised. With moist silver oxide (AgOH), sulphonium iodide gives the sulphonium hydroxide.

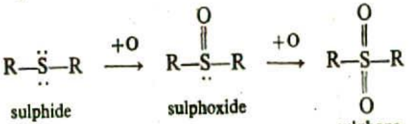


$$CH_3-\overset{+}{\underset{\underset{CH_3}{|}}{\ddot{S}}}-CH_3\bar{I} + AgOH \longrightarrow CH_3-\overset{+}{\underset{\underset{CH_3}{|}}{\ddot{S}}}-CH_3\bar{O}H + AgI$$

trimethyl sulphonium hydroxide

Alkyl sulphonium hydroxides ($R_3\overset{+}{S}\bar{O}H$), like quaternary ammonium salts ($R_4\overset{+}{N}\bar{O}H$), are strong bases and upon heating undergo decomposition to form alkenes.

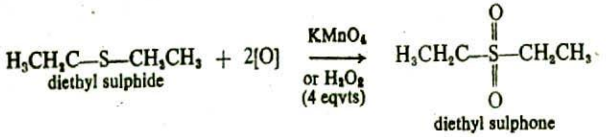
(2) **Oxidation to Sulphoxide and Sulphone.** As already stated, alkyl sulphides are highly nucleophilic substances and are therefore easily oxidised. They utilise one or both lone pairs of electrons on sulphur for union with one or two oxygen atoms.



$$R-\ddot{\underset{..}{S}}-R \xrightarrow{+O} R-\overset{\overset{O}{\|}}{\underset{..}{S}}-R \xrightarrow{+O} R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-R$$

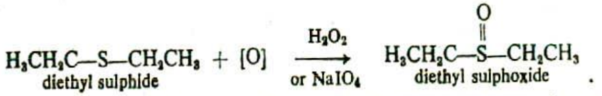
sulphide sulphoxide sulphone

Thus when a sulphide is oxidised with potassium permanganate or excess of hydrogen peroxide (in acetic acid), it is directly converted to **Sulphone**.



$$\underset{\text{diethyl sulphide}}{H_3CH_2C{-}S{-}CH_2CH_3} + 2[O] \xrightarrow[\substack{\text{or } H_2O_2 \\ (4\text{ eqvts})}]{KMnO_4} \underset{\text{diethyl sulphone}}{H_3CH_2C{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}CH_2CH_3}$$

However, when oxidation of sulphide is carried with one equivalent of H_2O_2 (in acetic acid) or sodium metaperiodate (at low temperature), **Sulphoxide** is the product.

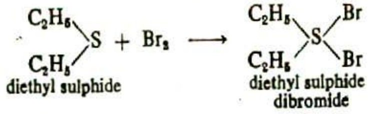


$$\underset{\text{diethyl sulphide}}{H_3CH_2C{-}S{-}CH_2CH_3} + [O] \xrightarrow[\text{or } NaIO_4]{H_2O_2} \underset{\text{diethyl sulphoxide}}{H_3CH_2C{-}\overset{\overset{O}{\|}}{S}{-}CH_2CH_3}$$

In fact, a reagent which can oxidise a sulphide to sulphone can also oxidise a sulphoxide to sulphone.

Dimethyl Sulphoxide or **DMSO** (mp 18°, bp 189°) is an exceptionally powerful solvent for both polar and non-polar compounds. It is becoming increasingly important as a reaction medium, particularly for bimolecular nucleophilic reactions in which nucleophile bears a negative charge. DMSO is useful as a medicine for its ability to penetrate tissue and allay pain.

(3) **Addition of Halogens.** Alkyl sulphides add halogens forming dihalides.



$$\underset{\text{diethyl sulphide}}{(C_2H_5)_2S} + Br_2 \longrightarrow \underset{\text{diethyl sulphide dibromide}}{(C_2H_5)_2SBr_2}$$

Ethers do not form similar dihalides with halogens.

(4) **Hydrolysis with Alkalis.** When boiled with aqueous NaOH or KOH solution, alkyl sulphides are hydrolysed forming the parent alcohol and H_2S gas.

$$\underset{\text{diethyl sulphide}}{CH_3{-}CH_2{-}S{-}CH_2{-}CH_3} + 2H_2O \longrightarrow 2\underset{\text{ethyl alcohol}}{CH_3{-}CH_2{-}OH} + H_2S$$

This reaction shows that alkyl sulphides are diesters of hydrogen sulphide.

MUSTARD GAS, β, β′-dichlorodiethyl sulphide,

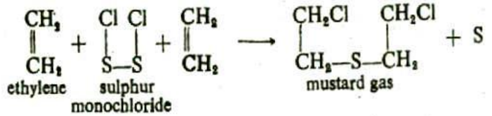
$$Cl{-}\overset{\beta}{C}H_2{-}\overset{\alpha}{C}H_2{-}S{-}\overset{\alpha'}{C}H_2{-}\overset{\beta'}{C}H_2{-}Cl$$

It was used as a 'poison gas' in the First World War (1914—18) under the name *Mustard gas.*

Preparation. (1) It was originally prepared by Germans from ethylene by reaction with HOCl to form ethylene chlorohydrin and then treating it with Na_2S and HCl in two operations to yield mustard gas.

$$\underset{\text{ethylene}}{CH_2{=}CH_2} \xrightarrow{+HOCl} \underset{\text{ethylene chlorohydrin}}{CH_2OH{-}CH_2Cl} \xrightarrow{Na_2S} (CH_2OH{-}CH_2)_2S \xrightarrow{HCl} \underset{\text{mustard gas}}{(CH_2Cl{-}CH_2)_2S}$$

(2) The English and the Americans produced it by passing ethylene into sulphur monochloride, S_2Cl_2.

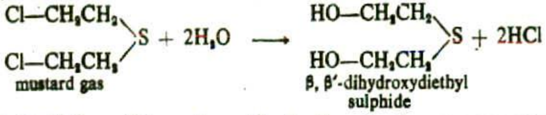


$$\underset{\text{ethylene}}{CH_2{=}CH_2} + \underset{\text{sulphur monochloride}}{S_2Cl_2} + CH_2{=}CH_2 \longrightarrow \underset{\text{mustard gas}}{ClCH_2CH_2{-}S{-}CH_2CH_2Cl} + S$$

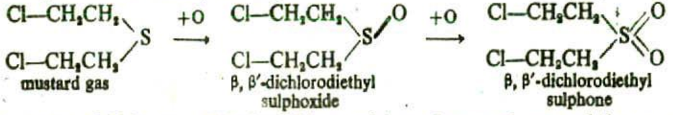
Properties. Mustard gas is not a gas but an oily liquid, bp 215°. It, however, vaporises when sprinkled by means of bursting shells. It produces painful blisters on the skin and has very destructive effect on the lungs and air passages. It is generally known to have a prolonged action, causing death after about four days.

Chemically mustard gas combines the reactions of an alkyl halide and organic sulphide.

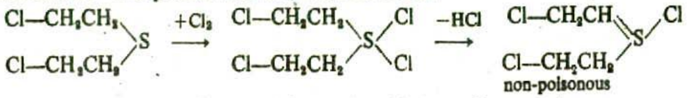
(1) *Hydrolysis.* The chlorine atoms are readily hydrolysed even in water solution.



(2) *Oxidation.* It is easily oxidised with potassium permanganate or hydrogen peroxide to form the sulphoxide and finally the sulphone.



(3) *Action of Chlorine.* Chlorine adds to sulphur of mustard gas and then a molecule of HCl is eliminated. The product has no poisonous action.



Since the products of chlorination and oxidation of mustard gas are non-poisonous substances, the above reactions can be employed to destroy mustard gas. The destruction of mustard gas is best accomplished by treating the affected region with free chlorine gas or bleaching powder.

QUESTIONS

1. Outline the methods of preparation and properties of thioalcohols and thioethers. *(Vikram BSc, 1993)*
2. What happens when ethanethiol is treated with NaOH ? *(Nehu BSc Hons, 1994)*
3. What happens when ethyl mercaptan is added to lead acetate solution ? *(Berhampur BSc, 1994)*
4. What is mustard gas ? What are its uses ? *(Kerala BSc, 1994)*
5. How will you synthesise sulphonal from acetone ? *(Madras BSc, 1993; Dibrugarh BSc Hons, 1994)*
6. How will you synthesise allyl disulphide from allyl alcohol ?

Answer.

$$\underset{\text{ALLYL ALCOHOL}}{CH_2{=}CHCH_2OH} \xrightarrow{PCl_5} CH_2{=}CHCH_2Cl \xrightarrow[\text{excess}]{NaSH} CH_2{=}CHSH$$

$$\xrightarrow[\text{or } H_2O_2]{I_2} \underset{\text{ALLYL DISULPHIDE}}{CH_2{=}CHCH_2S{-}SCH_2CH{=}CH_2}$$

7. Explain : Dimethyl sulphoxide (bp 189°C) has a much higher boiling point than dimethyl sulphide (bp 37°C).

Answer. The sulphur-oxygen bond in dimethyl sulphoxide is highly polar, with a + charge on sulphur and a − charge on the oxygen. This polarity causes the molecules of dimethyl sulphoxide to associate. Energy (heat) is required to break up this molecular association. Therefore, the boiling point of dimethyl sulphoxide is much higher than that of dimethyl sulphide.

8. *n*-Propyl bromide reacts with excess NaSH to form (A), C_3H_8S. Compound (A) reacts with concentracted HNO_3 to give (B), $C_3H_8O_3S$. Compound (B) reacts with PCl_5 and gives a chloride (C). Identify (A), (B) and (C).

Answer. (A) = $CH_3CH_2CH_2SH$ (*n*-Propanethiol)

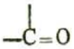
(B) = $CH_3CH_2CH_2SO_3H$ (*n*-Propylsulphonic acid)

(C) = $CH_3CH_2CH_2SO_2Cl$ (*n*-Propylsulphonyl chloride)

Chapter **20**

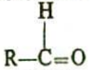
Aldehydes and Ketones—The carbonyl Compounds

Aldehydes and ketones are classes of compounds both of which contain a carbon doubly bonded to oxygen,



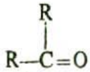
$$-\overset{|}{C}=O$$ (carbon-oxygen double bond)

The group $C=O$ known as the *carbonyl group* determines the chemistry of aldehydes and ketones, and hence these compounds are collectively called as **Carbonyl Compounds.** In aldehydes the carbonyl carbon is linked to one hydrogen atom and one alkyl group (formaldehyde in which CO is joined to two H atoms being an exception), while in ketones it is linked to two alkyl groups. Their type formulas are :



$$R-\overset{\overset{\displaystyle H}{|}}{C}=O$$

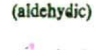
aldehyde



$$R-\overset{\overset{\displaystyle R}{|}}{C}=O$$

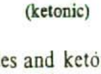
ketone

The ketones are called **Symmetrical ketones** or **Unsymmetrical Ketones** according as the two alkyl groups attached to the carbonyl group are the same or different.



$$R-\overset{\overset{\displaystyle R}{|}}{C}=O$$

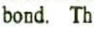
symmetrical ketone



$$R-\overset{\overset{\displaystyle R'}{|}}{C}=O$$

unsymmetrical ketone

The functional groups characteristic of aldehydes and ketones respectively are



$$-\overset{\overset{\displaystyle H}{|}}{C}=O$$

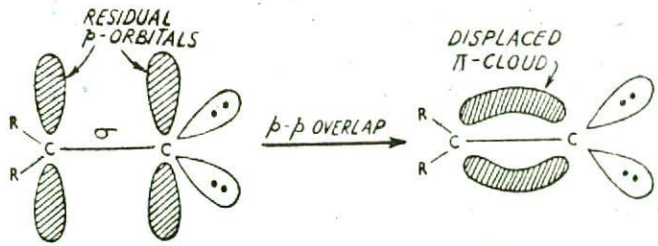
(aldehydic)

$$-\overset{|}{C}=O$$

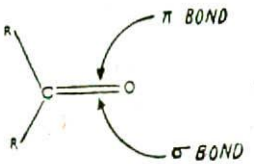
(ketonic)

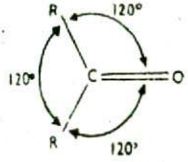
STRUCTURE

The carbon-oxygen double bond in aldehydes and ketones can be formulated in a manner similar to the carbon-carbon double bond in alkenes. Here we assume that both the carbon and oxygen of the carbonyl group are sp^2 hybridized. One sp^2 orbital of carbon overlaps with a sp^2 orbital of oxygen to form a σ bond, while the residual p orbitals of the two atoms overlap in a sidewise fashion to from a π bond. Therefore, a carbonyl double bond is, in fact, made of one σ bond and one π bond. Thus,



It may be noted that in the above model of a carbonyl compound, all the three sp^2 orbitals of carbon form σ bonds. On the other hand, only one sp^2 orbital of oxygen forms a σ bond and the two unused ones are occupied by pairs of electrons. Also, since the electronegativity of oxygen is much higher than that of carbon, the π electron cloud is displaced towards the oxygen as shown in the above model. This causes net polarisation of the bond. The carbon becomes slightly positive and oxygen slightly negative. Thus the carbonyl double bond can be represented as :





The carbonyl double bond thus differs from the carbon-carbon double bond of alkenes which is non-polar.

The above structure of carbonyl compounds accounts for their high dipole moment (2·3 to 2·8 D). The electron diffraction and spectroscopic studies reveal that the carbon, oxygen and the other two atoms or groups attached to carbonyl carbon lie in the same plane and have bond angles roughly 120°. These facts support the formulation of the structure of aldehydes and ketones described above.

NOMENCLATURE

Aldehydes and ketones are named according to the Common and the IUPAC systems.

(1) **Aldehydes.** The COMMON NAMES of aldehydes are derived from those of the carboxylic acids to which they are oxidised. The portion '*–ic* acid' of the name of the corresponding acid is replaced by the suffix '–aldehyde'. Thus CH_3CHO is oxidised to acetic acid and is named as acetaldehyde,

acetic acid — *ic acid* + aldehyde ⟶ acetaldehyde

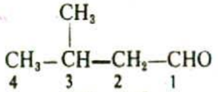
In the IUPAC system, aldehydes are named as *alkanals* and the name of an individual aldehyde is obtained by dropping the terminal '*e*' of the name of the parent hydrocarbon (having same carbon skeleton) and adding the suffix '–al'. Thus HCHO is called methanal, the parent hydrocarbon being methane,

methane – *e* + al ⟶ methanal

The common and IUPAC names of some aldehydes are given below.

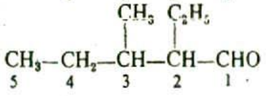
Formula	*Common Name*	*IUPAC Name*
HCHO	formaldehyde	methanal
CH_3CHO	acetaldehyde	ethanal
CH_3CH_2CHO	propionaldehyde	propanal
$CH_3CH_2CH_2CHO$	butyraldehyde	butanal
$CH_2{=}CHCHO$	acrolein	propenal

While assigning IUPAC names to complex aldehydes, the longest carbon chain including the —CHO group is selected as the parent chain. It is numbered from the carbon of the —CHO group which is assigned number '1'. The substituents on the chain are given positional numbers and named in the usual fashion. Since the aldehydic group —CHO is always at the end of the chain, it is unnecessary to specify its position in the systematic name. Thus,



$$\underset{4}{CH_3}-\underset{3}{\overset{\overset{\displaystyle CH_3}{|}}{CH}}-\underset{2}{CH_2}-\underset{1}{CHO}$$

3-methylbutanal



$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{\overset{\overset{\displaystyle CH_3}{|}}{CH}}-\underset{2}{\overset{\overset{\displaystyle C_2H_5}{|}}{CH}}-\underset{1}{CHO}$$

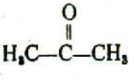
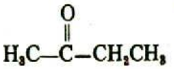
2-ethyl-3-methylpentanal

(2) **Ketones.** According to the COMMON SYSTEM, symmetrical ketones are named as *dialkyl ketones*. First member of the series CH_3COCH_3 is, however, popularly called *acetone*.

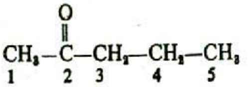
The common names of unsymmetrical ketones are obtained by naming the alkyl groups as separate words in alphabetic order and adding the third word 'ketone'.

The IUPAC name of ketones is *alkanones* and the name of an individual member on the system is derived by dropping the final '*e*' of the parent hydrocarbon (containing same number of C-atoms) and adding the suffix '*one*'.

The common and systematic names of a few ketones are given below.

Formula	*Common Name*	*IUPAC Name*
 $H_3C-\overset{\overset{O}{\|}}{C}-CH_3$	acetone, dimethyl ketone	propanone
 $H_3C-\overset{\overset{O}{\|}}{C}-CH_2CH_3$	ethyl methyl ketone	butanone

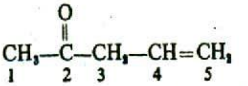
While naming higher ketones on IUPAC system, it becomes necessary to assign positional number to the carbonyl group.



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_3}$$

2-pentanone

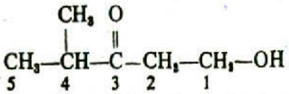
In complex compounds, where prefixing of the positional number to the ketone name gives rise to confusion it is inserted before the suffix *-one*.



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH_2}-\underset{4}{CH}=\underset{5}{CH_2}$$

4-penten-2-one

For naming a compound which in addition to carbonyl contains another functional group, the term *oxo* is also used to indicate the position of carbonyl on the hydrocarbon chain. For example,

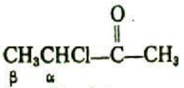


$$\underset{5}{CH_3}-\underset{4}{\overset{\overset{CH_3}{|}}{CH}}-\underset{3}{\overset{\overset{O}{\|}}{C}}-\underset{2}{CH_2}-\underset{1}{CH_2}-OH$$

4-methyl-3-oxo-1-pentanol

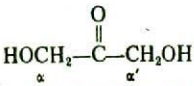
Sometimes, while naming substituted ketones, the positions of the side-chains or substituents on the parent chain are denoted by Greek letters α, β, γ etc.

The carbon adjacent to the carbonyl group is called α, the one next to it β, and so no. Thus,



$$CH_3\underset{\beta}{CH}\underset{\alpha}{Cl}-\overset{\overset{O}{\|}}{C}-CH_3$$

α-chlorobutanone



$$HO\underset{\alpha}{CH_2}-\overset{\overset{O}{\|}}{C}-\underset{\alpha'}{CH_2}OH$$

α, α′-dihydroxypropanone

ISOMERISM

Like other classes of organic compounds *aldehydes* and ketones also exhibit the following types of isomerism.

(1) **Chain Isomerism.** Both aldehydes and ketones show chain isomerism. Thus *n*-butyraldehyde, $CH_3CH_2CH_2CHO$, and isobutyraldehyde, $(CH_3)_2CHCHO$, are chain isomers. Similarly methyl *n*-propyl ketone $CH_3COCH_2CH_2CH_3$, and isopropyl methyl ketone $CH_3COCH(CH_3)_2$, are also chain isomers.

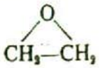
(2) **Positional Isomerism.** Aldehydes do not show positional isomerism because the —CHO group in them has to be present at the end of the chain. On the other hand a ketonic

carbonyl can be situated any where within the chain and hence ketones exhibit positional isomerism. Thus 2-pentanone, $CH_3COCH_2CH_2CH_3$, and 3-pentanone, $CH_3CH_2COCH_2CH_3$ are positional isomers.

(3) **Functional Isomerism**. Ketones show functional isomerism with aldehydes and unsaturated alcohols. For example, the formula C_3H_6O represents the following compounds.

$$\underset{\text{acetone}}{CH_3COCH_3} \qquad \underset{\text{propanal}}{CH_3CH_2CHO} \qquad \underset{\text{allyl alcohol}}{CH_2{=}CHCH_2OH}$$

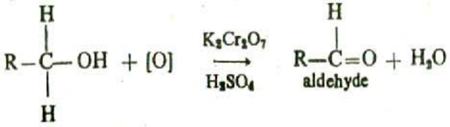
Aldehydes also exhibit functional isomerism with cyclic ethers. Thus acetaldehyde (CH_3CHO) is isomeric with ethylene oxide,



METHODS OF PREPARATION

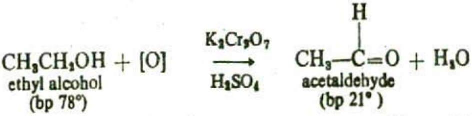
Aldehydes and ketones are similar in structure and there are several synthetic methods applicable to the preparation of these types of compounds. Also, there are methods useful for the preparation of aldehydes only and some for the preparation of ketones only.

