Oxygen Containing Organic Compounds - I

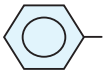
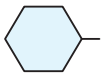
(Alcohols, Phenols, Ethers, Glycols & Glycerol)

ALCOHOLS — Section - 1

The compounds in which hydroxyl group (–OH) is attached to a saturated carbon atom are called as Alcohols. The compounds in which a hydroxyl group is attached to an unsaturated carbon atom of a double bond are called as Enols. The saturated carbon may be that of an alkyl, allyl, cycloalkyl or benzyl group. However if a hydroxyl group is attached to a benzene ring, the compounds are called as Phenols.

The alcohols are further classified as : Monohydric (containing one –OH group), Dihydric (containing two –OH groups) and Trihydric (containing three –OH groups).

Some important Monohydric alcohols are :

CH_3OH (Methanol), CH_3CH_2OH (Ethanol), $(CH_3)_2CHOH$ (Propan-2-ol / Isopropyl alcohol), $(CH_3)_3C\text{-}OH$ (2-Methylpropan-2-ol / Tert. butyl alcohol), $CH_2 = CHCH_2OH$ (Prop-2-en-1-ol / Allyl alcohol), $HC \equiv CCH_2OH$ (Prop-2-yn-1-ol), C_6H_5OH (Phenol),  CH_2OH (Benzyl alcohol),  OH (Cyclohexanol).

Monohydric alcohols are further classified as: Primary (1°) $RCH_2\text{-}OH$, Secondary (2°) $R_2CH\text{-}OH$ and Tertiary (3°) $R_3C\text{-}OH$.

Preparations of Alcohols

1. **Hydrolysis of alkyl halides :** Alkyl halides undergo hydrolysis when heated with aqueous alkalies or moist silver oxide. The hydrolysis occurs by a nucleophillic substitution reaction.

$$R - X + NaOH \xrightarrow{H_2O} R - OH + NaX$$

$$C_2H_5 - Br + KOH(aq) \longrightarrow C_2H_5 - OH + KBr$$

Sometimes this method is not satisfactory as *Olefins* (alkenes) are also formed as side products specially if halide is tertiary. If R is 3°, then alkyl halides mainly give alkenes, when NaOH is concentrated (–OH as base).

$$(CH_3)_3C - Br + NaOH(conc.) \longrightarrow \underset{\text{Major product}}{(CH_3)_2C = CH_2} + \underset{\text{Minor product}}{(CH_3)_3C - OH}$$

However satisfactory results are obtained by using moist Silver oxide (AgOH) or aqueous K_2CO_3.

$$RI + AgOH \longrightarrow R - OH + AgI$$

2. From alkenes :

(a) By acid-catalysed hydration of alkenes : Alkenes react with cold concentrated H_2SO_4 to give alkyl hydrogen sulphates following Markovnikov's addition.

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H-\underset{\text{Cold}}{OSO_3H} \longrightarrow \underset{\underset{\text{Isopropylhydrogensulphate}}{OSO_3H}}{CH_3-\overset{|}{C}H-CH_3} \xrightarrow[\Delta]{H_2O} \underset{OH}{CH_3-\overset{|}{C}H-CH_3}$$

Note : Alkyl hydrogen sulphate when boiled with water give alcohols.

(b) Hydroboration - Oxidation of alkenes : Alkenes react with diborane in presence of THF as solvent to form alkyl boranes (*Hydroboration*). Alkyl boranes are then oxidised and hydrolysed by the addition of hydrogen peroxide in aqueous base.

$$CH_3CH=CH_2 \xrightarrow[2.\ H_2O_2/OH^-, H\text{-}OH]{1.\ B_2H_6\ /\ THF} \underset{H\quad OH}{CH_3\overset{|}{C}H\overset{|}{C}H_2}$$

Here the net addition (*syn*) of H – OH to alkenes is in accordance with Anti-Markovnikov's rule and *free from any rearrangement.* It is an important method for preparing 1° alcohols.

Note : In the above addition reaction, 'H' comes from B_2H_6 and 'OH' comes from H_2O molecule.