(1) **Direct Oxidation of Alcohols**. Aldehydes are obtained by the direct oxidation of primary alcohols. The oxidants most commonly used are potassium dichromate in sulphuric acid or potassium permanganate in alkaline solution.



$$R-\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{aldehyde}}{R-\overset{\overset{\large H}{|}}{C}=O} + H_2O$$

primary alcohol



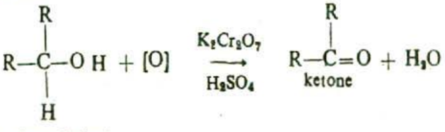
$$\underset{\substack{\text{ethyl alcohol}\\ \text{(bp 78°)}}}{CH_3CH_2OH} + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\substack{\text{acetaldehyde}\\ \text{(bp 21°)}}}{CH_3-\overset{\overset{\large H}{|}}{C}=O} + H_2O$$

The aldehydes formed in the above process are readily oxidised to carboxylic acid if allowed to remain in the reaction mixture.

$$\underset{\text{aldehyde}}{RCHO} + [O] \longrightarrow \underset{\text{acid}}{RCOOH}$$

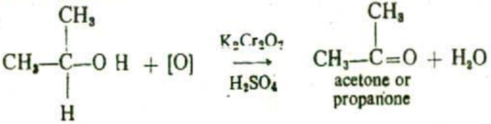
Therefore, the aldehyde formed must be removed from the reaction mixture before it gets opportunity to be oxidised to the acid. The aldehydes, however, have lower boiling points than the corresponding alcohols. Thus the reaction is carried at a temperature slightly above the boiling point of the aldehyde when the latter can be distilled as it is formed. In the oxidation of ethyl alcohol (78°), if the reaction mixture is maintained at about 25°, the acetaldehyde (bp 21°) formed distils over leaving the alcohol behind.

Ketones also may be prepared by oxidation of secondary alcohols with potassium dichromate in sulphuric acid.



$$R-\overset{\overset{\large R}{|}}{\underset{\underset{\large H}{|}}{C}}-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{ketone}}{R-\overset{\overset{\large R}{|}}{C}=O} + H_2O$$

secondary alcohol

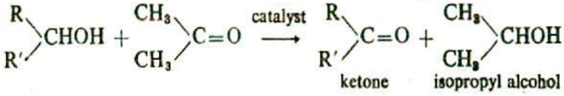


$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large H}{|}}{C}}-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\substack{\text{acetone or}\\ \text{propanone}}}{CH_3-\overset{\overset{\large CH_3}{|}}{C}=O} + H_2O$$

2-propanol

Ketones, unlike aldehydes, are not easily oxidised further (carbon-carbon bonds must be broken), and can be obtained in high yield by this method.

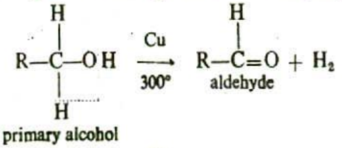
Another alternative procedure for this oxidation of alcohols is by refluxing them with acetone in the presence of aluminium tert-butoxide, Al(O—tert—Bu)$_3$, as catalyst. This is called **Oppenauer oxidation.** Here the alcohol is oxidised at the expense of acetone which is reduced.



This method is more commonly used for the preparation of ketones which contain oxidisable function (say, carbon-carbon double bond). The reaction cannot be ordinarily employed for the synthesis of aldehydes because most of them undergo condensation in the presence of aluminium tert-butoxide.

(2) **Catalytic Dehydrogenation of Alcohols.** When vapours of an appropriate primary alcohol are passed over a catalyst such as reduced copper or silver at 300°, the alcohol is dehydrogenated to give an aldehyde. Similarly ketones can be prepared from secondary alcohols.

(*i*)

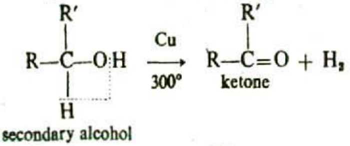


$$\underset{\text{primary alcohol}}{R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH} \xrightarrow[300^\circ]{Cu} \underset{\text{aldehyde}}{R-\overset{\displaystyle H}{C}=O} + H_2$$

e.g.,

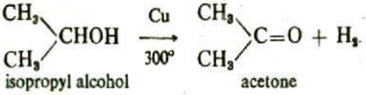
$$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[300^\circ]{Cu} \underset{\text{acetaldehyde}}{CH_3CHO} + H_2$$

(*ii*)

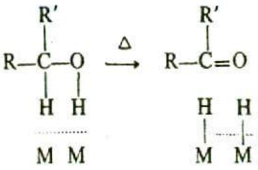


$$\underset{\text{secondary alcohol}}{R-\overset{\displaystyle R'}{\underset{\displaystyle H}{C}}-OH} \xrightarrow[300^\circ]{Cu} \underset{\text{ketone}}{R-\overset{\displaystyle R'}{C}=O} + H_2$$

e.g.,

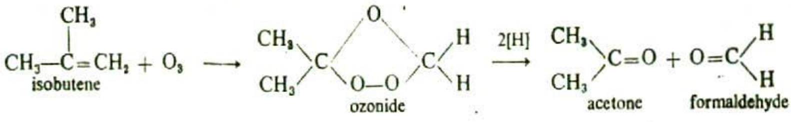


The above reactions could be explained as the reverse of hydrogenation process taking place on metal surface,



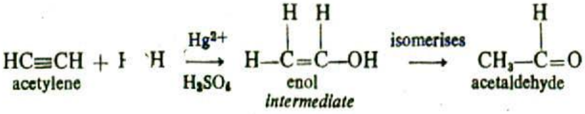
$$\begin{array}{c} R' \\ | \\ R-C-O \\ |\quad\;\; | \\ H\quad H \\ \\ M\quad M \end{array} \xrightarrow{\Delta} \begin{array}{c} R' \\ | \\ R-C=O \\ \\ H\quad H \\ |\quad\;\; | \\ M\quad M \end{array}$$

(3) **Oxidation of Alkenes with Ozone.** Some aldehydes and ketones can be obtained by the oxidation of alkenes with ozone. The ozonides formed are not isolated since they are often explosive in the dry state. Instead the reaction mixture is treated under reducing conditions (Zn + acetic acid; or Pd, H$_2$) to yield aldehydes and ketones.



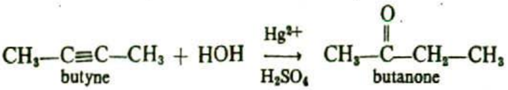
The ozonolysis reaction of alkenes described above has its great value as a diagnostic procedure, not as a preparative method.

(4) **Hydration of Alkynes.** Acetaldehyde is made by hydration of acetylene in the presence of a solution of mercuric sulphate and sulphuric acid.



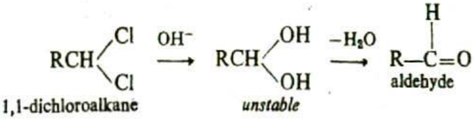
$$\underset{\text{acetylene}}{HC\equiv CH} + H{-}OH \xrightarrow[H_2SO_4]{Hg^{2+}} \underset{\substack{\text{enol}\\ \textit{intermediate}}}{H{-}\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}OH} \xrightarrow{\text{isomerises}} \underset{\text{acetaldehyde}}{CH_3{-}\overset{H}{\overset{|}{C}}{=}O}$$

Homologues of acetylene on similar hydration yield methyl ketones.



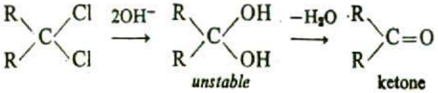
$$\underset{\text{butyne}}{CH_3{-}C\equiv C{-}CH_3} + HOH \xrightarrow[H_2SO_4]{Hg^{2+}} \underset{\text{butanone}}{CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_3}$$

(5) **Hydrolysis of gem-Dihalides.** Aldehydes can be prepared by the alkaline hydrolysis of gem-dihalides in which two halogen atoms are attached to the terminal carbon atom. The halogen atoms are first replaced by OH groups and the unstable glycol splits out a molecule of water to form an aldehyde.



$$\text{Thus,}\quad \underset{\text{1,1-dichloroethane}}{CH_3CHCl_2} \xrightarrow{OH^-} \underset{\textit{unstable}}{CH_3CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{acetaldehyde}}{CH_3CHO} + H_2O$$

Ketones are prepared by the hydrolysis of such gem-dihalides in which the two halogens are attached to any carbon atom other than the terminal carbon atom.



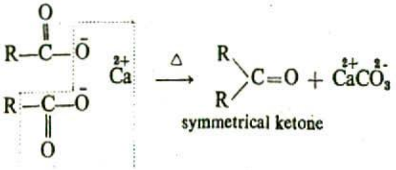
Thus,

$$\underset{\text{2,2-dibromopropane}}{CH_3{-}CBr_2{-}CH_3} \xrightarrow{2OH^-} \underset{\textit{unstable}}{CH_3{-}C(OH)_2{-}CH_3} \xrightarrow{-H_2O} \underset{\text{acetone}}{CH_3{-}CO{-}CH}$$

The dihalides required for the preparation of ketones can be obtained by the reaction of halogen acids (H−X) with alkynes.

This method is not generally useful because aldehydes and ketones are attacked by alkalis.

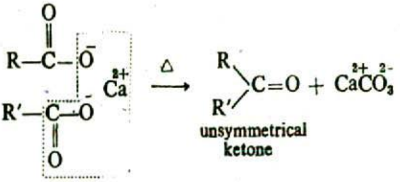
(6) **Pyrolysis of Salts of Carboxylic acids.** Aldehydes and ketones can be prepared by thermal decomposition (pyrolysis) of suitable calcium salts of carboxylic acids. This method is mainly valuable for synthesising symmetrial ketones.



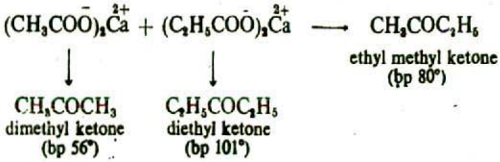
e.g.,

$$\underset{\text{calcium acetate}}{(CH_3{-}CO{-}O)_2\overset{2+}{Ca}} \xrightarrow{\Delta} \underset{\text{acetone}}{(CH_3)_2CO} + \overset{2+}{Ca}\overset{2-}{CO_3}$$

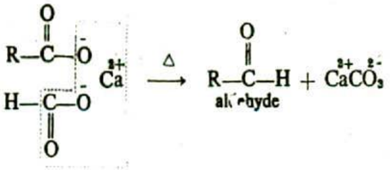
Unsymmetrical ketons are obtained by heating a mixture of calcium salts of two carboxylic acids (excluding formic acid).



The product is accompanied by the ketones RCOR and R'COR' formed from the two individual salts, necessitating separation. Thus when calcium acetate and calcium propionate are heated, a mixture of three ketones is obtained from which ethyl methyl ketone is separated by fractional distillation.



If one of the two calcium salts taken is derived from formic acid, an aldehyde is obtained.



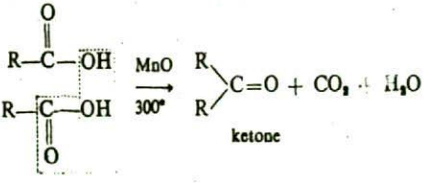
The aldehyde product is, of course, accompanied by the ketone and formaldehyde.

$$(\mathrm{RCO\overset{-}{O}})_2\overset{2+}{\mathrm{Ca}} \xrightarrow{\Delta} \mathrm{RCOR} + \overset{2+}{\mathrm{Ca}}\overset{2-}{\mathrm{CO_3}}$$

$$(\mathrm{HCO\overset{-}{O}})_2\overset{2+}{\mathrm{Ca}} \xrightarrow{\Delta} \underset{\text{formaldehyde}}{\mathrm{H_2CO}} + \overset{2+}{\mathrm{Ca}}\overset{2-}{\mathrm{CO_3}}$$

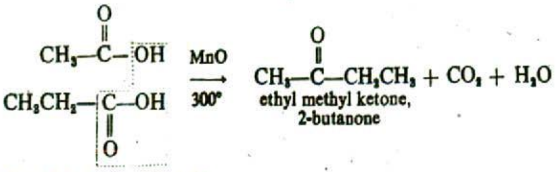
In general, yields of aldehydes and ketones in the above reaction are low and can be improved by taking barium, manganese or thorium salts instead of calcium salts.

(7) **Catalytic Decomposition of Carboxylic acids.** Simple ketones can be prepared in very good yield (90%) by passing the vapours of a suitable carboxylic acid (other than formic acid) over the heated oxide of manganese or thorium.



e.g., $\underset{\text{acetic acid}}{2\mathrm{CH_3COOH}} \xrightarrow[300^\circ]{\mathrm{MnO}} \underset{\text{acetone}}{(\mathrm{CH_3})_2\mathrm{CO}} + \mathrm{CO_2} + \mathrm{H_2O}$

Unsymmetrical ketones are obtained by passing a mixture of vapours of acids other than formic acid.

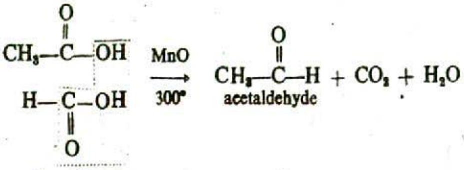


$$\begin{matrix} CH_3-\overset{O}{\overset{\|}{C}}-OH \\ CH_3CH_2-\underset{\underset{O}{\|}}{C}-OH \end{matrix} \xrightarrow[300^\circ]{MnO} \underset{\text{ethyl methyl ketone, 2-butanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3} + CO_2 + H_2O$$

acetic acid and propionic acid

The yield would be low since acetone and diethyl ketone are also formed simultaneously.

Aldehydes are prepared by passing a mixture of the vapours of formic acid and any other acid over the heated catalyst.

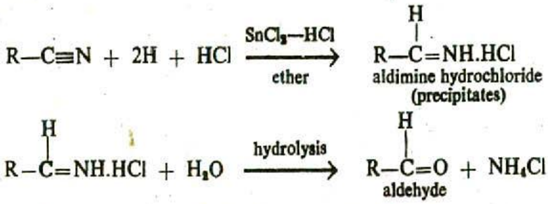


$$\begin{matrix} CH_3-\overset{O}{\overset{\|}{C}}-OH \\ H-\underset{\underset{O}{\|}}{C}-OH \end{matrix} \xrightarrow[300^\circ]{MnO} \underset{\text{acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + CO_2 + H_2O$$

acetic acid and formic acid

The aldehyde product is admixed with acetone, necessitating separation.

(8) **Stephens reduction of Nitriles.** It is a useful procedure to prepare aldehydes. Alkanenitriles are first reduced in ether solution by hydrogen chloride gas and stannous chloride at room temperature. The aldimine hydrochloride produced is filtered off and subsequently hydrolysed with warm water.

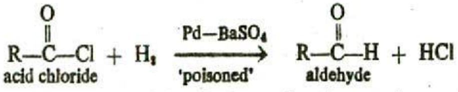


$$R-C\equiv N + 2H + HCl \xrightarrow[\text{ether}]{SnCl_2-HCl} \underset{\substack{\text{aldimine hydrochloride}\\\text{(precipitates)}}}{R-\overset{H}{\overset{|}{C}}=NH.HCl}$$

$$R-\overset{H}{\overset{|}{C}}=NH.HCl + H_2O \xrightarrow{\text{hydrolysis}} \underset{\text{aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} + NH_4Cl$$

This method is not applicable to the synthesis of ketones.

(9) **Rosenmund reduction of Acid chlorides.** Aldehydes can be prepared by the reduction of acid chlorides with H_2 gas in the presence of a palladium catalyst supported over barium sulphate at 140°C.



$$\underset{\text{acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + H_2 \xrightarrow[\text{'poisoned'}]{Pd-BaSO_4} \underset{\text{aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + HCl$$

Normally the aldehyde formed would be further reduced to a primary alcohol. But the barium sulphate poisons the palladium catalyst which is deactivated so as not to permit the further reduction of the aldehyde product. This is called *Rosenmund reduction*. Formaldehyde cannot be made by this method because formyl chloride, HCOCl, is very unstable at ordinary temperatures.

According to a more recent method, an acid chloride can be reduced to aldehydes using a modified hydride reagent, lithium tri-*t*-butoxyaluminium hydride.

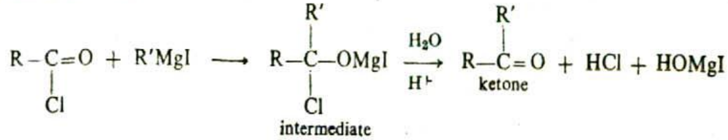
$$RCOCl + LiAl(O\text{-}t\text{-}Bu)_3H \xrightarrow{-78^\circ} RCHO + LiCl + Al(O\text{-}t\text{-}Bu)_3$$

This reaction is preferred to Rosenmund reaction as it proceeds at low temperature and the reducing agent is easy to prepare. It may be noted that $LiAlH_4$ alone would have reduced the aldehyde product to primary alcohol.

(10) **From Grignard Reagents.** Aldehydes can be synthesised by the action of Grignard reagents with excess of formic ester.

$$RMgCl + \underset{\text{ethyl formate}}{H-\overset{\overset{O}{\|}}{C}-OC_2H_5} \longrightarrow R-\overset{\overset{O}{\|}}{C}-H + ClMgOC_2H_5$$

Ketones are obtained by the addition of Grignard reagents to acid chlorides and subsequent acid hydrolysis.



$$R-\underset{\underset{Cl}{|}}{C}=O + R'MgI \longrightarrow \underset{\text{intermediate}}{R-\overset{\overset{R'}{|}}{\underset{\underset{Cl}{|}}{C}}-OMgI} \xrightarrow[H^+]{H_2O} \underset{\text{ketone}}{R-\overset{\overset{R'}{|}}{C}=O} + HCl + HOMgI$$

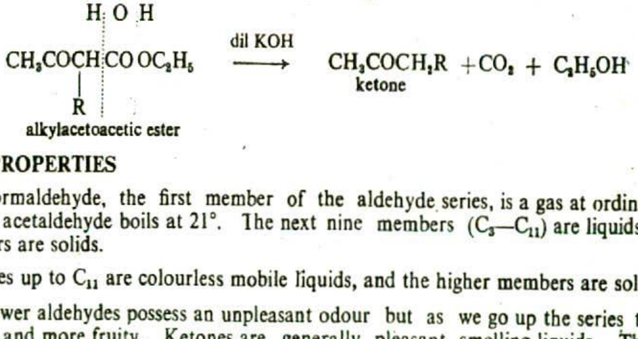
Recently organocadmium compounds have been used for the preparation of ketones from acid halides, in preference to Grignard reagents, since they do not react further with ketone product to form alcohol.

$$RMgCl + CdCl_2 \longrightarrow \underset{\substack{\text{cadmium}\\\text{grignard}}}{RCdCl} + MgCl_2$$

$$R'COCl + RCdCl \longrightarrow R'COR + CdCl_2$$

The reaction of a Grignard reagent with a nitrile and subsequent acid hydrolysis also yields a ketone.

(11) **From Acetoacetic esters.** Alkyl derivatives of acetoacetic ester, $CH_3COCH_2COOC_2H_5$, upon hydrolysis with dilute alkalis give the corresponding ketones.



$$\underset{\text{alkylacetoacetic ester}}{CH_3CO\underset{\underset{R}{|}}{C}H\,\overset{H\;O\;H}{\vdots}\,COOC_2H_5} \xrightarrow{\text{dil KOH}} \underset{\text{ketone}}{CH_3COCH_2R} + CO_2 + C_2H_5OH$$

PHYSICAL PROPERTIES

(1) Formaldehyde, the first member of the aldehyde series, is a gas at ordinary temperature while acetaldehyde boils at 21°. The next nine members (C_3—C_{11}) are liquids and the higher members are solids.

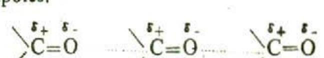
Ketones up to C_{11} are colourless mobile liquids, and the higher members are solids.

(2) Lower aldehydes possess an unpleasant odour but as we go up the series the smell becomes more and more fruity. Ketones are generally pleasant smelling liquids. The higher aldehydes (C_8—C_{13}) and ketones are used in perfumery.

(3) The first few members of the aldehyde and ketone series are soluble in water but the solubility falls rapidly with the increase in the size of the hydrocarbon groups attached to carbonyl group. Those with five or more carbon atoms are sparingly soluble or insoluble.

The solubility of aldehydes and ketones is accounted for by the electrostatic attractions between the polar carbonyl group and the water dipoles. Beyond C_5, however, the electrostatic forces of attraction between the polar group and water dipoles are insufficient to hold the molecule in solution since the large hydrocarbon-like nature of alkyl groups becomes dominant.

(4) Aldehydes and ketones being quite polar compounds (acetaldehyde 2·70 D ; acetone 2·85 D), there is a good deal of intermolecular association due to electrostatic attraction between opposite ends of C=O dipoles.



Hcence the boiling points of carbonyl compounds are higher than the non-polar alkanes of comparable molecular weight. The dipole-dipole attraction between molecules of aldehydes or ketones, however, is weaker than the analogous hydrogen bonding attraction between alcohol molecules. Thus the boiling points of the carbonyl compounds are lower than those of corresponding alcohols. For illustration, acetone, propionaldehyde and butane (having molecular weights 58, 58, 60) show boiling points 56°, 49° and −0·5° respectively.

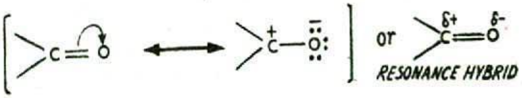
(5) In general melting points, boiling points of the members of both the aldehyde and ketone series show regular increase as we ascend the respective series. The physical constants of some of the carbonyl compounds are given below.

Table. Physical constants of some Aldehydes and Ketones

Name	*formula*	*mp °C*	*bp °C*	*solubility g/100 g H_2O*
Aldehydes :				
Formaldehyde	HCHO	−92	−21	$\propto$
Acetaldehyde	CH_3CHO	−124	20	∞
Propionaldehyde	CH_3CH_2CHO	−81	50	20
n-Butyraldehyde	$CH_3(CH_2)_2CHO$	−97	75	7
n-Valeraldehyde	$CH_3(CH_2)_3CHO$	−92	103	Sl.S
n-Caproaldehyde	$CH_3(CH_2)_4CHO$		131	Sl.S
Ketones :				
Acetone	CH_3COCH_3	−94	56	∞
Ethyl methyl ketone	$CH_3COCH_2CH_3$	−86	80	26
2-Pentanone	$CH_3COCH_2CH_2CH_3$	−84	102	Sl.S
3-Pentanone	$CH_3COCH_2CH_2CH_3$	−40	102	5
2-Hexanone	$CH_3CO(CH_2)_3CH_3$	−35	150	2
3-Hexanone	$CH_3CH_2COCH_2CH_2CH_3$		124	Sl.S

NATURE OF REACTIONS OF CARBONYL COMPOUNDS

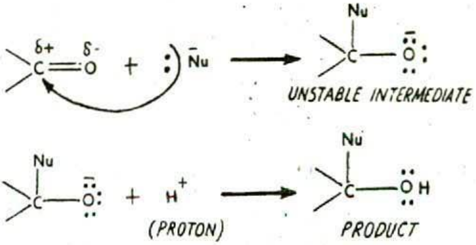
We have said earlier that the carbon-oxygen bond in aldehydes and ketones is polar. The greater electronegativity of oxygen than carbon shifts the electrons constituting the π bond partially towards oxygen. Thus carbon becomes slightly positive and oxygen slightly negative. Also, the carbonyl double bond can be represented as a resonance hybrid of the canonical forms I and II.



Hence, the carbon-oxygen bond is highly polarised. It implies that the carbon atom of the carbonyl group is electron-deficient, while the oxygen atom is electron-rich. This makes the C=O group an extremely reactive function in aldehydes and ketones. The basic principles involved in the general reactions of this class of compounds are discussed below.

(1) **Nucleophilic addition reactions.**

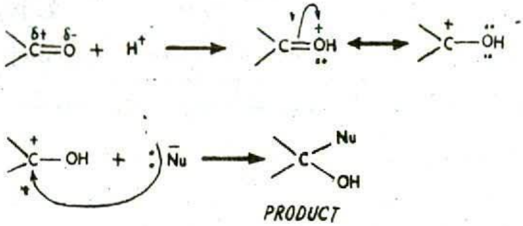
The electron-deficient carbon of the carbonyl group is easily attacked by a nucleophile which can supply an electron pair. Thus many addition reactions of the carbonyl compounds are initiated by nucleophiles. A general mechanism of such reactions is given on the next page.



First the nucleophile (: $\bar{Nu}$) adds to the carbonyl carbon to form an unstable intermediate. The intermediate then yields the final product by abstracting a proton from the solvent or the reacting agent. It is noteworthy that the entire process consisting of the above two steps is frequently reversible under certain conditions when the product is transformed back into the starting carbonyl compound.

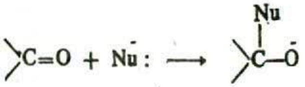
The nucleophilic addition reactions of carbonyl group are catalysed by acids or bases.

(*i*) **Acid-catalysed addition.** The proton released by the acid combines with the carbonyl oxygen and thus attenuates the electron deficiency of the carbon atom. In this way the positivity of the carbonyl carbon atom is increased and the attack of the nucleophile enhanced.

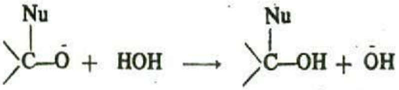


(*ii*) **Base-catalysed addition.** Here the nucleophile (: $\bar{Nu}$) is generated from its conjugate acid (Nu—H) in the presence of a base ($\bar{O}H$) and the addition takes place as described before.

$$Nu{-}H + \bar{O}H \longrightarrow \bar{Nu}: + HOH$$



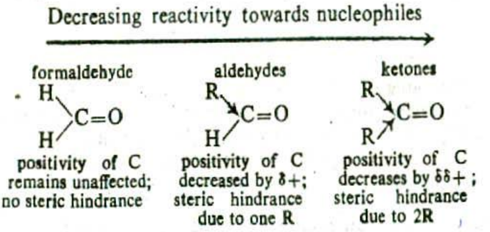
$$>C{=}O + \bar{Nu}: \longrightarrow >\overset{Nu}{\overset{|}{C}}{-}\bar{O}$$



$$>\overset{Nu}{\overset{|}{C}}{-}\bar{O} + HOH \longrightarrow >\overset{Nu}{\overset{|}{C}}{-}OH + \bar{O}H$$

It may be noted that whether the addition is acid-catalysed or base-catalysed, the product obtained is the same. An acid catalyst promotes nucleophilic attack by increasing the nucleophilic character of the carbonyl carbon, while a base does so by increasing the nucleophilicity of the reagent.

Relative Reactivities of Aldehydes and Ketones. For maximum reactivity towards nucleophiles, the carbonyl carbon atom should be as positive as possible and not sterically hindered by adjacent groups. The ketones have two alkyl groups on the carbonyl carbon while aldehydes have one alkyl group only. Each alkyl group being electron-releasing decreases the positivity of the carbon atom and on account of its bulk offers steric hindrance to the approaching reagents. For both these reasons, the nucleophilic attack on the carbonyl carbon is retarded. Thus the carbonyl group in ketones being influenced by two alkyl groups is less reactive than in aldehydes where the carbonyl group is under the influence of one alkyl group only. Formaldehyde having no alkyl group on carbonyl carbon is more reactive than all other aldehydes which are again more reactive than the ketones.

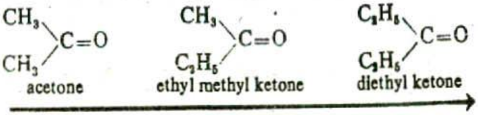


positivity of C remains unaffected; no steric hindrance

positivity of C decreased by $\delta+$; steric hindrance due to one R

positivity of C decreases by $\delta\delta+$; steric hindrance due to 2R

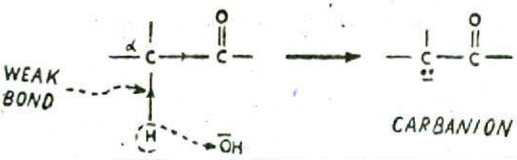
As we go higher in the series of carbonyl compounds, the electron-releasing power of the alkyl group is reduced and their shielding effect enhanced. Thus the reactivity of the carbonyl group in them is progressively decreased. For example,



Decreasing reactivity towards nucleophiles

(2) **Acidity of α-Hydrogen atom.** Another type of reactions of the carbonyl compounds are due to the acidity of the hydrogen atoms on carbon adjacent to carbonyl, or α-carbon atom. The acid character of the α-hydrogen atoms (attached to α-carbon) is explained as follows.

The carbonyl carbon is positive and, therefore, attracts the electrons in the single bond shared with α-carbon. The α-carbon in turn pulls towards it the electrons in the next single bond joining hydrogen. The drift of the electrons away from the hydrogen atom weakens the carbon-hydrogen bond. Thus there is a tendency for α-hydrogen atom to split off as proton in the presence of strong basic reagents.

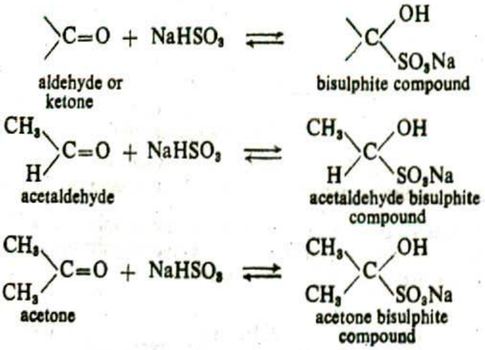


The removal of proton leaving an electron pair gives a carbanion or enolate ion which is resonance stabilised. The two contributing forms to the hybrid are

The carbanion thus produced is a good nucleophile and can attack carbonyl group of another molecule. The formation of the carbanion followed by its addition to a carbonyl group, is the process involved in all the condensation reactions of aldehydes and ketones.

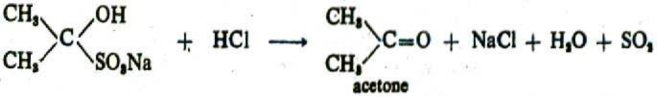
A. NUCLEOPHILIC ADDITION REACTIONS

(1) **Addition of Sodium bisulphite.** Saturated solution of sodium bisulphite ($NaHSO_3$) in water, when mixed with aldehydes and some ketones forms nicely crystalline 'bisulphite addition compounds'. Thus,



Almost all aldehydes form bisulphite addition compounds but only a few ketones of the type CH_3COR, where R is a primary alkyl group up to C_3 in size, undergo this addition. Ketones with bulky alkyl groups fail to react with sodium bisulphite presumably because of steric hindrance and shielding the electrophilic carbon atom of the carbonyl group.

The bisulphite addition compounds get decomposed back to the original carbonyl compounds in presence of acids or alkalis. Thus,

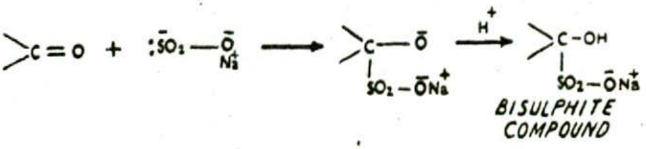


Hence the formation and decomposition of the bisulphite compounds serves as a powerful means of purification and separation of carbonyl compounds from non-carbonyl substances.

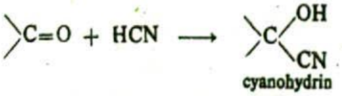
MECHANISM. Sodium bisulphite ionises to form sulphite ions.

$$NaHSO_3 \rightleftharpoons \overset{+}{Na} + \overset{+}{H} + \underset{\text{sulphite ion}}{:\ddot{S}O_2-\overset{-}{O}:}$$

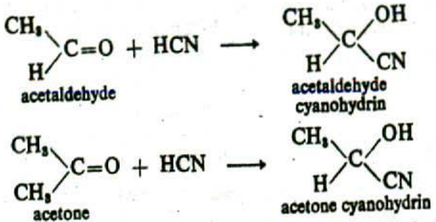
The negatively charged sulphite ion becomes the nucleophilic agent which attacks the positively charged carbonyl carbon atom. This is followed by the addition of a proton to the negatively charged oxygen atom to form the required bisulphite compound.



(2) **Addition of Hydrogen Cyanide.** Hydrogen cyanide adds on to all aldehydes and methyl ketones to yield *Cyanohydrins*, when the reaction is carried with a basic catalyst. Thus,



e.g.,



$$\mathrm{CH_3(H)C{=}O + HCN \longrightarrow CH_3(H)C(OH)(CN)}$$

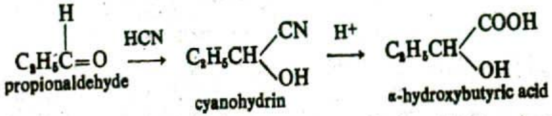
acetaldehyde — acetaldehyde cyanohydrin

$$\mathrm{(CH_3)_2C{=}O + HCN \longrightarrow CH_3(H)C(OH)(CN)}$$

acetone — acetone cyanohydrin

Hydrogen cyanide, a highly toxic gas, is never handled directly but is produced in the reaction mixture by treating sodium or potassium cyanide with a mineral acid ($NaCN + H_2SO_4$).

The hydrogen of cyanohydrins either in acid or basic solution will convert the nitrile group to the carboxylic acid. Since cyanohydrins are α-hydroxynitriles, this provides a useful route for the preparation of α-hydroxy acids. For example,



$$\mathrm{C_2H_5C(H){=}O \xrightarrow{HCN} C_2H_5CH(CN)(OH) \xrightarrow{H^+} C_2H_5CH(COOH)(OH)}$$

propionaldehyde — cyanohydrin — α-hydroxybutyric acid

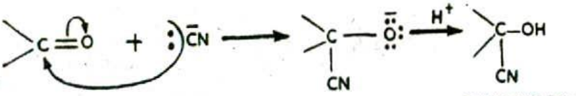
The α-hydroxy acid contains one more carbon than the original carbonyl compound.

MECHANISM. The presence of a base ($\bar{O}H$) promotes the ionization of HCN to give $\bar{C}N$ ions.

$$\mathrm{H{-}CN} + \dot{O}H \longrightarrow H_2O + :\bar{C}N$$

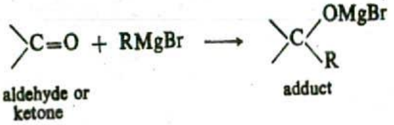
(nucleophile)

The reaction then proceeds by the nucleophilic attack of $\bar{C}N$ on the carbonyl carbon atom. This is followed by the addition of H^+ (supplied by H_2O) to the negative oxygen atom of the carbonyl group to form the required cyanohydrin.



CYANOHYDRIN

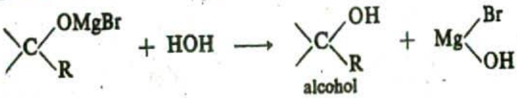
(3) **Addition of Grignard Reagents.** Almost all aldehydes and ketones react with Grignard reagent to form complex adducts,



$$\mathrm{{>}C{=}O + RMgBr \longrightarrow {>}C(OMgBr)(R)}$$

aldehyde or ketone — adduct

These upon hydrolysis with acid yield alcohols.

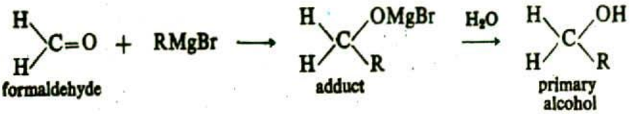


$$\mathrm{{>}C(OMgBr)(R) + HOH \longrightarrow {>}C(OH)(R) + Mg(Br)(OH)}$$

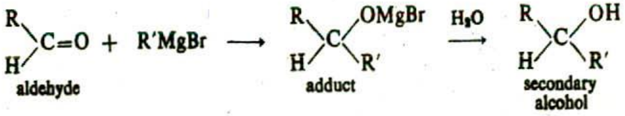
alcohol

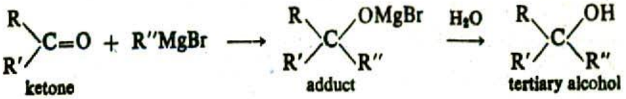
Thus the addition of Grignard Reagents to carbonyl compounds provides an excellent route for the synthesis of alcohols.

Formaldehyde gives a primary alcohol and this reaction is particularly useful for increasing the carbon chain by one carbon.

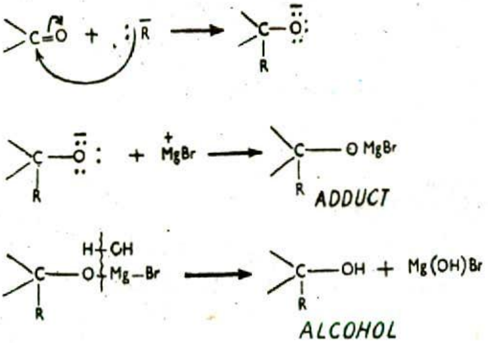


Other aldehydes yield secondary alcohols and ketones form tertiary alcohols.

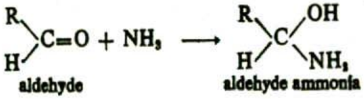




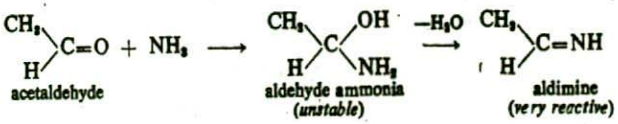
MECHANISM. As we have pointed out earlier, Grignard reagents have considerable ionic character and may be represented as $\overset{-}{R}\overset{+}{M}gBr$. The carbanion :$\bar{R}$ is a powerful nucleophile and attacks the carbonyl carbon atom which is followed by the association of $\overset{+}{M}gBr$ with the oxygen atom.

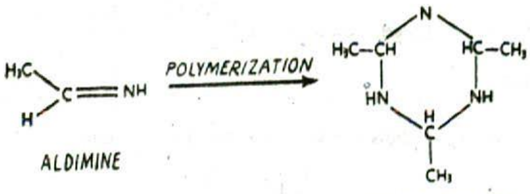


(4) **Addition of Ammonia.** Aldehydes react with ammonia to form aldehyde ammonias.



The aldehyde ammonias are unstable and lose water immediately to form aldimine. The dehydration product is not usually obtained because, in most cases, it immediately polymerises to form cyclic trimers. Thus for acetaldehyde,



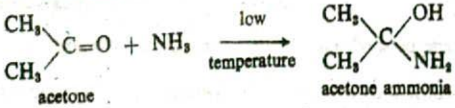


ALDIMINE

CYCLIC TRIMER

In actual practice only the final product of the reaction is isolated. Formaldehyde reacts in a different way yielding hexamethylenetetramine (*See formaldehyde*).

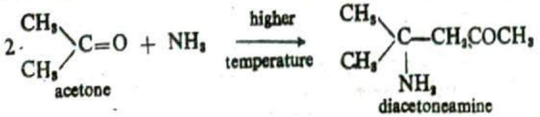
Ketones also give ketone-ammonias but these cannot be isolated. Acetone reacts slowly with ammonia to form first acetone ammonia and then a complex compound.



$$(CH_3)_2C{=}O + NH_3 \xrightarrow[\text{temperature}]{\text{low}} (CH_3)_2C(OH)NH_2$$

acetone — acetone ammonia

Acetone upon treatment with ammonia at higher temperature gives diacetoneamine.

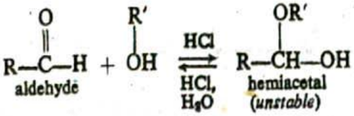


$$2\,(CH_3)_2C{=}O + NH_3 \xrightarrow[\text{temperature}]{\text{higher}} (CH_3)_2C(NH_2){-}CH_2COCH_3$$

acetone — diacetoneamine

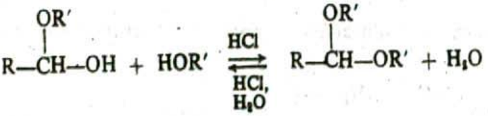
B. NUCLEOPHILIC ADDITION REACTIONS FOLLOWED BY LOSS OF WATER

(1) **Reaction with Alcohols.** In the presence of an acidic (or basic) catalyst, alcohols add to the carbonyl group of aldehydes to form adducts known as **Hemiacetals** (half-acetals). Hemiacetal is an unstable intermediate which at once reacts with another molecule of alcohol to yield a stable compounds called **Acetal.**



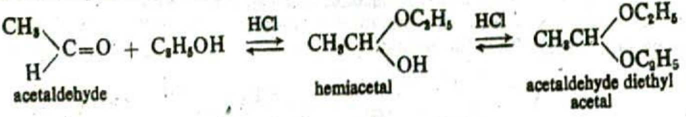
$$R{-}\overset{O}{\overset{\|}{C}}{-}H + \overset{R'}{\overset{|}{O}}H \underset{\substack{HCl,\\ H_2O}}{\overset{HCl}{\rightleftharpoons}} R{-}\overset{OR'}{\overset{|}{C}}H{-}OH$$

aldehyde — hemiacetal (*unstable*)



$$R{-}\overset{OR'}{\overset{|}{C}}H{-}OH + HOR' \underset{\substack{HCl,\\ H_2O}}{\overset{HCl}{\rightleftharpoons}} R{-}\overset{OR'}{\overset{|}{C}}H{-}OR' + H_2O$$

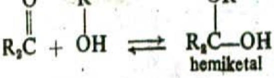
The forward reaction is catalysed by dry HCl, while the reverse reaction is catalysed by aqueous HCl. For example, acetaldehyde is converted to acetal as follows.



$$CH_3(H)C{=}O + C_2H_5OH \overset{HCl}{\rightleftharpoons} CH_3CH(OC_2H_5)(OH) \overset{HCl}{\rightleftharpoons} CH_3CH(OC_2H_5)_2$$

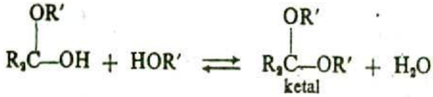
acetaldehyde — hemiacetal — acetaldehyde diethyl acetal

Ketones would react similarly to form **Hemiketals** and **Ketals.**



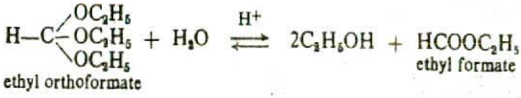
$$R_2\overset{O}{\overset{\|}{C}} + \overset{R'}{\overset{|}{O}}H \rightleftharpoons R_2\overset{OR'}{\overset{|}{C}}{-}OH$$

hemiketal



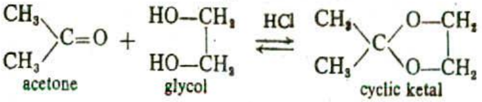
$$R_2C(OR')-OH + HOR' \rightleftharpoons \underset{\text{ketal}}{R_2C(OR')-OR'} + H_2O$$

The above equilibria lie far to the left and are unfavourable to the formation of ketals. But if the equilibria are tilted to the right by removing water produced during the reaction, ketals are prepared in satisfactory yield. This is done by the addition of orthoformic ester.