(c) Oxymercuration and demercuration : Mercuric acetate ($Hg(OAc)_2$) in presence of water - tetrahydrofuran solution reacts with alkene to form alkyl mercury compound. The mercury compound is reduced with $NaBH_4$ when alcohol is formed.

$$R-CH=CH_2 \xrightarrow[2.\ NaBH_4,\ OH^-]{1.\ Hg(OAc)_2\,/\,THF,\ H\text{-}OH} \underset{\text{addition}}{R-\overset{|}{C}H-\overset{H}{\overset{|}{C}}H_2} \quad \underset{(2^\circ\ \text{Alcohol})}{\overset{|}{OH}}$$

The above addition reaction (*anti*) occurs in accordance with Markovnikov's addition (unlike hydroboration reaction). The 'H' becomes attached to the carbon atom of the double bond with greater number of hydrogen atoms. *It too does not involve rearrangement.*

Note : In the above reaction, 'OH' comes from H_2O and 'H' comes from $NaBH_4$.

3. Reduction of Aldehydes and Ketones : Aldehydes and Ketones on reduction yield alcohols. A number of reducing agents like H_2/Ni or Na/C_2H_5OH or Zn/HCl or $LiAlH_4$ in ether or $NaBH_4$ in alkali or H_2O can be used for this purpose.

(a) Bouveault - Blanc reduction : The reducing agent used is sodium and ethanol. The aldehydes and ketones are reduced by nascent hydrogen into corresponding alcohols.

$$RCHO + 2[H] \xrightarrow[EtOH]{Na} RCH_2OH \qquad (1^\circ\ \text{alcohol})$$

$$\begin{matrix} R \\ \diagdown \\ \quad CO \\ \diagup \\ R' \end{matrix} + 2[H] \xrightarrow[EtOH]{Na} \begin{matrix} R \\ \diagdown \\ \quad CHOH \\ \diagup \\ R' \end{matrix} \qquad (2^\circ\ \text{alcohol})$$

(b) Reduction with $LiAlH_4$: It is a better reducing agent for the conversion of carbonyl compounds into alcohols. $LiAlH_4$ is soluble in ether, the common solvent and it does not reduce the carbon – carbon double bond.

$$CH_3 - CH = CH - CHO \xrightarrow[\text{ether}]{LiAlH_4} CH_3CH = CHCH_2OH$$

Note : **(i)** $NaBH_4$ also does not reduce carbon – carbon double bond. Also, $NaBH_4$ is a mild reducing agent.

(ii) Catalytic hydrogenation reduces carbon – carbon double bond as well as carbonyl group.

$$CH_2 = CHCHO + 4[H] \xrightarrow[\text{Catalyst}]{Ni} CH_3CH_2CH_2OH$$

Catalytic hydrogenation of esters produce primary alcohol.

(iii) Ketones are reduced to secondary alcohols by Aluminium isopropoxide in Isopropyl alcohol. The reduction by this method is known as *Meerwin-Pondorrf-Verley* (MPV) reduction and is considered as an important method for the formation of secondary alcohols.

$$R_2C = O \xrightarrow[\text{in Isopropyl alcohol}]{[(CH_3)_2CH-O]_3Al} R_2CH - OH$$

(iv) As a special case, $LiAlH_4$ also reduces double bond if conjugated with a phenyl group, in α, β-unsatured carbonyl compound along with carbonyl group.

$$Ph - CH = CH - CHO \xrightarrow[\text{ether}]{LiAlH_4} Ph - CH_2 - CH_2 - CH_2OH$$

(v) $NaBH_4$ can reduce aldehydes, ketones and acyl chlorides to alcohols.
$LiAlH_4$ can reduce carboxylic acids, esters (to alcohols) and amides (to amines) also.

4. Hydrolysis of Ester : (*Base or Acid catalysed*)

Esters on hydrolysis by mineral acids or alkalies form alcohols and carboxylic acids. Hydrolysis of ester takes place by acyl-o-cleavage reaction mechanism.

$$R - CO - \overset{*}{O}R' + H - OH \xrightarrow[\Delta]{H^+ \text{ or } OH^-} R'\overset{*}{O}H + RCOOH$$

Alcohols being more volatile than acids can be easily separated by distillation.

5. From Ethers :

(a) Hydrolysis : Ethers when heated with dil. sulphuric acid under pressure are hydrolysed to the corresponding alcohols.

$$R - OR' + H_2O \xrightarrow[\text{dil.}]{H_2SO_4} ROH + R'OH$$ (Separated by fractional distillation)

(b) With concentrated HI :

(i) If symmetric : $R - O - R \xrightarrow{HI} ROH + RI$

(ii) If mixed : $R - O - R' \xrightarrow{HI} ROH + R'I$ (Iodide contains smaller alkyl group except when R′ is 3°)

$$C_2H_5 - O - CH_3 \xrightarrow{HI} C_2H_5OH + CH_3I$$

Note : **(i)** The details of this reaction is given in Section - 3 (Ethers)

(ii) In this reaction, refluxing the products with KI(aq) gives only alcohols.

$$C_2H_5OCH_3 \xrightarrow{HI} C_2H_5OH + CH_3I \xrightarrow[HI(aq)/H^+]{KI/H^+} C_2H_5OH + CH_3OH$$

6. Action of Nitrous acid on primary amines : Alcohols are formed when primary amines (only) are treated with nitrous acid (HNO_2).

$$RNH_2 + HONO \longrightarrow ROH + N_2 + H_2O$$

$$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$$

The details of this reaction will be covered later in chapter of 'Amines'.

Note : Under similar condition, Methylamine does not yield Methanol. The product formed is Methylnitrite or Dimethyl ether.

$$CH_3NH_2 + 2HNO_2 \longrightarrow CH_3 - O - N = O + 2H_2O + N_2$$

or $$2CH_3NH_2 + 2HNO_2 \longrightarrow CH_3 - O - CH_3 + 3H_2O + 2N_2$$

7. Reduction of Carboxylic acid and its derivatives :

(a) Catalytic Hydrogenation : It follows the order : $RCOCl > RCOOR' > RCOOH$.

However, catalytic hydrogenation is not used in industries because extremely high pressures and temperatures are required.

(b) Bouveault – Blanc reduction :

$$RCOOC_2H_5 \xrightarrow[EtOH]{Na} RCH_2OH + C_2H_5OH$$

(c) Reduction by $LiAlH_4$: The acids can be reduced to primary alcohols by $LiAlH_4$ (not by $NaBH_4$).

$$RCOOH \xrightarrow[2.\ H_2O]{1.\ LiAlH_4 \text{ in ether}} RCH_2OH$$

Esters are more easily reduced than carboxylic acids by $LiAlH_4$. Two alcohols are formed from each ester molecule; one is derived form the acyl part and other from the alcoholic part.

$$R - \overset{\overset{O}{\|}}{C} - OR' \xrightarrow[2.\ H_2O]{1.\ LiAlH_4} R - CH_2OH + R'OH$$

8. From Grignard Reagent : All the three types of monohydric alcohols can be prepared by the use of Grignard reagents.

(a) Primary alcohols : Primary alcohols are obtained when Grignard reagent is reacted with oxygen or Formaldehyde or Ethylene oxide.

(i) $$RMgX + \frac{1}{2}O_2 \longrightarrow R - O - MgX \xrightarrow{H_2O} ROH + Mg\begin{matrix}OH\\X\end{matrix}$$

The alcohol has same number of carbon atoms as present in the alkyl group of the Grignard reagent.

(ii) $$HCHO + RMgX \longrightarrow RCH_2O - MgX \xrightarrow{H_2O} RCH_2OH + Mg\begin{matrix}OH\\X\end{matrix}$$

The alcohol has one carbon atom more than the alkyl group of the Grignard reagent.

(b) Ethanol : $[C_2H_5OH]$

(i) Fermentation of Molasses $(C_{12}H_{22}O_{11})$:

$$\underset{\text{Molasses}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2\uparrow$$

From molasses, both glucose and fructose are formed, which are converted to ethyl alcohol by zymase.

(ii) From Starch $(C_6H_{10}O_5)_n$:

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} \xrightarrow[\text{Diastase}]{n\,H_2O} \underset{\text{Maltose}}{n(C_{12}H_{22}O_{11})} \xrightarrow[H_2O]{\text{Maltase}} \underset{\text{Glucose}}{n(C_6H_{12}O_6)} + \underset{\text{Fructose}}{n(C_6H_{12}O_6)}$$

From starch, both glucose and fructose are formed, which are converted to ethyl alcohol by zymase.

(c) For 1° alcohols (OXO - Process) :

$$CH_2 = CH_2 + CO + H_2 \xrightarrow[[CoH(CO)_4]]{\text{high temp. pressure}} CH_3CH_2CHO \xrightarrow{H_2/Ni} CH_3CH_2CH_2OH$$

$$CH_3CH = CH_2 + CO + H_2 \xrightarrow[[Co(CO)_4]_2]{\text{high temp. pressure}} CH_3CH_2CH_2CHO + CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CHO$$

➤ These can be reduced to give corresponding 1° and 2° alcohols.