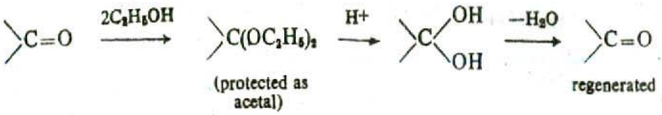


$$\underset{\text{ethyl orthoformate}}{H-C(OC_2H_5)_3} + H_2O \overset{H^+}{\rightleftharpoons} 2C_2H_5OH + \underset{\text{ethyl formate}}{HCOOC_2H_5}$$

Cyclic ketals are obtained by reaction with glycol in the presence of acid and in the absence of alkyl formate. Thus,

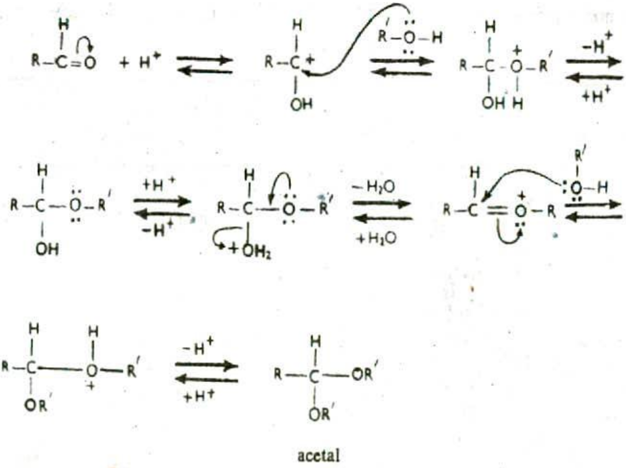


It is sometimes necessary to protect or mask an aldehyde or ketone group in a molecule to prevent it from reacting during the course of a transformation of some other functional group in the molecule. This is done by converting the carbonyl group into an acetal or cyclic ketal. After the reaction, the carbonyl group is regenerated by acid hydrolysis.

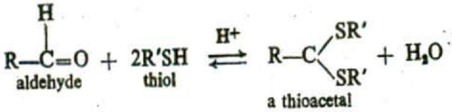


$$>C=O \xrightarrow{2C_2H_5OH} \underset{\text{(protected as acetal)}}{>C(OC_2H_5)_2} \xrightarrow{H+} >C(OH)_2 \xrightarrow{-H_2O} \underset{\text{regenerated}}{>C=O}$$

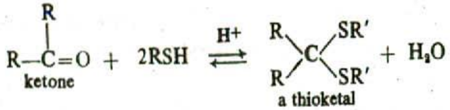
MECHANISM :



(2) **Reactions with Thiols or Thioalcohols.** Aldehydes and ketones both react with thiols (or thioalcohols) even more readily than with alcohols, to form **Thioacetals** and **Thioketals** respectively.



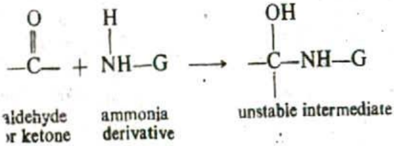
$$R{-}CH{=}O + 2R'SH \underset{}{\overset{H^+}{\rightleftharpoons}} R{-}CH(SR')_2 + H_2O$$

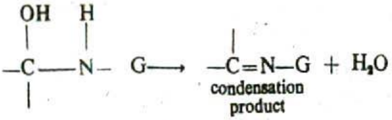


$$R_2C{=}O + 2RSH \overset{H^+}{\rightleftharpoons} R_2C(SR')_2 + H_2O$$

Thioacetals and thioketals are resistant to acid hydrolysis but can be readily converted to the original aldehydes and ketones when subjected to hydrolysis in the presence of $HgCl_2{-}CdCO_3$ mixtures. The formation of thioacetals and thioketals is also employed for masking the carbonyl group of aldehydes and ketones in organic synthesis.

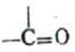
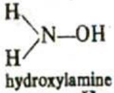
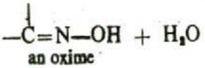
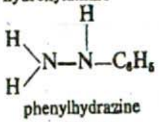
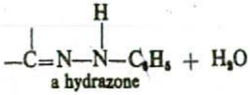
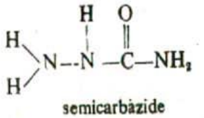
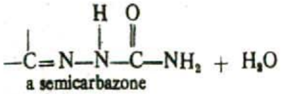
(3) **Reaction with Ammonia Derivatives, GNH_2.** Certain derivatives of ammonia which contain the primary amine group $-NH_2$, add to the carbonyl group of aldehydes and ketones to form unstable intermediates. These immediately lose a molecule of water to yield the respective 'condensation product'.





G stands for the general group bonded to $-NH_2$ group in the ammonia derivative.

The common ammonia derivatives used for the reaction and the products obtained are listed below.

Aldehyde or Ketone	*Ammonia derivative, NH_2-G*	*Product*
	+  hydroxylamine	→  an oxime
	+  phenylhydrazine	→  a hydrazone
	+  semicarbazide	→  a semicarbazone

The reaction product in each case is named *as oxime* (aldoxime or ketoxime), *phenylhdrazone* or *semicarbazone* of the carbonyl compound from which it was obtained. Thus the various ammonia derivatives react with acetaldehyde and acetone as follows.

(*a*) *With hydroxylamine*, H_2NOH

$$\underset{\text{acetaldehyde}}{CH_3CH{=}O} + H_2NOH \longrightarrow \underset{\text{acetaldoxime}}{CH_3CH{=}N{-}OH} + H_2O$$

$$\underset{\text{acetone}}{(CH_3)_2C{=}O} + H_2NOH \longrightarrow \underset{\text{dimethyl ketoxime}}{\underset{\text{acetone oxime,}}{(CH_3)_2C{=}N{-}OH}} + H_2O$$

(*b*) *With phenylhydrazine*, $H_2NNHC_6H_5$

$$CH_3CH{=}O + H_2NNHC_6H_5 \longrightarrow \underset{\text{acetaldehyde phenylhydrazone}}{CH_3CH{=}NNHC_6H_5} + H_2O$$

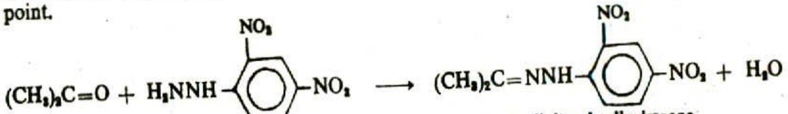
$$(CH_3)_2C{=}O + H_2NNHC_6H_5 \longrightarrow \underset{\text{actone pheylhydrazone}}{(CH_3)_2C{=}NNHC_6H_5} + H_2O$$

(*c*) *With Semicarbazide*, $H_2NNHCONH_2$

$$CH_3CH{=}O + H_2NNHCONH_2 \longrightarrow \underset{\text{acetaldehyde semicarbazone}}{CH_3CH{=}NNHCONH_2} + H_2O$$

$$(CH_3)_2C{=}O + H_2NNHCONH_2 \longrightarrow \underset{\text{acetone semicarbazone}}{(CH_3)_2C{=}NNHCONH_2} + H_2O$$

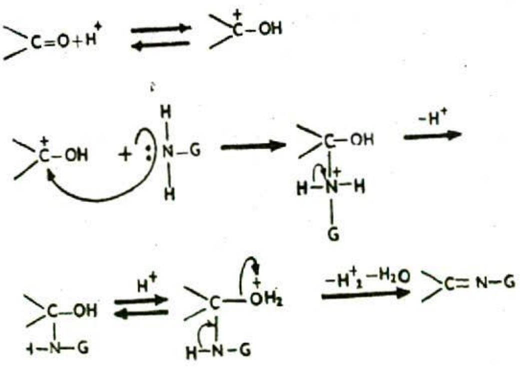
The product of reaction of aldehydes and ketones with the various ammonia derivatives are mostly crystalline solids having sharp melting points. For this reason they are frequently employed for the characterisation and identification of carbonyl compounds. The semicarbazones are usually high melting solids than are the oximes or the pheylhydrazones. Should the oxime or the phenylhydrazone of an unknown carbonyl compound be a low melting solid or oil, the semicarbazone will usually serve to identify it. If not, 2,4-dinitrophenylhydrazine may be used in place of phenylhydrazine and the product 2,4-dinitrophenylhydrazone has a high melting point.



2,4-dinitrophenylhydrazine

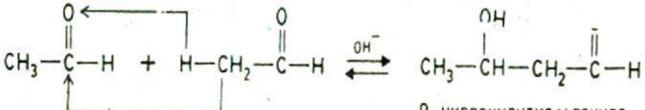
acetone 2,4-dinitrophenlhydrazone

MECHANISM. The reactions between ammonia derivatives and carbonyl compounds are acid catalysed. The first step in the mechanism is the protonation of the carbonyl group. The protonated spieces is then attacked by the ammonia derivarive (GNH_2) which acts as a nucleophile since it has a lone pair of electrons on the nitrogen atom. The adduct then rapidly loses a proton and a water molecule to give the final product.



C. REACTIONS INVOLVING ALKYL GROUP

(1) Aldol Condensation. Aldehydes undergo a reversible self addition in presence of dilute base to give condensation product which is both an aldehyde and alcohol. This is called **aldol** and the reaction is known as *aldol condensation*. It proceeds by addition of one molecule of aldehyde to the carbonyl group of another, with a simultaneous cleavage of carbon-hydrogen bond in α-position. Thus acetaldehyde when warmed with dilute sodium hydroxide gives β-hydroxybutyraldehyde (acetaldol).



β-HYDROXYBUTYRALDEHYDE

(3-hydroxybutanal)

When a mixture of two different aldehydes, each possessing an α-hydrogen, is treated with base, four different aldol products are formed; two from condensation of the two aldehydes with like molecules and two from condensation of two different aldehydes in two different ways. Thus,

$$RCH_2CH{=}O + CH_3CHO \xrightarrow{\bar{O}H} RCH_2CH(OH)CH_3CHO$$

crossed aldol

$$RCH_2CH{=}O + CH_2RCHO \xrightarrow{\bar{O}H} RCH_2CH(OH)CHRCHO$$

simple aldol

$$CH_3CH{=}O + CH_2RCHO \xrightarrow{\bar{O}H} CH_3CH(OH)CHRCHO$$

crossed aldol

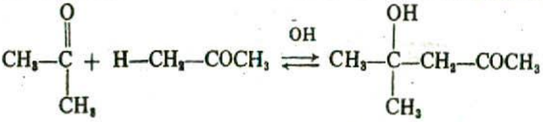
$$CH_3CH{=}O + CH_3CHO \xrightarrow{\bar{O}H} CH_3CH(OH)CH_2CHO$$

simple aldol

Because of the mixtures of aldols obtained, the reactions between two different aldehydes are of little preparative value.

It is noteworthy that any aldol condensation takes place with aldehydes having at least one α-hydrogen but not at all with those having no α-hydrogen, such as trimethylacetaldehyde, $(CH_3)_3CCHO$.

Ketones containing α-hydrogen also undergo aldol condensation to a smaller extent than do aldehydes. This is presumably as a consequence of steric hindrance to the carbonyl addition. Thus acetone in the presence of a base would establish the following equilibrium.



$$CH_3-\underset{CH_3}{\overset{O}{\overset{\|}{C}}} + H-CH_2-COCH_3 \overset{\bar{O}H}{\rightleftharpoons} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-COCH_3$$

diacetone alcohol,
4-hydroxypentan-2-pentanone
(aldol)

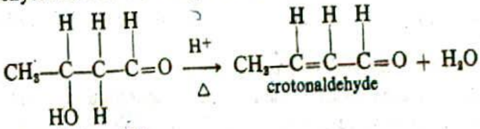
Ordinarily the equilibrium as above in case of ketones lies far towards the left and is unfavourable to aldol formation. However, diacetone alcohol (*i.e.*, aldol) may be obtained in excellent yield by using barium hydroxide as catalyst in a Soxhlet thimble through which hot acetone is allowed to percolate. The aldol product that accumulates in the Soxhlet extractor flask is kept out of contact with the catalyst so that it does not change back to give acetone.

Aldol condensation is not confined to aldehydes alone but can also take place between an aldehyde and a ketone (Cross **aldol condensation**), Thus accetaldehyde and acetone condense in presence of KCN to form 4-hydroxypentan-2-one.

$$CH_3CH{=}O + CH_3COCH_3 \xrightarrow{KCN} CH_3CH(OH)CH_2COCH_3$$

acetaldehyde acetone 4-hydroxypentan-2-one

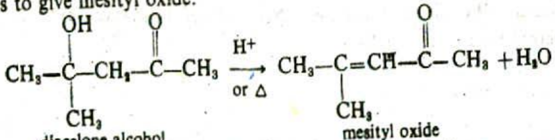
Dehydration of Aldols. Sometimes the aldol products are stable enough to be isolated. In other cases water may be lost spontaneously to form unsatuated aldehyde or ketone. Acetaldol itself may undergo dehydration on warming or in the presence of an acid to form crotonaldehyde.



$$CH_3-\underset{HO}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{H}{C}{=}O \xrightarrow[\Delta]{H^+} CH_3-\overset{H}{C}{=}\overset{H}{C}-\overset{H}{C}{=}O + H_2O$$

acetaldol or aldol crotonaldehyde

Similarly, diacetone alcohol (aldol of acetone) upon heating or in the presence of dilute mineral acid, dehydrates to give mesityl oxide.

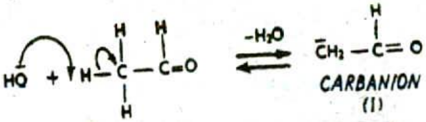


$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{or } \Delta]{H^+} CH_3-\underset{CH_3}{C}{=}CH-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$$

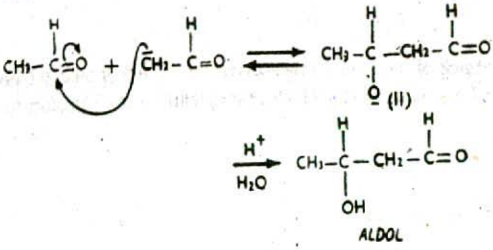
diacelone alcohol mesityl oxide

MECHANISM. The aldol condensation in case of aldehydes will be illustrated by taking example of acetaldehyde.

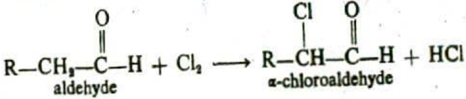
(*a*) The base ionises to form $\bar{O}H$ ion which removes a proton (H^+) from α-carbon, so forming a negatively charged residue or Carbanion.



(*b*) The nucleophilic attack of the carbanion (I) on the carbonyl carbon results in the formation of anion (II) which picks up a proton from H_2O to form aldol.

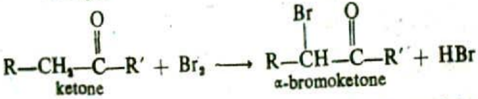


(2) **Halogenation**. Aldehydes and ketones are readily halogenated whereby the hydrogen atoms on the carbon next to the carbonyl group are readily replaced by Cl, Br or I atoms.



$$R-CH_2-\overset{O}{\overset{\|}{C}}-H + Cl_2 \longrightarrow R-\overset{Cl}{CH}-\overset{O}{\overset{\|}{C}}-H + HCl$$

aldehyde α-chloroaldehyde

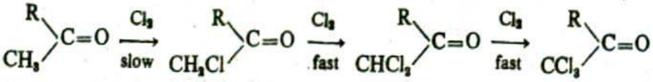


$$R-CH_2-\overset{O}{\overset{\|}{C}}-R' + Br_2 \longrightarrow R-\overset{Br}{CH}-\overset{O}{\overset{\|}{C}}-R' + HBr$$

ketone α-bromoketone

Thus acetaldehyde upon chlorination yields α-chloroacetaldehyde, CH_2ClCHO, and acetone upon bromination gives α bromoacetone, $CH_2BrCOCH_3$.

The second and third α-hydrogens in a carbonyl compound can be substituted by halogen atoms depending on the reaction time and conditions.



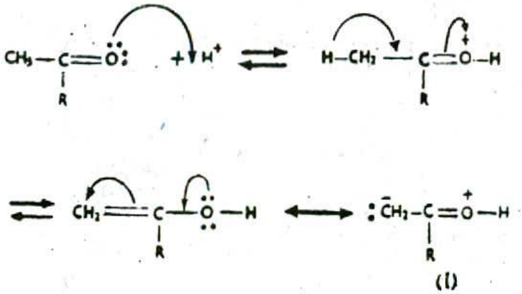
The introduction of the first halogen atom is slow but further substitution takes place more rapidly due to the addtional electron withdrawl of the halogen atom already present.

The halogenation of aldehydes and ketones is catalysed by acids and bases, but occurs more rapidly with the latter. Acid catalysis is used if the monoketone is required as the overall rate of halogenation is slower than base catalysis.

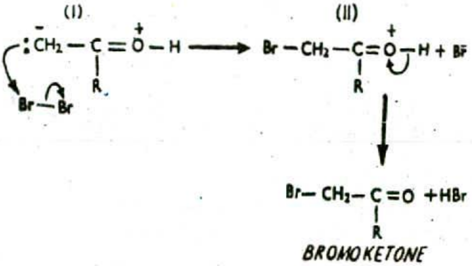
MECHANISM. Acid catalysed and base catalysed halogenation of aldehydes and ketones takes place *via* enolic form. We will illustrate the mechanism of both types by taking example of bromination of a methyl ketone, $RCOCH_3$.

(*a*) *Acid catalysed reaction* :

(*i*) In the presence of acids (H^+) the ketone gives the enolic form (I).

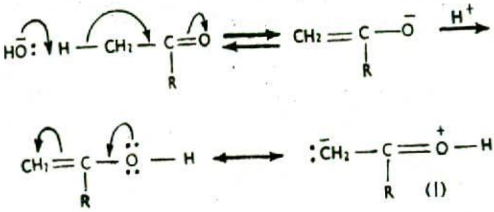


(*ii*) Nucleophilic attack of the enol (I) then takes place over molecular bromine resulting in the potonated form of α-bromoketone (II) which subsequently loses a proton to bromine ion to furnish α-bromoketone.



(*b*) *Base catalysed reaction* :

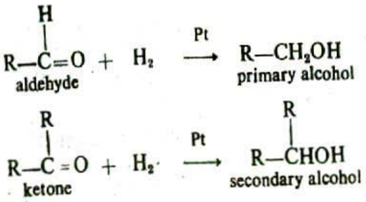
(*i*) Enol I is formed as follows.



(*ii*) Enol form (I) then reacts in a fashion as described in step (*ii*) of acid catalysed mechanism to give α-bromoketone.

D. REDUCTION OF CARBONYL COMPOUNDS

(1) **Reduction to Alcohols.** The carbonyl group of aldehydes and ketones can be reduced to give a primary and secondary alcohol respectively This reaction can be carried with hydrogen in the presence of metal catalysts such as platinum, palladium, nickel or copper chromite.

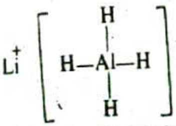


$$\underset{\text{aldehyde}}{R-\overset{\displaystyle H}{\overset{|}{C}}=O} + H_2 \xrightarrow{Pt} \underset{\text{primary alcohol}}{R-CH_2OH}$$

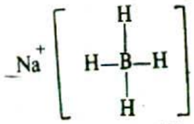
$$\underset{\text{ketone}}{R-\overset{\displaystyle R}{\overset{|}{C}}=O} + H_2 \xrightarrow{Pt} \underset{\text{secondary alcohol}}{R-\overset{\displaystyle R}{\overset{|}{C}}HOH}$$

The catalytic hydrogenation of aldehydes and ketones to get alcohols, on account of drastic conditions of the reaction, is no longer used in the laboratory. However, the method remains useful on an industrial scale because hydrogen gas is quite cheap.