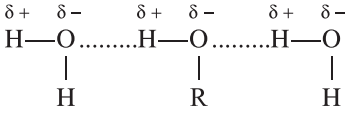
Note : Absolute alcohol (100% pure ethyl alcohol). Rectified spirit (containing 95.87 % C_2H_5OH + 4.13 % H_2O) cannot be converted into absolute alcohol simply by distillation because the mixture of ethanol and water in the ratio of 95.87 : 4.13 (a ratio present in rectified spirit) is a constant boiling mixture (azeotropic mixture) having b.p. 78.13°C.

Methylated spirit (Denaturated alcohol) It is rectified spirit (industrial alcohol) mixed with poisonous substances like CH_3OH, pyridine, acetone, etc. to make it unfit for drinking purposes. The usual composition of denatured alcohol is 85 — 90% rectified spirit + 10 — 15% methanol.

Power alcohol. Alcohol used for the generation of power is called power alcohol. It is a mixture of petrol and alcohol in the ratio of 4 : 1 in presence of benzene or ether.

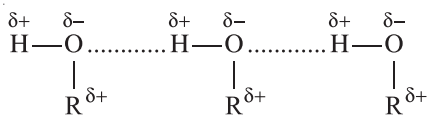
Physical Properties

1. The lower alcohols are readily soluble in water and the solubility decreases with the increase in molecular weight. The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarised –OH groups present both in alcohol and water.



Relative solubility of isomeric alcohols in water is 1° > 2° > 3°.

2. Boiling points of alcohols are much higher than those of the corresponding alkanes and ethers. It is due to the formation of hydrogen bonding between the hydroxyl groups of the two molecules of an alcohol with the result several molecules are associated to form a large molecules.



Among the isomeric alcohols, b.p. show the following trend:

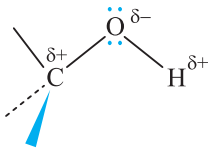
Primary > Secondary > Tertiary (e.g. visualise isomers of C_4H_9OH.)

3. Lower alcohols form solid addition compounds with anhydrous metallic salts like $CaCl_2$ and $MgCl_2$, viz., $CaCl_2.4C_2H_5OH$ and $MgCl_2.6C_2H_5OH$.

By analogy to water of crystallisation, these alcohol molecules are referred to as alcohol of crystallisation. For this reason, alcohols cannot be dried over anhydrous calcium chloride.

4. Methanol is highly toxic. Ingestion of even small quantities of methanol can cause blindness ; large quantities can cause death. Methanol poisoning can also occur by inhalation of the vapours or by prolonged exposure to the skin. Ethanol is a hypnotic (sleep producer). Ethanol is much less toxic than methanol.

Reactions of Alcohols

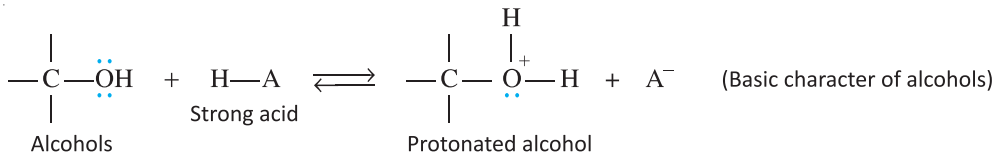


Let us examine the electron distribution in the alcoholic functional group, and its impact on the reactivity :

(i) Oxygen atom of an alcohol polarizes both C—O bond and the O—H bond of an alcohol. Polarization of the O—H bond makes the hydrogen partially positive and explains why alcohols are weak acids. In such reactions alcohols act as acids and cleavage of the O—H bond takes place. The order of reactivity of different alcohols for such reactions is :

$CH_3OH > 1° > 2° > 3°$ alcohols.

(ii) Polarisation of the C—O bond makes the carbon atom partially positive, and hence it would have been susceptible to nucleophilic attack if OH^- were not a strong base, i.e., if OH^- were not a poor leaving group.



Protonated alcohols easily undergo nucleophilic substitution which may be S_N2 or S_N1 depending upon the class of alcohol.

Mechanism of Nucleophilic substitution reactions of Alcohols (S_N1 and S_N2 paths) :

Note that alcohols do not give typical nucleophillic substitution reaction since OH^- ion being a strong base is a poor leaving group.

$ROH + Nu^- \not\longrightarrow R - Nu + OH^-$ Strong base (Poor leaving group)

But alcohols do give nucleophillic substitution in presence of halogen acids. In presence of acids, leaving group is H_2O instead of –OH group. Primary alcohols having β-carbon as 1° or 2° always give S_N2 reaction. Secondary alcohols having β-carbon as 1° also give S_N2 reaction. All tertiary alcohols give S_N1 reaction.