At present, chemical reducing agents such as lithium aluminium hydride, $LiAlH_4$, and sodium borohydride, $NaBH_4$, are extensively used for the reduction of carbonyl compounds, Their structural formulae are

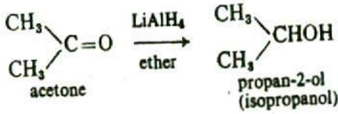


lithium aluminium hydride



sodium borohydride

The hydride reagent is dissolved in the appropriate solvent and its solution mixed with solution of the carbonyl compound. The reaction takes place in a short time at room temperature. $LiAlH_4$ solution is prepared in ether because it reacts with water and alcohol much as Grignard reagent does. Thus,



acetone

propan-2-ol (isopropanol)

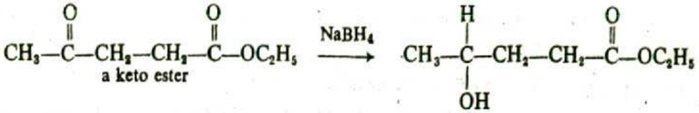
Sodium borohydride is not sensitive to water and alcohol. Its solution for reduction of carbonyls are prepared in these solvents.

Metal hydrides have a distinct advantage over catalytic hydrogenation because these do not reduce carbon-carbon double bond. Thus when 2-butenal is reduced with $LiAlH_4$, the carbonyl group is reduced to alcohol without affecting the carbon-carbon double bond in the molecule.

$$\underset{\text{2-butenal}}{CH_3CH{=}CHCHO} \xrightarrow[\text{ether}]{LiAlH_4} \underset{\text{2-buten-1-ol}}{CH_3CH{=}CHCH_2OH}$$

However, lithium aluminium hydride is a strong reducing agent for carbonyl groups not only of aldehydes and ketones but also of carboxylic acids, esters and other acid derivatives.

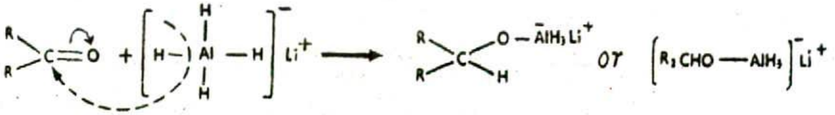
Sodium borohydride is a milder reducing agent than lithium aluminium hydride and unlike the latter it does not reduce carbonyl groups of other functions. Thus with its help we can reduce selectively carbonyl groups without affecting ester, amide and carboxylic groups in the same molecule. For example,



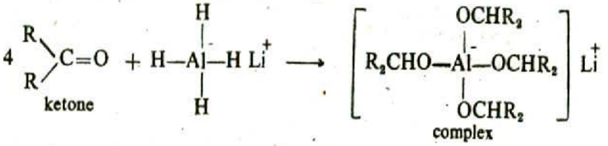
$$\underset{\text{a keto ester}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5} \xrightarrow{NaBH_4} CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5$$

(ester group remains unaffected)

MECHANISM. The reduction of carbonyl compounds with lithium aluminium hydride $\overset{+}{Li}AlH^-_4$ (or $\overset{+}{Na}BH^-_4$) proceeds by the following steps. A hydride ion (H^-) adds to a carbonyl carbon and the aluminium (or B) atom attached to the carbonyl oxygen, giving a complex. The complex when decomposed with water yields the alcohol, $Al(OH)_3$ and LiOH.



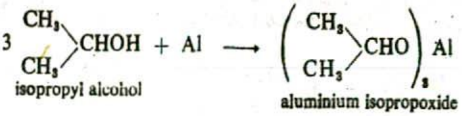
Likewise all four hydrogens on aluminium can be utilised to form the complex. This receives four protons from water and reduction is complete.



$$4\underset{\text{ketone}}{R_2C{=}O} + H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{\bar{Al}}}-H\ \overset{+}{Li} \longrightarrow \underset{\text{complex}}{\left[R_2CHO-\overset{\overset{\displaystyle OCHR_2}{|}}{\underset{\underset{\displaystyle OCHR_2}{|}}{\bar{Al}}}-OCHR_2\right]}\overset{+}{Li}$$

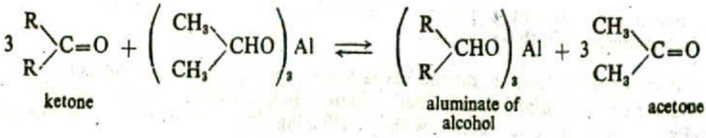
$$\xrightarrow{+4H_2O} \underset{\text{alcohol}}{4R_2CHOH} + Al(OH)_3 + LiOH$$

Another important reducing agent which is specific for the reduction of carbonyl compounds to alcohols is aluminium isopropoxide, prepared from aluminium and isopropyl alcohol.



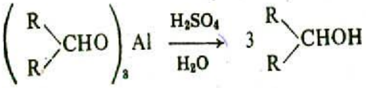
$$3\underset{\text{isopropyl alcohol}}{(CH_3)_2CHOH} + Al \longrightarrow \underset{\text{aluminium isopropoxide}}{\left((CH_3)_2CHO\right)_3Al}$$

In this reaction which is known as **Meerwein-Poundorf-Verley reduction**, the aldehyde or ketone is allowed to react with aluminium isopropoxide in isopropyl alcohol as solvent.



$$3\underset{\text{ketone}}{R_2C{=}O} + \left((CH_3)_2CHO\right)_3Al \rightleftharpoons \underset{\text{aluminate of alcohol}}{\left(R_2CHO\right)_3Al} + 3\underset{\text{acetone}}{(CH_3)_2C{=}O}$$

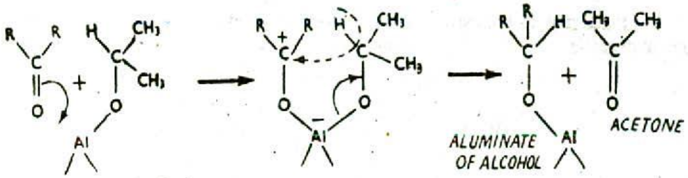
Acetone is distilled and the equilibrium is pushed to the right-hand side. The resulting aluminate is then treated with dilute acid to yield the alcohol.



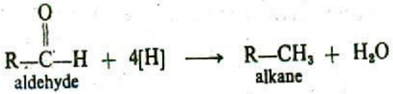
$$\left(R_2CHO\right)_3Al \xrightarrow[H_2O]{H_2SO_4} 3\,R_2CHOH$$

Meerwein-Poundorf-Verley reduction is useful because other reducible groups like double bonds, nitro groups etc., present in the carbonyl compound remain unaffected.

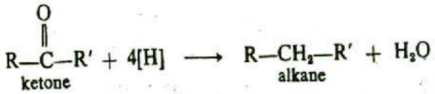
MECHANISM. The reaction is initiated by donation of a pair of electrons from the carbonyl double bond to the incomplete shell of aluminium. This is followed by direct hydride (H^-) transfer to the carbonyl carbon to give aluminate of the alcohol product.



(2) **Reduction to Hydrocarbons.** The carbonyl group of aldehydes and ketones may be reduced to methylene group, yielding hydrocarbons.



$$\underset{\text{aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + 4[H] \longrightarrow \underset{\text{alkane}}{R-CH_3} + H_2O$$



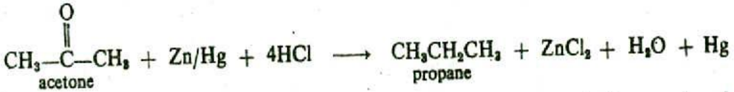
$$\underset{\text{ketone}}{R-\overset{O}{\overset{\|}{C}}-R'} + 4[H] \longrightarrow \underset{\text{alkane}}{R-CH_2-R'} + H_2O$$

This is done by two general methods :

(*i*) *The Clemmensen reduction* ;

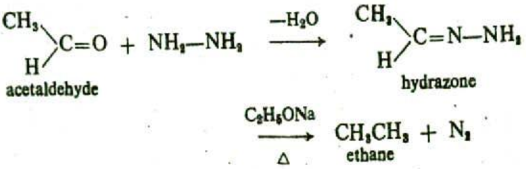
(*ii*) *The Wolff-Kishner reduction.*

Clemmensen Reduction uses amalgamated Zinc (Zn/Hg) and hydrochloric acid as the reducing agent. For illustration,



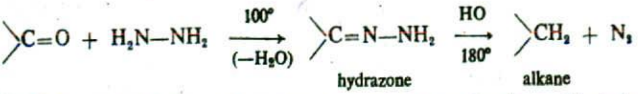
$$\underset{\text{acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + Zn/Hg + 4HCl \longrightarrow \underset{\text{propane}}{CH_3CH_2CH_3} + ZnCl_2 + H_2O + Hg$$

Wolff-Kishner reduction utilises hydrazine ($NH_2.NH_2$) as a reducing agent and sodium ethoxide as catalyst. First the aldehyde or ketone is converted to hydrazone which is then heated with sodium ethoxide ($Na+C_2H_5OH$) to give the hydrocarbon. Thus,



$$\underset{\text{acetaldehyde}}{CH_3(H)C{=}O} + NH_2-NH_2 \xrightarrow{-H_2O} \underset{\text{hydrazone}}{CH_3(H)C{=}N-NH_2} \xrightarrow[\Delta]{C_2H_5ONa} \underset{\text{ethane}}{CH_3CH_3} + N_2$$

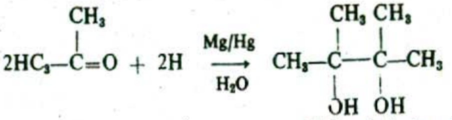
According to *Huang-Minlon modification* (1946) of this method, the hydrazone of the carbonyl compound is prepared, and while still in solution, is heated in a high boiling solvent (diethylene glycol) with alkali until it is decomposed.



The advantage of this method is that it is convenient and the product is readily isolated in pure state.

Both Clemmensen method and Kishner method are widely used for converting aldehydes and ketones to hydrocarbons, the latter being preferable for aldehydes and the former for ketones.

(3) **Reduction to Pinacols.** Ketones when reduced in neutral or alkaline medium, form 1,2-diols or *pinacols*. Thus with magnesium amalgam and water, acetone is reduced as follows.

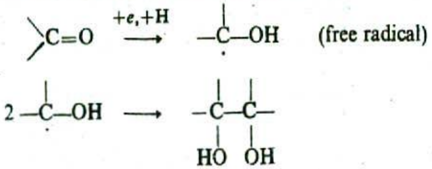


$$2HC_3-\overset{CH_3}{\overset{|}{C}}=O + 2H \xrightarrow[H_2O]{Mg/Hg} CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

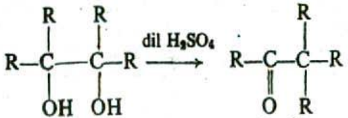
2,3-dimethylbutane,
2,3-diol (pinacol)

Aldehydes do not undergo 'pinacol reduction'.

The mechanism of pinacol reduction is believed to involve the intermediate free radical.



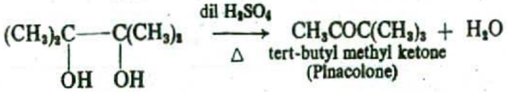
Pinacol-Pinacolone Rearrangement. Upon treatment with hot dil H_2SO_4, pinacol undergoes a rearrangement *and deyhdration* to form a monoketone called *pinacolone.* This is known as pinacol-pinacolone rearrangement.



$$R-\underset{OH}{\overset{R}{C}}-\underset{OH}{\overset{R}{C}}-R \xrightarrow{dil\ H_2SO_4} R-\underset{\underset{O}{\|}}{C}-\underset{R}{\overset{R}{C}}-R$$

pinacol pinacolone

e.g.,



$$(CH_3)_2\underset{OH}{C}-\underset{OH}{C}(CH_3)_2 \xrightarrow[\Delta]{dil\ H_2SO_4} CH_3COC(CH_3)_3 + H_2O$$

Pinacol

tert-butyl methyl ketone
(Pinacolone)

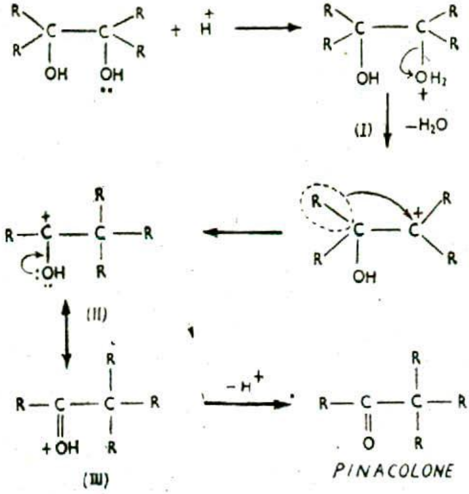
MECHANISM. It is considered to take place by the following steps.

(*i*) The basic OH group accepts a proton from a strong acid to form protonated glycol (I).

(*ii*) The ion (I) readily ionises, losing H_2O and forming the carbonium ion (II).

(*iii*) The alkyl group R with its bonding electrons, migrates to generate a better carbonium ion (III) (*i.e.*, with greater resonance stablisation).

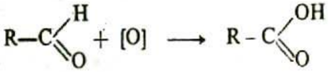
(*iv*) The carbonium ion (III) loses a proton to give pinacolone.



E. OXIDATION REACTIONS

(1) **Oxidation to Carboxylic acids.** Aldehydes are oxidised to the corresponding carboxylic acids. Ketones are oxidised with difficulty giving acids with smaller number of carbon atoms. The ease with which the oxidation reaction takes place provides a simple method of distinguishing between aldehydes and ketones.

(*a*) When oxidised with the usual strong oxidising agents such as chromic acid and potassium permanganate, aldehydes are converted to carboxylic acids in good yield.



$$R{-}C\begin{matrix}\nearrow H\\ \searrow O\end{matrix} + [O] \longrightarrow R-C\begin{matrix}\nearrow OH\\ \searrow O\end{matrix}$$

This oxidation can also be achieved by using milder oxidants such as (*i*) ammoniacal solution of silver nitrate (*Tollen's reagent*); (*ii*) alkaline solution of cupric ions. Since cupric hydroxide is insoluble it is made soluble by complex formation either with tartarate ions (*Fehling's solution*) or with citrate ions (*Benedict's solution*).

Tollen's Reagent. It contains the soluble silver ammonia ion, $[Ag(NH_3)_2]^+$. The oxidation of aldehyde is accompanied by reduction of silver ion to metallic silver which appears as mirror under proper conditions. Hence ths reaction is also called *silver mirror test* for aldehydes.

$$AgNO_3 + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+NO_3^-$$

$$RCHO + 2[Ag(NH_3)_2]^+ + 3\bar{O}H \longrightarrow RCOOH + \underset{\text{silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

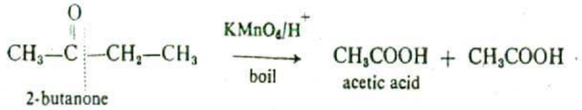
Fehlings' Solution. It contains complex cupric ions and is prepared by adding Fehling A solution which contains copper sulphate, to Fehling B solution which contains sodium hydroxide and Rochelle salt (sodium potassium tartarate). During the oxidation of aldehydes to acids, the cupric ions are reduced to cuprous ions which are precipitated as red cuprous oxide.

$$RCHO + 2\overset{2+}{Cu} + 3O\bar{H} \longrightarrow RCO\bar{O} + 2\overset{+}{Cu} + 2H_2O$$

$$2\overset{+}{Cu} + 2\bar{O}H \longrightarrow \underset{\substack{\text{cuprous oxide}\\ (\textit{red})}}{Cu_2O\downarrow} + H_2O$$

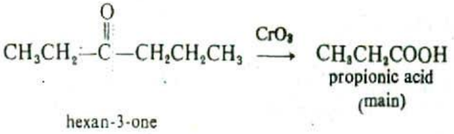
Ketones are not oxidised by the above reagents and hence are used to distinguish between aldehydes and ketones.

Ketones can, however, be oxidised under drastic conditions which involves the cleavage of carbon-carbon bonds. Consequently the acids thus produced contain fewer carbon atoms than the original ketone. When oxidised with acid potassium permanganate or hot chromic acid, the ketone molecule cleaves at the C–CO bond to give a mixture of carboxylic acids. Two such bonds are present and both are liable to attack, increasing the range of products. If one of the α-carbon atoms has fewer hydrogen atoms than the other, then this is attacked preferentially (**Popoff's Rule**). Thus,

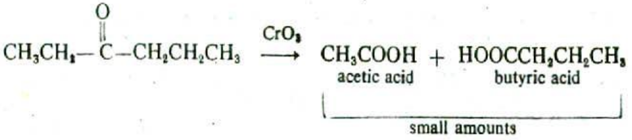


$$\underset{\text{2-butanone}}{CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}CH_2{-}CH_3} \xrightarrow[\text{boil}]{KMnO_4/\overset{+}{H}} \underset{\text{acetic acid}}{CH_3COOH + CH_3COOH}$$

If the carbon atoms adjacent to the carbonyl group have the same number of hydrogen atoms, the carbonyl group remains chiefly with the smaller alkyl group. Thus the oxidation of hexan-3-one gives propionic acid as the main product with small amounts of butyric acid and acetic acid.

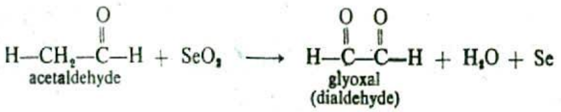


$$\underset{\text{hexan-3-one}}{CH_3CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}CH_2CH_2CH_3} \xrightarrow{CrO_3} \underset{\substack{\text{propionic acid}\\ \text{(main)}}}{CH_3CH_2COOH}$$

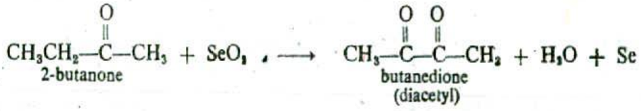


$$CH_3CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}CH_2CH_2CH_3 \xrightarrow{CrO_3} \underbrace{\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{butyric acid}}{HOOCCH_2CH_2CH_3}}_{\text{small amounts}}$$

(2) **Formation of Dicarbonyl Compounds.** Aldehydes and ketones also undergo a special oxidation reaction which does not involve the cleavage of carbon-carbon bonds. Selenium oxide SeO_2, oxidisises a methyl group which is adjacent to the carbonyl group to form a dicarbonyl compound. Thus,

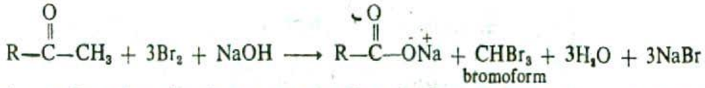


$$\underset{\text{acetaldehyde}}{H{-}CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}H} + SeO_2 \longrightarrow \underset{\substack{\text{glyoxal}\\ \text{(dialdehyde)}}}{H{-}\overset{\overset{\large O}{\|}}{C}{-}\overset{\overset{\large O}{\|}}{C}{-}H} + H_2O + Se$$



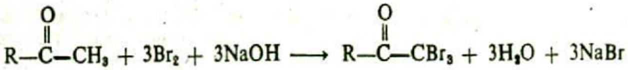
$$\underset{\text{2-butanone}}{CH_3CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3} + SeO_2 \longrightarrow \underset{\substack{\text{butanedione}\\ \text{(diacetyl)}}}{CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3} + H_2O + Se$$

(3) **Haloform Reaction.** When a methyl ketone is treated with a halogen in sodium hydroxide solution, it is oxidised to a carboxylic acid containing one carbon less than the original molecule with the simultaneous formation of trihalomethane. Thus,

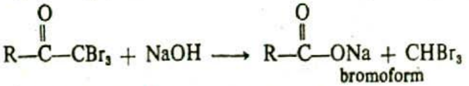


$$R{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3 + 3Br_2 + NaOH \longrightarrow R{-}\overset{\overset{\large O}{\|}}{C}{-}\overset{-}{O}\overset{+}{Na} + \underset{\text{bromoform}}{CHBr_3} + 3H_2O + 3NaBr$$

This reaction, in fact takes place in two stages. First the three hydrogen atoms of methyl group are replaced by three halogen atoms and then the molecule is cleaved to give an acid and trihalomethane.



$$R-\overset{\overset{O}{\|}}{C}-CH_3 + 3Br_2 + 3NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-CBr_3 + 3H_2O + 3NaBr$$



$$R-\overset{\overset{O}{\|}}{C}-CBr_3 + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-ONa + \underset{\text{bromoform}}{CHBr_3}$$

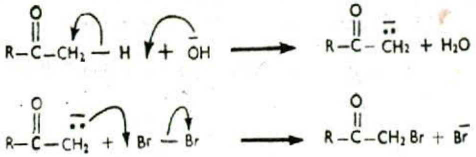
The reaction yields trihalomethanes-chloroform, bromoform, or iodoform depending on the halogen used. Since the common name for halomethanes is 'haloform', it is called **Haloform Reaction**. Acetaldehyde is the only aldehyde which gives haloform reaction.

The haloform reation is used as a diagnostic test for the presence of $-COCH_3$ group. For this purpose, the reaction is carried with iodine and alkali because the iodoform produced being a yellow crystalline solid is then precipitated. This is known as **Iodoform Test** and is given by methyl ketones, acetaldehyde and compounds such as CH_3CHOHR and CH_3CH_2OH which are oxidised to appropriate carbonyl compounds under conditions used for the reaction.

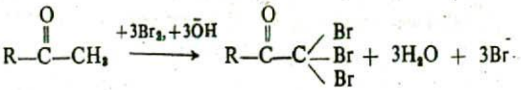
The haloform reaction is useful for distinguishing methyl ketones from other ketones. It is also used in synthesis for the preparation of carboxylic acid with one carbon less than the original methyl ketone.

MECHANISM. It involves the following steps :

(*i*) The hydrogen atoms of the $-CH_3$ group are replaced by halogens in alkali solution. The methyl ketone enolises and the halogen reacts with the enolate ion.

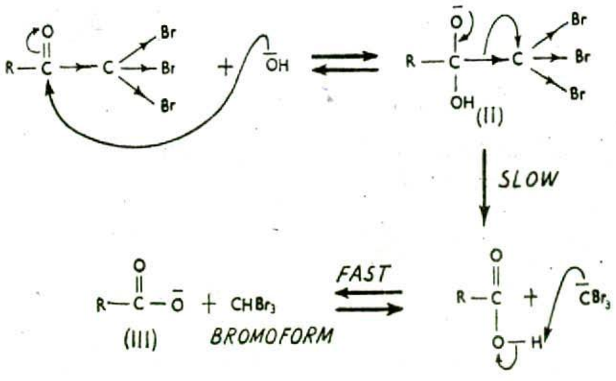


Due to the electron-withdrawing effect of the Br atom, the remaining two hydrogen atoms of the methyl group become even more acidic and the displacement continues till all the hydrogen atoms are successively replaced by halogen atoms.



$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{+3Br_2, +3\bar{O}H} R-\overset{\overset{O}{\|}}{C}-C\begin{smallmatrix}Br\\Br\\Br\end{smallmatrix} + 3H_2O + 3Br^-$$

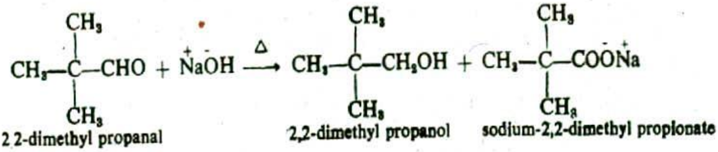
(*ii*) Due to the inductive effect of the halogen atoms, the positivity of the carbonyl carbon increases and by a nucleophilic attack on it, anion (II) is formed. This then cleaves to give a molecule of iodoform and the carboxylate ion (III).



(4) **Action of Sodium hydroxide; Cannizzaro Reaction.** Aldehydes (except formaldehyde) upon treatment with concentrated alkali are converted into dark brown resinous products which presumably arise through a series of aldol condensations. Ketones, however, do not form resins when treated with concentrated alkali.

Formaldehyde and other aldehydes which lack an α-hydrogen, when heated with a concentarted sodium or potassium hydroxide solution, undergo a very interesting novel reaction. Two molecules of the aldehyde react by mutual oxidation-reduction forming one molecule of each of the corresponding alcohol and acid. In other words, one molecule of the aldehyde is oxidised at the expense of the other which is reduced. Thus,

$$2HCHO + \overset{+}{Na}\overset{-}{O}H \xrightarrow{\Delta} \underset{\text{methyl alcohol}}{CH_3OH} + \underset{\text{sod formate}}{HCO\overset{-}{O}\overset{+}{Na}}$$



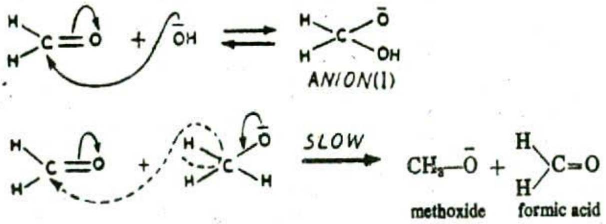
$$\underset{\text{2 2-dimethyl propanal}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CHO} + \overset{+}{Na}\overset{-}{O}H \xrightarrow{\Delta} \underset{\text{2,2-dimethyl propanol}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2OH} + \underset{\text{sodium-2,2-dimethyl propionate}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CO\overset{-}{O}\overset{+}{Na}}$$

The reaction involving simultaneous oxidation and reduction of an aldehyde to give an acid and alcohol is called **Disproportionation** or **Cannizzaro Reaction.**

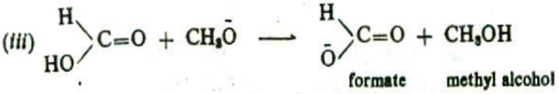
MECHANISM. The mechanism of Cannizzaro reaction, is illustrated by taking example of formaldelyde.

(*i*) Nucleophilic addition of the hydroxy ion ($\overset{-}{O}H$) on the carbonyl group gives a complex anion (I).

(*ii*) The anion I transfers a hydride ion ($\overset{-}{H}$) to another molecule of formaldehyde reducing it to methoxide ion (CH_3O^-) while the anion I itself is oxidised to formic acid.



(*iii*) The resulting methoxide ion and formic acid exchange a proton (acid-base reaction) to form the methyl and formate ion.



$$(iii)\quad \begin{matrix}H\\HO\end{matrix}\!\!>C=O + CH_3\overset{-}{O} \longrightarrow \underset{\text{formate}}{\begin{matrix}H\\\overset{-}{O}\end{matrix}\!\!>C=O} + \underset{\text{methyl alcohol}}{CH_3OH}$$

The formate ion in the presence of alkali ($\overset{+}{Na}\overset{-}{O}H$) gives $HCO\overset{-}{O}\overset{+}{Na}$.

If a mixture of formaldehyde and another aldehyde be taken, the expected alcohols and carboxylic acids are formed. Such a reaction is called *Crossed Cannizzaro Reaction*.

Cannizzaro reaction is used for reducing aldehydes where all other conventional methods fail.

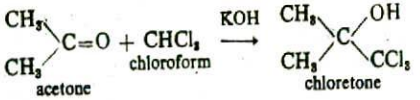
(5) **Tischenko Reaction.** All aldehydes in presence of aluminium ethoxide, $Al(OC_2H_5)_3$, undergo modified cannizzaro reaction. Under these conditions, the alcohol and the acid formed as a result of Cannizzaro reaction combine to give an ester and the reaction is then known as *Tischenko Reaction*. Thus acetaldehyde gives ethyl acetate and propionaldehyde gives propyl propionate.

$$\underset{\text{acetaldehyde}}{2CH_3CHO} \xrightarrow{Al(OC_2H_5)_3} \underset{\text{ethyl acetate}}{CH_3COO{-}C_2H_5}$$

$$\underset{\text{propionaldehyde}}{2CH_3CH_2CHO} \xrightarrow{Al(OC_2H_5)_3} \underset{\text{propyl propionate}}{CH_3CH_2COO-CH_2CH_2CH_3}$$

F. MISCELLANEOUS REACTIONS

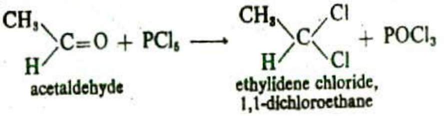
(1) **Reaction with Chloroform.** Ketones, unlike aldehydes, condense with chloroform in the presence of potassium hydroxide to form chlorohydroxy compounds.

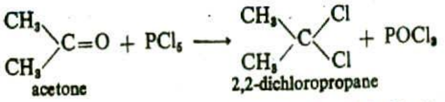


(2) **Polymerization.** The first few members of the aldehyde series readily undergo polymerization to give a variety of products (for details see formaldehyde and acetaldehyde). Ketones, however, are not much susceptible to polymerization.

(3) **Schiff's Test.** Dilute solutions of aldehydes when added to Schiff's reagent (rosaniline hydrochloride dissolved in water and its red colour decolourised by passing sulphur dioxide) restores its red colour. This is known as Schiff's test for aldehydes. Generally, ketones do not respond to this test. Acetone, however, gives a positive test but slowly.

(4) **Reaction with Phosphourus Pentachloride.** Both aldehydes and ketones react with phosphorus pentachloride to form *gem*-dichloroalkanes when the oxygen atom of the carbonyl group is replaced by two chlorine atoms. Thus,





The yield of *gem*-dichlorides is usually good with aldehydes but poor with ketones.

TESTS OF ALDEHYDES AND KETONES

(1) **Resin test.** Aldehydes when warmed with concentrated NaOH solution form dark coloured resins which rise to the surface. Formaldehyde and ketones do not give this test.

(2) **Schiff's test.** When dilute solution of an aldehyde is added to magenta solution decolourised by sulphur dioxide, the intense red colour of the original dye is restored.

(3) **Formation of Bisulphite compounds.** On adding 1—2 ml of a cold saturated solution of sodium bisulphite to about the same volume of an aldehyde or ketone, and shaking, a crystalline bisulphite compound separates out.

(4) **2, 4-dinitrophenylhydrazone (DNP) test.** 2, 4-dinitrophenylhydrazine solution is prepared by dissolving it in alcohol and then warming followed by the addition of two drops of conc sulphuric acid. Addition of 2-3 ml of this reagent to 1·0 ml of aldehyde or ketone in about 5—10 ml of alcohol produces a yellow, red or orange 2, 4-DNP which is filtered, dried recrystallised from alcohol.

(5) **Silver mirror test.** Ammonium hydroxide is added dropwise to a 10% solution of silver nitrate. When the precipitate first formed is redissolved, the solution is warmed with a little aldehyde solution. A shining silver mirror is deposited on the inner wall of the test tube. Ketones, however, do not respond to this test.

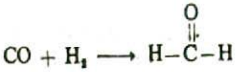
(6) **Fehling's Solution test.** A little dilute solution of the aldehyde is added to Fehling's solution taken in a test tube. Then it is warmed in a water bath for 1-2 minutes. Reddish brown precipitate of cuprous oxide separates out. Ketones do not give this test.

INDIVIDUAL ALDEHYDES

FORMALDEHYDE, *Methanal*, H—CH=O

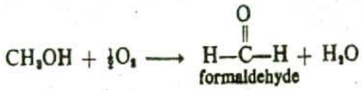
It is the first member of the homologous series of aldehydes. Traces of formaldehyde are produced by the incomplete combustion of coal, wood, sugar, etc.

Preparation. (1) *By reduction of Carbon monoxide.* Formaldehyde is produced from carbon monoxide and hydrogen when a mixture of these gases (*water gas*) is passed at low pressure through an electric discharge of low intensity.



$$CO + H_2 \longrightarrow H-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

(2) *By oxidation of Methyl alcohol.* Large quantities of formaldehyde are prepared by passing a mixture of methyl alcohol vapour and air over heated copper or silver.



$$CH_3OH + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{formaldehyde}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-H} + H_2O$$

A catalyst composed of molybdenum trioxide and ferric oxide converts 95 per cent of methyl alcohol to formaldehyde.

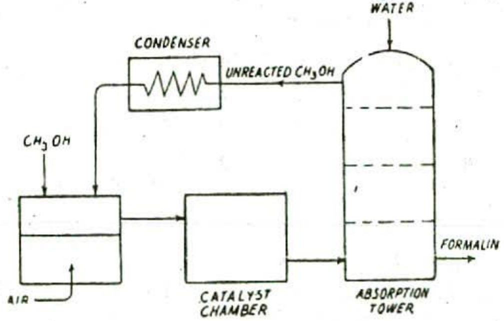
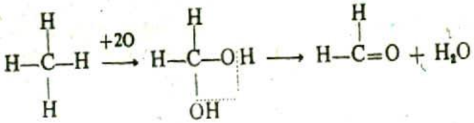


Fig. 20·1. Manufacture of formalin.

Since formaldehyde is a gas, the product is sold in the market as 40 per cent aqueous solution under the name *Formalin.*

(3) It is also manufactured in USA by the controlled oxidation of methane under pressure.



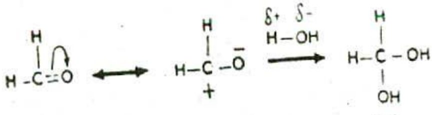
$$H-\underset{H}{\overset{H}{C}}-H \xrightarrow{+2O} H-\underset{OH}{\overset{H}{C}}-OH \longrightarrow H-\overset{H}{C}=O + H_2O$$

LABORATORY MEHOD. Formaldehyde is prepared in the laboratory by the oxidation of methyl alcohol in the presence of platinum.

$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow{\Delta,Pt} HCHO + H_2O$$

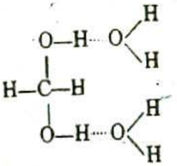
Properties. (*Physical*). Formaldehyde is a colourless gas at ordinary temperature and pressure. It is easily condensed to a liquid which boils at —21°. It has a very pungent and penetrating odour. It is readily soluble in water. In the gaseous state or when dissolved in water, formaldehyde is a powerful disinfectant.

Formaldehyde forms an unstable hydrate with water. It is decidedly more stable than the hydrate of acetaldehyde, the latter being unstable owing to the presence of the electron repelling methyl group. Mechanism of hydrate formation may be depicted as

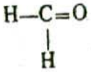


(I) (II) (III)

The presence of a methyl group in place of H-atom would exert its inductive effect (*electron repelling*) and reduce the magnitude of positive charge on C-atom in formula II). (*See acetaldehyde*).



(*Chemical*). Structuraliy, formaldehyde differs from other aldehydes in that it has a hydrogen linked to the—CHO group instead of the alkyl group.



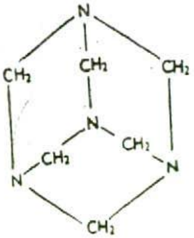
$$\underset{H}{\underset{|}{H-C}}=O$$

Consequently it does not duplicate all of the general reactions of the higher aldehydes and is actually more reactive. The following reactions of formaldehyde are noteworthy.

(1) **Reaction with Ammonia**. Unlike other aldehydes, it does not form aldehydeammonia but instead gives a white crystalline compound **hexamethylenetetramine.**

$$6CH_2O + 4NH_3 \longrightarrow \underset{\substack{\text{hexamethylene}\\ \text{tetramine}}}{(CH_2)_6N_4} + 6H_2O$$

The proposed structural formula for the compound is indicated. It is used in medicine as a urinary antiseptic under the name **Urotropine**.

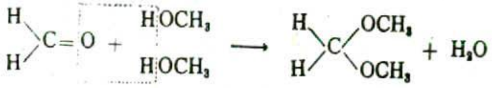


Hexamethylenetetramine

(2) Reaction with Sodium Hydroxide. Formaldehyde differs from other aldehydes as it does not form a resin with dilute sodium hydroxide solution. However, when treated with a concentrated alkali solution, it undergoes *Cannizzaro Reaction.*

$$\begin{array}{l} HCHO \\ HCHO \end{array} + H_2O \longrightarrow \begin{array}{l} HCOOH \\ CH_3OH \end{array}$$

(3) **Reaction with Alcohols**. Like other aldehydes, it reacts with alcohols forming **acetals.** Thus in the presence of hydrogen chloride and fused chloride; formaldehyde reacts with methyl alcohol to form **methylal**.



$$H_2C{=}O + \begin{array}{l} HOCH_3 \\ HOCH_3 \end{array} \longrightarrow H_2C(OCH_3)_2 + H_2O$$

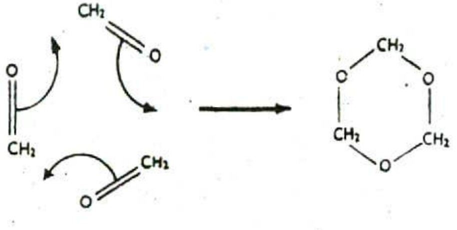
(4) Polymerisation Reactions. (*i*) When an aqueous solution of formaldehyde is evaported to dryness, a white crystalline solid, mp 121—123°, is obtained. This is called **paraformaldehyde** and possesses the structure

$$HOCH_2-\left[OCH_2\right]_{n-2}-O-CH_2OH$$

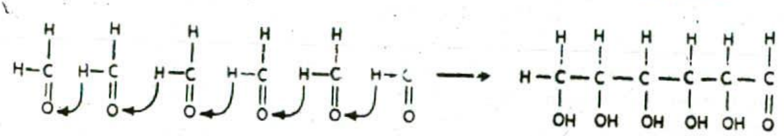
where *n* lies between 6 and 50. Paraformaldehyde regenerates formaldehyde on heating.

(*ii*) Formaldehyde on treatment with concentrated sulphuric acid gives polyoxymethylene $(CH_2O)n{\cdot}2H_2O$, where *n* is greater than 100. Polyoxymethylenes are insoluble white solids which regenerate formaldehyde on heating.

(*iii*) When formaldehyde gas is allowed to stand at room temperature, it slowly undergoes polymerization and yields a white solid called meta-formaldehyde or trioxymethylene or trioxan $(CH_2O)_3$, mp 61-62°. This trimer is insoluble in water and does not possess reducing properties characteristic of formaldehyde. Hence it possesses a cyclic structure as shown below.



(*iv*) When a dilute solution of formaldehyde containing a weak alkali (baryta or lime) is allowed to stand, it polymerizes to a mixture of sugars of formula $C_6H_{12}O_6$, called *Formose* or *α-Acrose*. These sugars are presumably formed through a chain of aldol condensations.



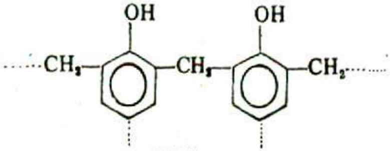
This demonstrates beautifully as to how formaldehyde formed as a result of reduction of carbon dioxide in plants is converted to sugars by photosynthesis.

$$[illegible] \longrightarrow CH_2O + O_2$$

$$n([illegible]) \longrightarrow C_6H_{12}O_6$$

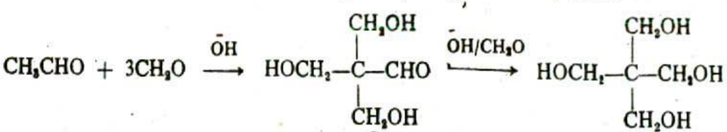
(5) Condensation with Phenol. Formaldehyde on condensation with phenol gives artificial resins and plastics which are used for making electric equipment under the name **Bakelite.**

When phenol is refluxed with 40% formaldehyde in presence of 0·88 ammonia (catalyst), an oily liquid separates. This upon heating and finally cooling by dropping in water, gives a hard and brittle mass known as *Bakelite.*



Bakelite

(6) **Condensation with Acetaldehyde.** When acetaldehyde is treated with excess of formaldehyde in presence of calcium hydroxide it undergoes mixed aldol condensation to form (I). This compound having no α-hydrogen atom undergoes 'Crosesd Cannizzaro reaction' with another molecule of formaldehyde to produce pentaerythritol. Pentaerythritol is an important industrial product because its tetra-nitrate (PETN) is a powerful explosive.



$$CH_3CHO + 3CH_2O \xrightarrow{\bar{O}H} HOCH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CHO \xrightarrow{\bar{O}H/CH_2O} HOCH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2OH$$

(I) pentaerythritol

Uses. Formaldehyde is placed in the market as 40 per cent aqueous solution under the name *'formalin'* and is used as such for most purposes.

(1) The vapour of formaldehyde, produced by the action of heat on formalin is used as a disinfectant. Formalin is used for sterilising surgical instruments.

(2) Formalin is used for preserving biological and anatomical specimens, since it makes the tissues hard and insoluble.

(3) On account of its hardening effect on hide-proteins formalin in used for tanning.

(4) Formalin is used in the production of plastics including well-known '*Bakelite*' which is obtained by heating phenol with formalin.

(5) Formalin is used as reducing agent for decolorising of *vat dyes* and also making mirrors.

Tests. Formaldehyde can be identified by the usual reactions of aldehydes. It also gives the following special test not given by other aldehydes.

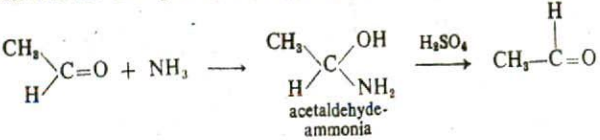
A freshly prepared solution of pyrogallol is mixed with the solution of formaldehyde and excess of concentrated hydrochloric acid is added. In a few minutes, a white precipitate is formed which rapidly turns pink and then deep red.

Acetaldehyde, *Ethanal,* $CH_3CH=O$

It is the second member of the aldehyde series. It is formed as an intermediate compound in the alcoholic fermentation of glucose and is present in wines.