S_N1 path :

1st step : $(CH_3)_3C-OH \xrightarrow[\text{fast}]{HX} (CH_3)_3C-\overset{+}{O}H_2$

2nd step : $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\overset{+}{O}H_2 \xrightarrow[\text{RDS}]{\text{slow}} (CH_3)_3-C^+ + H_2O$ ($3°C^+$; highly stable)

3rd step : $(CH_3)_3-C^+ + X^- \longrightarrow (CH_3)_3-C-X$

Note that it is almost similar to S_N1 in alkyl halides. Allyl and benzyl alcohols also follow the same path (S_N1).

S_N2 path : $RCH_2OH \xrightarrow{HX} RCH_2\overset{+}{O}H_2$

$X^- + RCH_2-\overset{+}{O}(H)-H \xrightarrow{\text{Slow step}} \left[X\cdots C\cdots \overset{+}{O}-H\right] \longrightarrow X-CH_2R + H_2O$ (S_N2 product)

Note : (i) In S_N2 reactions, X^- being weak base do not bring elimination by removing β-hydrogen. However in S_N1 reaction, carbocations formed may lose proton to give alkenes (E1).

(ii) Another method to bring out substitution in alcohols especially by S_N2 path is to convert them into halides with PX_3 or into sulphonates with TsCl.

$RCH_2OH + Cl-SO_2-C_6H_4-CH_3 \longrightarrow RCH_2-O-SO_2-C_6H_4-CH_3 + HCl$

Tosyl chloride (TsCl) Alkyl Tosylate (R-OTs)

(iii) At a high temperature, and in the absence of a good nucleophile, protonated alcohols are capable of undergoing elimination reactions.

1. With active metals:

Alcohols are acidic in nature and hence react with alkali metals to form metal alkoxides with the evolution of hydrogen gas.

$$2ROH + 2M \longrightarrow 2R-\bar{O}M^+ + H_2 \qquad (\text{where } M \equiv Na, K, Mg, Al, \text{etc.})$$

$$2CH_3OH + 2Na \longrightarrow 2CH_3-ONa + H_2$$

Note : (i) Alcohols behave like acids when O – H bond cleaves.

(ii) Reactivity of alcohols with metals is in order : $CH_3OH > 1° > 2° > 3°$

(iii) $R-O^-Na^+$ can be decomposed by H_2O to give back alcohol. However alcohols do not react with NaOH.

$$RO^-Na^+ + H_2O \longrightarrow ROH + NaOH$$

(iv) Since most alcohols are weaker acids than water, most alkoxide ions are stronger bases than the hydroxide ions. $(CH_3)_3CO^- > C_2H_5O^- > OH^- > CH_3O^-$ (Relative basic character).

Alcohols as acids

Alcohols have acidities similar to that of water. Methanol is a slightly stronger acid than water but most alcohols are somewhat weaker acids. In general, the order of acidity of alcohols is as follows :

$$H_2O > CH_3CH_2OH > (CH_3)_2-CH-OH > (CH_3)_3-C-OH.$$

The reason sterically hindered alcohols such as tert-butyl alcohol are less acidic arises from solvation effects. With unhindered alcohols, water molecules are able to surround and solvate the negative oxygen of the alkoxide ion formed when an alcohol loses a proton. Solvation stabilizes the alkoxide ion and increases the acidity of the alcohol. Any factor that stabilizes the conjugate base of an acid increases its acidity.

If the R– group of the alcohol is bulky, solvation of the alkoxide ion is hindered, and the alkoxide ion is not as effectively stabilized. The alcohol, consequently, is a weaker acid.

All alcohols, however, are much stronger acids than terminal alkynes, and are very much stronger acids than hydrogen, ammonia, and alkanes.

Relative Acidity $H_2O > ROH > RC\equiv CH > NH_3 > RH > H_2$

The conjugate base of an alcohol is an alkoxide ion. Sodium and potassium alkoxide can be prepared by treating alcohols with sodium or potassium metal or with the metal hydride. Because most alcohols are weaker acids than water, most alkoxide ions are stronger bases than the hydroxide ion.