Acetaldehyde can be prepared by almost all the general methods of preparation described earlier.

Laboratory Method. It is obtained in the laboratory by the oxidation of ethyl alcohol using a mixture of aqueous sodium or potassium dichromate and sulphuric acid as the oxidising agent. Acetaldehyde, as soon as it is formed, is distilled away to avoid its oxidation to acetic acid. The crude substance thus formed is purified by converting it into acetaldehyde-ammonia by treatment with ammonia. The crystals of acetaldehyde-ammonia are dried and distilled with dilute sulphuric acid and the regenerated acetaldehyde is collected in an ice-cooled receiver.



Manufacture. Acetaldehyde is obtained commercially :

(*i*) by the catalytic oxidation of ethyl alcohol with air in presence of silver at 250°.

$$CH_3CH_2OH \xrightarrow[250^\circ]{Ag} CH_3CHO + H_2O$$

(*ii*) by passing ethyl alcohol vâpours over copper at 300°.

$$CH_3CH_2OH \xrightarrow[300^\circ]{Cu} CH_3CHO + H_2$$

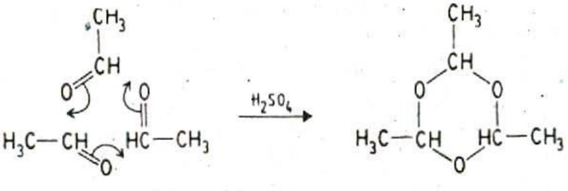
(*iii*) by the hydration of acetylene in presence of sulphuric acid and mercury salts.

$$HC{\equiv}CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO$$

Properties (*Physical*). Acetaldehyde is a colourless volatile liquid, bp 21°. It has a characteristic pungent odour.. It is readily soluble in water, alcohol, and ether. Its solutions in water, have an agreeable fruity odour.

(*Chemical*). All the chemical properties of acetaldehyde have already been discussed under the 'General Reactions' of aldehydes and ketones. Only a few polymerisation reactions will be described here

(1) With a drop of concentrated sulphuric acid, acetaldehyde polymerises with expolsive violence to form paraldehyde. Paraldehyde is a trimer and has a cyclic structure since it does not possess reducing properties.

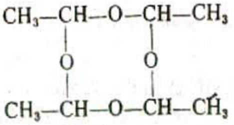


ACETALDEHYDE
(3 molecules)

PARALDEHYDE

Paraldehyde is a sweet smelling liquid, bp 128°, and is used in medicine as hypnotic.

(2) When acetaldehyde is treated with a few drops of conc H_2SO_4 at 0°, the tetramer, (CH_3CHO) · metaldehyde is formed. This is a white solid, mp 246° and has the structure.



Both the polymers regenerate acetaldehyde on distilling with sulphuric acid.

Uses. (1) Acetaldehyde is used in the technical preparation of a number of organic compounds including acetic acid, ethyl acetate and n-butyl alcohol.

(2) It has also been used for the silvering of mirrors.

(3) Paraldehyde is used in medicine as a hypnotic.

(4) Metaldehyde, under the name '*meto*' is used as a solid fuel in small lamps.

Tests. It gives the usual tests of aldehydes. In addition, acetaldehyde gives the following specific tests.

(1) *Iodoform Test.* Yellow crystals of iodoform are obtained when to an aqueous solution of acetaldehyde is added iodine and potassium hydroxide solution.

(2) It gives a blue coloration with sodium nitroprusside and piperidine.

(3) It gives a cherry-red colour when treated with a freshly prepared solution of sodium nitroprusside containing sodium hydroxide.

Chloral, *Trichloroacetaldehyde*, CCl_3CHO

Its systematic name would be *Trichloroethanal.*

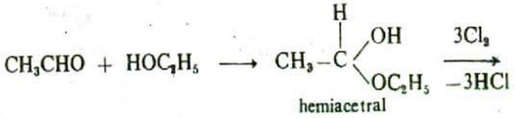
Preparation. *By direct chlorination of acetaldehyde.* Chloral can be prepared from acetaldehyde by direct chlorination in the presence of calcium carbonate.

$$\underset{\text{acetaldehyde}}{CH_3CHO} + 3Cl_2 \longrightarrow \underset{\text{chloral}}{CCl_3CHO} + 3HCl$$

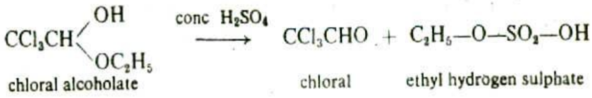
Calcium carbonate is needed to neutralise the hydrogen chloride produced which would otherwise cause the polymerisation of chloral.

(2) **By the action of Chlorine on Alcohol**. Chlorine is first passed into cold ethyl alcohol and then at 60° till no further absorption of chlorine takes place. The final product is chloral alcoholate which separates out as a crystalline solid. This on distillation withconcentrated sulphuric acid gives chloral. The reactions involved may be represented as follows.

$$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} + Cl_2 \longrightarrow \underset{\text{acetaldehyde}}{CH_3CHO} + Cl_2$$



$$CH_3CHO + HOC_2H_5 \longrightarrow \underset{\text{hemiacetral}}{CH_3-\overset{H}{\overset{|}{C}}\begin{cases}OH\\OC_2H_5\end{cases}} \xrightarrow[-3HCl]{3Cl_2}$$



$$\underset{\text{chloral alcoholate}}{CCl_3CH\begin{cases}OH\\OC_2H_5\end{cases}} \xrightarrow{\text{conc } H_2SO_4} \underset{\text{chloral}}{CCl_3CHO} + \underset{\text{ethyl hydrogen sulphate}}{C_2H_5-O-SO_2-OH}$$

Properties. Chloral is a colourless, oily liquid with a pungent odour and a sweetish taste, bp 98°. It is insoluble in water. When taken internally it induces sleep and hence its use as a hypnotic.

Chloral undergoes the usual reactions of aldehydes.

(1) *Addition Reactions.* Chloral combines with ammonia to give chloral-ammonia, $CCl_3.CH(OH)NH_2$; with hydrogen cyanide to form chloral cyanohydrin, $CCl_3CH(OH)CN$; and with sodium bisulphite to give bisulphite compound, $CCl_3CH(OH)SO_3Na$.

(2) *Condensation Reactions.* Chloral condenses with hydroxylanime to give oxime, $CCl_3CH=NOH$; with hydrazine to from hydrazone, $CCl_3CH=NNH_2$; and with phenylhydrazine to yield phenylhydrazone, $CCl_3CH=NNHC_6H_5$.

(3) *Oxidation.* Chloral reduces Fehling's solution to cuprous oxide, and Tollen's solution to metallic silver. In these reactions chloral itself is oxidised to trichloroacetic acid.

$$\underset{\text{chloral}}{CCl_3CHO} + O \longrightarrow \underset{\text{trichloroacetic acid}}{CCl_3COOH}$$

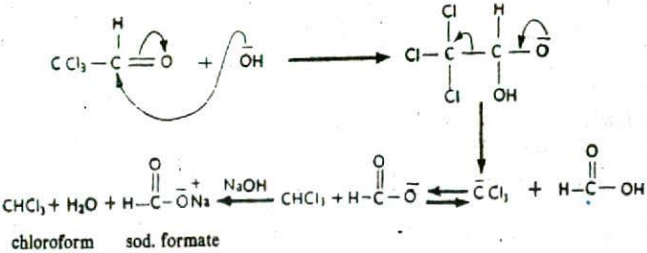
(4) *Reduction.* Chloral is reduced to trichloroethanol with aluminium ethoxide.

$$CCl_3CHO \xrightarrow{Al(OC_2H_5)_3} \underset{\text{trichloroethanol}}{CCl_3CH_2OH}$$

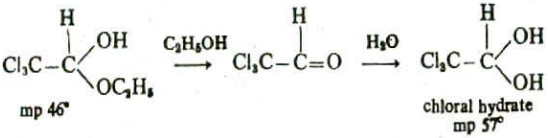
(5) *Reaction with Alkalis.* Chloral is hydrolysed by boiling aqueous alkali solution to form chloroform and metal formate.

$$CCl_3CHO + NaOH \longrightarrow CHCl_3 + \underset{\text{sod formate}}{HCOONa}$$

MECHANISM :



(6) *Reaction with Water and Alcohol.* When chloral is treated with water or ethyl alcohol, it forms chloral hydrate or chloral alcoholate with the evolution of heat. Both are crystalline solids.



These compounds are stable and water or ethyl alcohol can only be removed from them on treatment with concentrated sulphuric acid.

The stability of chloral hydrate is rather unexpected because the presence of two hydroxyl groups on the same carbon atom makes the molecule unstable and these readily lose a molecule of water.

Thus unexpected stability of chloral hydrate can be explained as follows. The strong inductive effect of the three chlorine atoms makes the carbon atom of the carbonyl group to acquire a small positive charge which prevents the release of a hydroxyl ion. Thus elimination of water is rendered impossible. Furthermore, Infrared studies of chloral hydrate indicate hydrogen bonding between the chlorine and hydrogen atoms as shown in Fig. 20·2.

Thus the stability of chloral hydrate may be attributed both to the inductive effect and hydrogen bonding.

(7) *Polymerisation.* In the presence of an acid, chloral readily polymerises to a white amorphous solid called *metachloral.*

Uses. Chloral is chiefly used in the manufacture of DDT, an important insecticide. It is also used in medicine as a hypnotic.

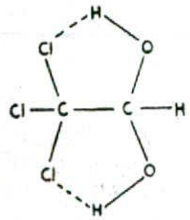


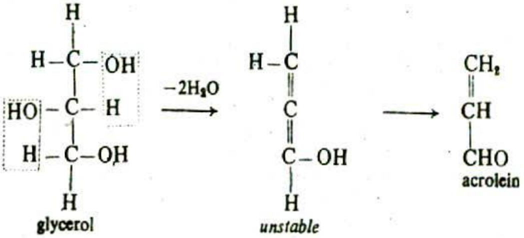
Fig. 20·2

UNSATURATED ALDEHYDES

Acrolein, *Acraldehyde*, Prop-2-en-1-al, $CH_2=CH-CHO$

This is the simplest and the best known 2, 3-unsaturated aldehyde. It is formed in small amounts when fats are overheated.

Preparation. Acrolein is prepared by dehydration of glycerol by heating with potassium hydrogen sulphate



Properties. Acrolein is a colourless liquid, bp 53°. It has an extremely pungent and penetrating odour and hence its name (*acer*=sharp ; *oleum*=oil). It has a strong irritating action upon eyes and nose, causing watering.

Acrolein molecule contains both an alkene linkage and an aldehyde group. Thus it behaves both as an alkene and as an aldehyde. However, acrolein shows a modified behaviour because it occurs as the following resonating structures.

$$CH_2=CH-CH=O \longleftrightarrow \overset{+}{C}H_2-CH=CH-\bar{O}$$

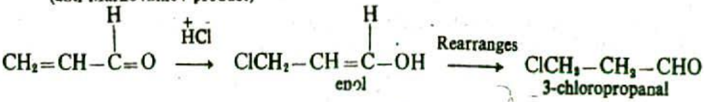
A. RECTIONS OF THE DOUBLE BOND

(1) Addition of Br_2 to acrolein gives 2, 3-dibromopropanal.

$$CH_2=CHCHO + Br_2 \longrightarrow \underset{\alpha,\ \beta\text{-dibromopropanal}}{CH_2BrCHBrCHO}$$

(2) Addition of HCl to acrolein gives 3-chloropropanal.

(anti-Markovnikov product)



$$CH_2=CH-\overset{\overset{\displaystyle H}{|}}{C}=O \xrightarrow{\overset{+}{H}\overset{-}{Cl}} \underset{\text{enol}}{ClCH_2-CH=\overset{\overset{\displaystyle H}{|}}{C}-OH} \xrightarrow{\text{Rearranges}} \underset{\text{3-chloropropanal}}{ClCH_2-CH_2-CHO}$$

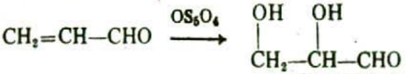
(3) Acrolein can be reduced to propanal with Raney nickel and hydrogen at low temperature and high pressure.

$$CH_2=CH-CHO \xrightarrow[H_2]{\text{Raney Ni}} \underset{\text{propanal}}{CH_3-CH_2-CHO}$$

(4) Reductive ozonolysis of acrolein gives a mixture of formaldehyde and glyoxal.

$$CH_2=CH-CHO \xrightarrow{O_3/H_2} \underset{\text{formaldehyde}}{HCHO} + \underset{\text{glyoxal}}{CHO-CHO}$$

(5) It can be hydroxylated to glyceraldehyde on treatment with OS_5O_4.

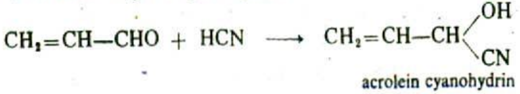


$$CH_2=CH-CHO \xrightarrow{OS_6O_4} \overset{\overset{\displaystyle OH}{|}}{C}H_2-\overset{\overset{\displaystyle OH}{|}}{C}H-CHO$$

glyceraldehyde,
2, 3-dihydroxy propanol

B. REACTIONS OF THE ALDEHYDIC GROUP

(1) With HCN it gives cyanohydrin.



$$CH_2{=}CH{-}CHO + HCN \longrightarrow \underset{\text{acrolein cyanohydrin}}{CH_2{=}CH{-}CH\begin{smallmatrix}OH\\ CN\end{smallmatrix}}$$

(2) It reduces ammoniacal silver nitrate and itself gets oxidised to acrylic acid.

$$CH_2{=}CH{-}CHO \xrightarrow{Ag(NH_3^+)_2} \underset{\text{acrylic acid}}{CH_2{=}CH{-}COOH}$$

(3) It can be reduced to allyl alcohol with $LiAlH_4$ at low temperature or with $NaBH_4$.

$$CH_2{=}CH{-}CHO \xrightarrow[\text{or } NaBH_4]{LiAlH_4} \underset{\text{allyl alcohol}}{CH_2{=}CH{-}CH_2OH}$$

(4) It condenses with hydroxylamine to form an oxime ; with hydrazine to give a hydrazone and with phenylhydrazine to produce a phenylhydrazone. Thus,

$$CH_2{=}CH{-}CHO + H_2N{-}G \xrightarrow{-H_2O} CH_2{=}CH{-}CH{=}N{-}G$$

where $G{=}OH$, NH_2, or NHC_6H_5.

(5) On treatment with $Al(OC_2H_5)_3$, it undergoes *Tischenko Reaction* to form allyl acrylate.

$$2\,CH_2{=}CH{-}CHO \xrightarrow{Al(OC_2H_5)_3} \underset{\text{allyl acrylate}}{CH_2{=}CHCO{-}O{-}CH_2CH{=}CH_2}$$

(6) Acrolein, however, does not undergo normal aldol condensation but gets cleaved to a molecule of formaldehyde and a molecule of acetaldehyde in presence of alkali.

$$CH_2{=}CH{-}CHO + H_2O \overset{NaOH}{\rightleftharpoons} HCHO + CH_3CHO$$

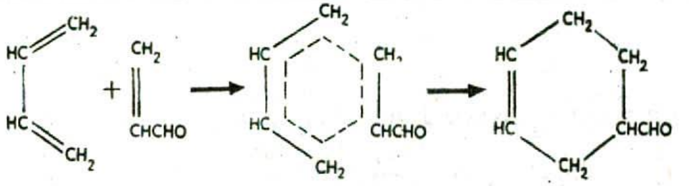
This reaction is actually the reversal of aldol condensation and is characteristic of α, β-unsaturated aldehydes.

C. MISCELLANEOUS REACTIONS

(1) Acrolein on reduction with metal and acid gives a mixture of allyl alcohol, 1-propanal 1-propanol and *pinacol*, a compound formed by bimolecular reduction.

$$CH_2{=}CH{-}CHO \xrightarrow{metal/H^+} \underset{\text{allyl alcohol}}{CH_2{=}CHCH_2OH} + \underset{\text{1-propanal}}{CH_3CH_2CHO} + \underset{\text{1-propanol}}{CH_3CH_2CH_2OH}$$
$$+ \underset{\text{pinacol}}{CH_2{-}CH{-}CHOH{-}CHOH{-}CH{=}CH_2}$$

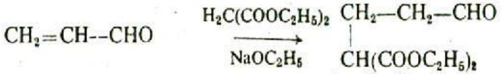
(2) It undergoes *Diels-Alder Reaction* with butadiene to form 1, 2, 3, 6-tetrahydrobenzaldehyde.



TRANSITION STATE

1,2,3,6-TETRAHYDRO BENZALDEHYDE

(3) Acrolein undergoes *Michael Reaction* when treated with diethyl malonate in presence of piperidine or sodium ethoxide.



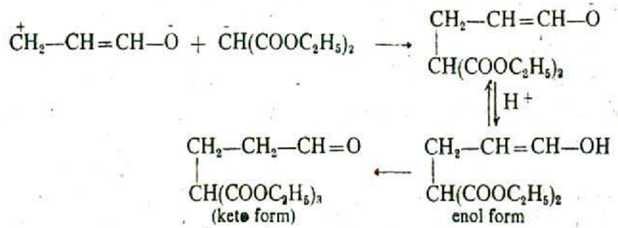
$$CH_2{=}CH{-}{-}CHO \xrightarrow[NaOC_2H_5]{H_2C(COOC_2H_5)_2} \begin{array}{l} CH_2{-}CH_2{-}CHO \\ | \\ CH(COOC_2H_5)_2 \end{array}$$

4, 4-dicarboxethoxypropanal

MECHANISM :

$$CH_2(COOC_2H_5)_2 \overset{NaOC_2H_5}{\rightleftharpoons} \bar{C}H(COOC_2H_5)_2 + \overset{+}{H}$$

$$CH_2{=}CH{-}CH{=}O \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH{-}\bar{O}$$



$$\overset{+}{C}H_2{-}CH{=}CH{-}\bar{O} + \bar{C}H(COOC_2H_5)_2 \longrightarrow \begin{array}{l} CH_2{-}CH{=}CH{-}\bar{O} \\ | \\ CH(COOC_2H_5)_2 \end{array}$$

$$\Big\Updownarrow H^+$$

$$\underset{\text{(keto form)}}{\begin{array}{l} CH_2{-}CH_2{-}CH{=}O \\ | \\ CH(COOC_2H_5)_3 \end{array}} \longleftarrow \underset{\text{enol form}}{\begin{array}{l} CH_2{-}CH{=}CH{-}OH \\ | \\ CH(COOC_2H_5)_2 \end{array}}$$

Uses. Acrolein is used : (1) as a synthetic reagent ; (2) as a warning agent for any leakage in refrigeration with methyl chloride ; (3) in the preparation of insecticides and acrolein-urea-formaldehyde resins.

Crotonaldehyde, 2-Butenal, $CH_3CH{=}CHCHO$

It is made by the aldol condensation of acetaldehyde followed by dehydration of the resulting aldol.

$$\underset{\text{aldol}}{CH_3CH(OH)CH_2CHO} \xrightarrow[I_2]{\Delta} \underset{\text{crotonaldehyde}}{CH_3CH{=}CHCHO} + H_2O$$

It is a pungent smelling liquid, bp 102·2°. It reacts in much the same way as does acrolein.

Crotonaldehyde is used as a solvent; insecticide and denaturant for alcohol ; and for preparing butyraldehyde and crotonic acid.

INDIVIDUAL KETONES

Acetone, *Dimethyl ketone, Propanone,* $CH_3{-}CO{-}CH_3$

It is the first and the best known member of the homologous series of ketones. Acetone is present in traces in normal urine but in conditions such as diabetes or starvation the amount is largely increased. It is a product of decomposition of cellulose, and is found in *wood spirit* obtained by the *dry* distillation of wood.

Preparation. (1) By the oxidation of isopropyl alcohol with sodium dichromate and sulphuric acid.

$$CH_3{-}CHOH{-}CH_3 + O \longrightarrow CH_3{-}CO{-}CH_3 + H_2O$$

This is also achieved by passing the vapours of alcohol mixed with oxygen over zinc oxide at 320°.

Isopropyl alcohol is also converted to acetone on industrial scale by the catalytic dehydrogenation.

(2) By the distillation of calcium acetate.

$$(CH_3COO)_2Ca \longrightarrow (CH_3)_2CO + CaCO_3$$

This method is used for the preparation of acetone in the laboratory.

(3) By passing acetic acid vapour over a copper catalyst at 300—400°.

$$2CH_3COOH \longrightarrow (CH_3)_2CO + CO_2 + H_2$$

(4) By passing a mixture of acetylene and steam over a catalyst (zinc and magnesium vanadates) at 420°.

$$2CH{\equiv}CH \longrightarrow \underset{\text{propene}}{CH_3{-}C{\equiv}CH} + C$$

$$CH_3C{\equiv}CH + H_2O \qquad \underset{\text{acetone}}{CH_3{-}CO{-}CH_3}$$

(5) By fermentation of starch or molasses by the bacterium *Chostridium acetobutylicum* (Weizmann). The starch is converted to sugars which undergo further decomposition giving acetone.

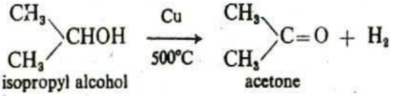
$$\underset{\text{glucose}}{3C_6H_{12}O_6} \longrightarrow \underset{\text{butyl alcohol}}{2C_4H_9OH} + \underset{\text{acetone}}{(CH_3)_2CO} + 7CO_2 + 4H_2 + H_2O$$

LABORATORY PREPARATION. Acetone is prepared in the laboratory by heating calcium acetate.

$$\underset{\text{calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\text{distil}} \underset{\text{acetone}}{(CH_3)_2C{=}O} + CaCO_3$$

INDUSTRIAL PREPARATION. Acetone is prepared on an industrial scale by (1) Catalytic dehydrogenation of isopropyl alcohol obtained from propylene in gases formed during the cracking of petroleum ; (2) Interaction of acetylene and steam ; (3) Fermentation of starch and molasses ; (4) Wood distillation, separation from pyroligneous acid and by heating calcium acetate (*see methyl alcohol*).

By Dehydrogenation of Isopropyl Alcohol. Most of the acetone at present is manufactured from isopropyl alcohol obtained from propane of cracked petroleum. It is dehydrogenated by passing its vapours over heated copper catalyst at 500°C.



$$\underset{\text{isopropyl alcohol}}{(CH_3)_2CHOH} \xrightarrow[500^\circ C]{Cu} \underset{\text{acetone}}{(CH_3)_2C{=}O} + H_2$$

Isopropyl alcohol-vapour is prepared and passed into a reactor packed with a copper catalyst. The reaction being endothermic the temperature is maintained at 500°C. The gaseous products from the reactor are passed through a cooler to a water scrubber for the complete recovery of acetone. The liquor obtained from the scrubber is fractionated to give pure acetone,

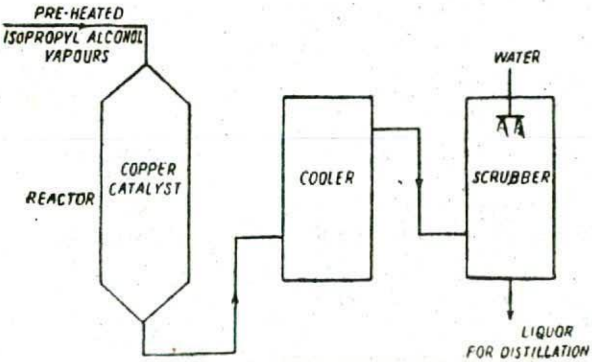


Fig. 20·3. Industrial preparation of acetone.

PROPERTIES

(*Physical*). Acetone is a colourless liquid, bp 56·5°. It has a characteristic pleasant odour and is pungent sweet taste. It mixes with water, alcohol and ether in all proportions. It is very volatile and inflammable. It has a specific gravity 0·792 at 20°.

(*Chemical*). Acetone gives all the general reactions of ketones described before.

(1) **Halogenation.** Chlorine reacts with acetone giving first monochloroacetone, $CH_2ClCOCH_3$, and ultimately hexachloroacetone, CCl_3COCCl_3. Bromine and iodine react to form ultimately $CHBr_2.CO.CHBr_2$ and $CH_2I.CO.CH_2I$ respectively.

(2) **Chloroform Reaction.** When acetone is distilled with bleaching powder ($CaOCl_2 = CaO + Cl_2$), which supplies both chlorine and alkali, it first forms trichloroacetone which upon hydrolysis yields chloroform

$$\underset{\text{acetone}}{CH_3{-}CO{-}CH_3} + 3Cl_2 \longrightarrow \underset{\text{trichloroacetone}}{CCl_3COCH_3} + 3HCl$$

$$CCl_3{-}CO{-}CH_3 + Ca(OH)_2 \longrightarrow \underset{\text{chloroform}}{CHCl_3} + CH_3COOH$$

The reaction is used for the preparation of chloroform. A similar reaction with iodine and alkali gives iadoform.

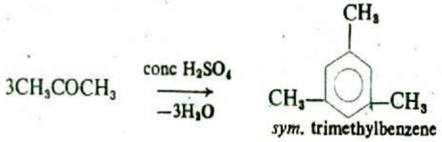
(3) **Condensation Reactions.** Acetone undergoes a variety of interesting condensation reactions.

(*i*) In the presence of dry hydrogen chloride gas, it gives first mesityl oxide and then phorone.

$$(CH_3)_2C{=}O + CH_3COCH_3 \xrightarrow[-H_2O]{\text{dry HCl}} \underset{\text{mesityl oxide}}{(CH_3)_2C{=}CH{-}CO{-}CH_3}$$

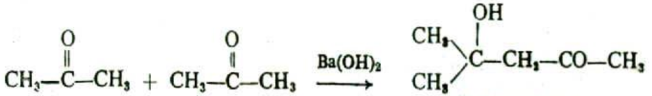
$$(CH_3)_2C{=}CH{-}CO{-}CH_3 + O{=}C(CH_3)_2 \xrightarrow[-H_2O]{\text{dry HCl}} \underset{\text{phorone}}{(CH_3)_2C{=}CH{-}CO{-}CH{=}C(CH_3)_2}$$

(*ii*) When treated with concentrated sulphuric acid, acetone gives mesitylene or *sym.* trimethyl benzene.



sym. trimethylbenzene

(*iii*) When treated with $Ba(OH)_2$, it undergoes aldol condensation to diacetone alcohol.



$$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3 + CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3 \xrightarrow{Ba(OH)_2} (CH_3)_2\overset{\overset{\large OH}{|}}{C}{-}CH_2{-}CO{-}CH_3$$

diacetone alcohol

Uses. (1) It is employed as a **solvent** in the manufacture of smokeless powders (*Cordite*), celluloid, collodion, paints and varnish removers, etc. It is an ingredient of liquid nail polish.

(2) Acetone is stored in solution in acetylene under pressure.

(3) It is used as a *raw material* for the production of iodoform, chloroform and sulphonal.

(4) It is a possible ingredient of motor fuel because it has high antinock value.

Tests. Acetone gives negative tests with sodium hydroxide, ammoniacal silver nitrate, Fehling's solution, and Schiff's reagent.

(1) *Iodoform Test.* If iodine solution be added drop by drop to a solution of acetone and ammonia (3 to 5 drops), a black precipitate of nitrogen iodide is formed. On warming it disappears and iodoform is obtained. Alcohol does not form iodoform in this way.

(2) *Nitroprusside or* **Legal's Test.** Freshly prepared solution of sodium nitroprusside (5 drops) is added to dilute acetone (5 ml) and sodium hydroxide (1 ml). A ruby red colour is produced which fades to yellow on standing.

(3) *Indigo Test.* A little *o*-nitrobenzaldehyde is dissolved in 2 ml of acetone and the solution stirred into 200 ml of water containing a little potassium hydroxide. A blue colour of *Indigotin* is produced.

Methyl Vinyl Ketone, But-3-ene-2-one, $CH_3—CO—CH=CH_2$

It is an α, β-unsaturated ketone and can be prepared by the following methods.

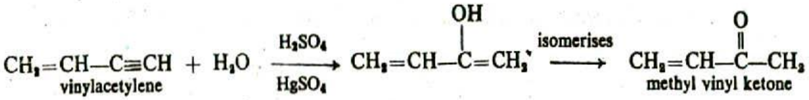
(1) By crossed aldol condensation between formaldehyde and acetone followed by dehydration of the 'aldol' on heating.

$$\underset{\text{acetone}}{CH_3COCH_3} + HCHO \xrightarrow{\text{dil NaOH}} \underset{\text{aldol}}{CH_3COCH_2—CH_2OH} \xrightarrow{\Delta} \underset{\text{methyl vinyl ketone}}{CH_3COCH = CH_2} + H_2O$$

(2) By the action of acetic anhydride on ethylene in the presence of zinc chloride as catalyst.

$$\underset{\text{ethylene}}{CH_2=CH_2} + (CH_3CO)_2O \xrightarrow{ZnCl_2} \underset{\text{methyl vinyl ketone}}{CH_2=CH—COCH_3} + CH_3COOH$$

(3) By the hydration of vinylacetylene in presence of dil sulphuric acid and mercuric sulphate.



$$\underset{\text{vinylacetylene}}{CH_2=CH—C\equiv CH} + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_2=CH—\overset{\overset{\displaystyle OH}{|}}{C}=CH_2 \xrightarrow{\text{isomerises}} \underset{\text{methyl vinyl ketone}}{CH_2=CH—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3}$$

This is also a commercial method for the preparation of methyl vinyl ketone (MVK).

Properties. Methyl vinyl ketone is a liquid, bp 79°. It gives the reactions of both an alkene and a ketone. It polymerises on standing.

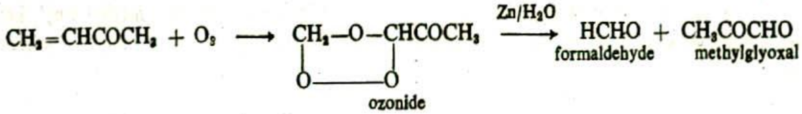
(1) *Addition of Bromine.* It adds on a molecule of bromine to form 3, 4-dibromo-butan-2-one.

$$CH_2=CH—CO—CH_3 + Br_2 \longrightarrow \underset{\text{3, 4-dibromo-butan-2-one}}{CH_2Br—CHBr—CO—CH_3}$$

(2) *Reduction.* Methyl vinyl ketone on reduction with H_2 in presence of Pt or Ni gives first 2-butanone which on further reduction gives 2-butanol.

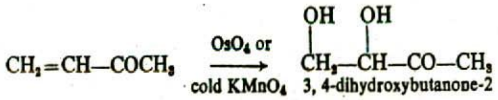
$$CH_2=CH—CO—CH_3 + H_2 \xrightarrow{\text{Pt or Ni}} \underset{\text{2-butanone}}{CH_3CH_2—CO—CH_3} \xrightarrow[\text{Pt or Ni}]{H_2} \underset{\text{2-butanol}}{CH_3CH_2—CHOH—CH_3}$$

(3) *Ozonolysis.* Ozone reacts with methyl vinyl ketone to form an ozonide which on reductive decomposition gives an equimolecular mixture of formaldehyde and methylglyoxal.



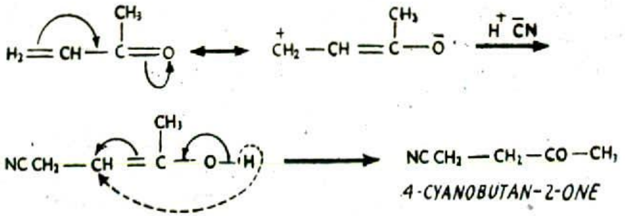
$$CH_2{=}CHCOCH_3 + O_3 \longrightarrow \underset{\text{ozonide}}{CH_2{-}O{-}CHCOCH_3} \xrightarrow{Zn/H_2O} \underset{\text{formaldehyde}}{HCHO} + \underset{\text{methylglyoxal}}{CH_3COCHO}$$

(4) *Hydroxylation.* Methyl vinyl ketone on treatment with osmium tetroxide or cold dilute potassium permanganate gives 3, 4-dihydroxybutanone-2.

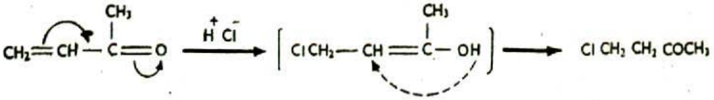


$$CH_2{=}CH{-}COCH_3 \xrightarrow[\text{cold } KMnO_4]{OsO_4 \text{ or}} \underset{\text{3, 4-dihydroxybutanone-2}}{\overset{OH}{CH_2}{-}\overset{OH}{CH}{-}CO{-}CH_3}$$

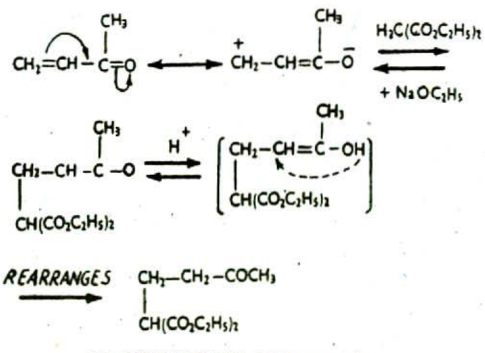
(5) *Addition of HCN.* Methyl vinyl ketone on treatment with HCN does not form a cyanohydrin but gives 4-cyanobutanone-2 arising from 1, 4 addition reaction.



(6) *Addition of HCl.* Similarly HCl reacts with MKV to form 4-chlorobutanone-2 which again arises from 1, 4-addition product.

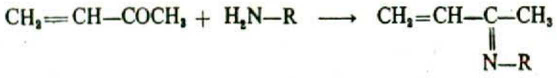


(7) *Michael Reaction.* Methyl vinyl ketone on treatment with diethyl malonate in presence of sodium ethoxide undergoes a 1, 4-addition of the carbanion to yield 5, 5-dicarbethoxybutanone-2.



5,5-DICARBETHOXY BUTAN-2 ONE

(8) Condensation with Ammonia derivatives. Like other ketones, methyl vinyl ketone also condenses with hydroxylamine, hydrazine, phenylhydrazine to form oximes, hydrazones and phenylhydrazones respectively.



$$CH_2{=}CH{-}COCH_3 + H_2N{-}R \longrightarrow CH_2{=}CH{-}\underset{\underset{N-R}{\|}}{C}{-}CH_3$$

where $R = -OH,\ -NH_2,\ -NHC_6H_5$ etc.

Uses. MVK is used commercially as a starting material for plastics.

INFRARED SPECTRA OF ALDEHYDES AND KETONES

The saturated aldehydes and ketones show a strong absorption band in the region 1740—1720 cm^{-1} and 1725—1705 cm^{-1} respectively due to $C{=}O$ stretching of the carbonyl group. In case of αβ-unsaturated aldehydes and ketones, this band occurs at a lower wave number (cm^{-1}). The –CHO group of an aldehyde displays a characteristic **C—H stretching** band near 2720 cm^{-1}. This in conjunction with the carbonyl bond, is diagnostic for **aldehydes.** The infrared spectrum of **ethyl methyl ketone** given below displays the various absorption **bands.**

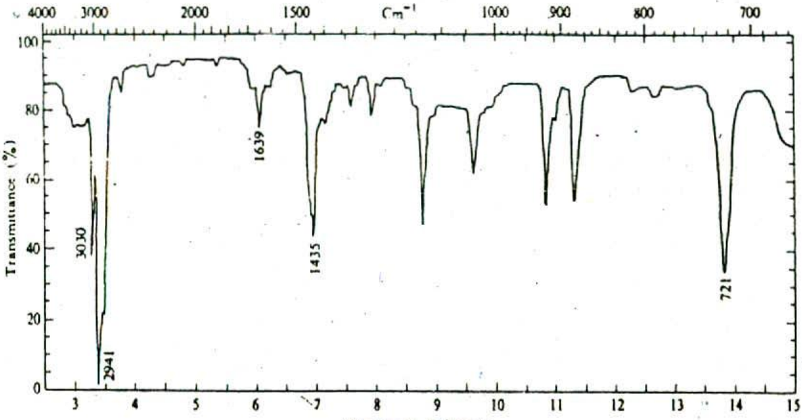


Fig. 20·3. Infrared spectrum of

COMPARISON OF ALDEHYDES AND KETONES

As pointed out before, aldehydes and ketones bear a marked structural similarity

R—CO—R′	Ketones
R—CO—H	Aldehydes

They have R—CO— in common and thus both classes give the reactions of the hydrocarbon radical R and >CO group. Aldehydes, however, are more reactive and possess reducing properties which are missing in ketones. The difference in behaviour is obviously due to the fact that the very active hydrogen linked to CO in aldehydes has been replaced by a comparatively inert alkyl group R′ in ketones.

Aldehydes	*Ketones*
Points of Resemblance :	
(1) Undergo halogenation in the hydrocarbon radical.	(1) Undergo halogenation like aldehydes.
(2) On reduction give primary alcohols.	(2) On reduction give secondary alcohols.
(3) React with HCN forming cyanohydrins.	(3) Form cyanohydrins like aldehydes.
(4) React with $NaHSO_3$ giving sodium bisulphite compounds.	(4) Give sodium bisulphite compounds like aldehydes.
(5) Give dihalogen derivatives with PCl_5, O being replaced by two Cl atoms.	(5) Give dihalogen derivatives similar to those obtained from aldehydes.
(6) React with NH_2OH by elimination of a water molecule to form *Aldoximes*.	(6) Form *Ketoximes* under similar conditions.
(7) React with $Ph.NH.NH_2$ by elimination of a water molecule to form *Phenylhydrazones*.	(7) React similarly to form *Phenylhydrazones*.
Points of difference :	
(1) React with ammonia to form *aldehyde-ammonias*.	(1) Give *complex compounds* instead of aldehydes ammonias.
(2) React with alcohols to form *acetals*.	(2) No action.
(3) Upon oxidation give fatty acids containing the same number of carbon atoms.	(3) Oxidised with difficulty giving fatty acids containing smaller number of carbon atoms than the original ketone.
(4) Reduce ammoniacal silver nitrate solution with the formation of mirror.	(4) Do not reduce ammoniacal silver nitrate.
(5) Reduce Fehling's solution with the formation of red cuprous oxide.	(5) Do not reduce Fehling's solution.
(6) Polymerise readily.	(6) Do not polymerise.
(7) Form brown resinous mass with NaOH solution.	(7) Do not form resins with NaOH solution.
(8) Restore pink colour of Schiff's reagent.	(8) Do not restore the colour of Schiff's reagent.

QUESTIONS

1. What are aldehydes and ketones ? Point out the structural relationship between the two types of compounds.

2. Describe the general methods of formation and properties of aldehydes.

3. Describe the preparation of acetaldehyde. Give its properties and how it reacts with Caustic potash, Ammonia and Potassium cyanide ?

4. How is acetone manufactured ? State its properties and uses.

6. Compare and contrast the chemical properties of aliphatic aldehydes and ketones.

7. (*a*) Describe the laboratory method of preparation of pure acetaldehyde.
   (*b*) In what respects does it differ from formaldehyde ?
   (*c*) Write with examples, what you know about the reducing character of acetaldehyde.

8. (a) How would you distinguish between a Ketone and an Aldehyde ?
(b) Write an account of the uses of ethyl acetoacetate in organic synthesis.

9. Give a method of preparation and two reactions of acrolein. *(Sambalpur BSc Hons, 1993)*

10. How will you distinguish between :
    - (a) Acetaldehyde and acetone
    - (b) 2,2-Dimethylpropanal and 2-butanone
    - (c) 3-Pentanone and cyclopentanone *(Gauhati BSc Hons. 1993)*

Hint. (a) Acetaldehyde forms silver mirror with Tollens' reagent ; (b) 2-Butanone gives Iodoform test ; and (c) Cyclopentanone forms addition compound with sodium bisulphite; 3-pentanone will not.

11. Write the mechanism for the reaction of acetaldehyde with HCN. *(Madurai BSc, 1994)*

12. Give the preparation of Crotonaldehyde. *(Goa BSc, 1994)*

13. Write a note on : Aldol condensation. *(Agra BSc, 1993; Annamalai BSc, 1994; Delhi BSc Hons., 1994)*

14. Write a note on : Cannizzaro reaction. *(Madras BSc, 1993 ; Saugar BSc 1993 ; Anna BSc, 1994)*

15. How will you synthesise acrolein from glycerol ? *(Osmania BSc Hons, 1994)*

16. An unknown compound has the formula C_7H_{14}. Ozonolysis (O_3, Zn/H_2O) gives two compounds, both of which react with 2,4-dinitrophenylhydrazine to give a solid derivative. One of the ozonolysis products gives both a positive Tollens' and a positive iodoform test; whereas the other is negative to both of these tests. What is the structure of the unknown ?

Answer. 3-Ethyl-2-pentene

17. Compound (A), $C_6H_{13}Br$, forms a Grignard reagent with magnesium in anhydrous ether. The Grignard reagent can be hydrolysed with water and acid to 2-methylpentane. When (A) is reacted with aqueous NaOH, compound (B), $C_6H_{14}O$, is formed, which is heated with copper metal to form (C), $C_6H_{12}O$. Compound (C) gives a negative Fehling's test, and a negative Tollens' test, but a positive iodoform test. From this information, deduce and write structural formulas of compounds (A), (B) and (C)

Answer. (A) is 2-Bromo-4-methylpentane ; (B) is 4-Methyl-2-pentanol and (C) is 4-Methyl-2-pentanone.