Relative basicity $H^- > R^- > NH_2^- > RC\equiv C^- > RO^- > OH^-$

Alcohols reacts with diazomethylene in presence of BF_3, Grignard reagent due to acidic nature.

$$ROH + \overset{-}{C}H_2 - \overset{+}{N} \equiv N \xrightarrow{BF_3} ROCH_3 + N_2$$

$$ROH + CH_3 - MgBr \xrightarrow{Ether} CH_4 + ROMgBr$$

2. Action of acids (Esterification):

(a) Ester of Carboxylic acids : $RCOOH + H - \overset{*}{O}R' \rightleftharpoons RCO\overset{*}{O}R' + H_2O \quad [* \to O^{18}]$

Reactivity in esterification :

- For alcohols : $CH_3OH > 1° > 2° > 3°$
- For acids : $HCOOH > CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3CCOOH$

Note : **(i)** Esterification reaction proceed by acyl-o-cleavage reaction mechanism.

(ii) Tert. alcohols react so slowly in acid-catalysed esterification that they usually undergo elimination to form alkenes.

(iii) Esters are also formed by the reaction of alcohols with acyl chlorides or acid anhydrides.

$$CH_3 - CO - O - CO - CH_3 + H - OR \longrightarrow CH_3 - CO - OR + CH_3 - COOH$$

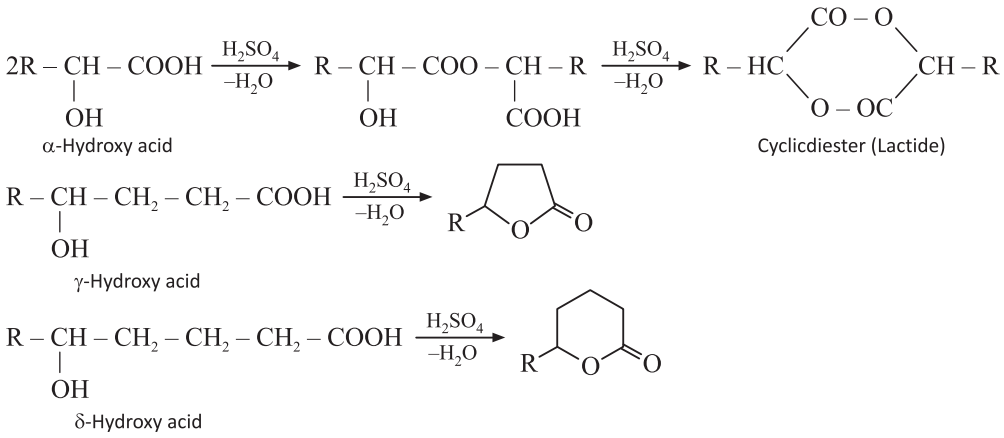
Unlike the reaction with carboxylic acids, these reactions are irreversible, hence yields of esters via this route are always high.

(iv) Reaction with acyl chlorides or acid anhydrides is used to determine number of hydroxyl groups in polyhydric alcohols.

$$\text{Number of OH groups} = \frac{\text{Molar mass of product} - \text{Molar mass of polyhydric alcohol}}{42}$$

(v) Suitable hydroxycarboxylic acid undergoes intramolecular esterification to form cyclic ester. (Called as Lactone)

The mechanism of the reaction will be discussed in Carboxylic Acids.



(b) Esters of Sulphonic acids : $CH_3 - SO_2 - Cl + H - OC_2H_5 \xrightarrow{\text{base}} CH_3 - SO_2 - OC_2H_5 + HCl$

Methyl sulphonyl chloride — Ethyl methyl sulphonate

(c) Esters of Inorganic acids : Alcohols react with inorganic acids, viz. HNO_3, H_2SO_4, H_3PO_3 and H_3PO_4 to form esters of inorganic acids.

$$ROH + HONO_2 \xrightarrow{H^+} RONO_2 + H_2O$$

$$2CH_3OH + H_2CO_3 \xrightarrow[-H_2O]{} (CH_3)_2CO_3$$ Dimethyl carbonate

$$CH_3OH + HO - SO_3H \longrightarrow CH_3OSO_3H \xrightarrow{CH_3OH} CH_3OSO_2OCH_3$$

Methyl hydrogen sulphate — Dimethyl sulphate

3. Conversion of alcohols into alkyl halides :

(a) Reaction with halogen acids : $R - OH + HX \xrightarrow[\text{anhyd.}]{ZnCl_2} R - X + H_2O$

The order of reactivity of the hydrogen halides is HI > HBr > HCl (HF is generally unreactive), and the order of reactivity of alcohols is 3° > benzyl ~ allyl > 2° > 1° > CH_3. This reaction follows nucleophillic substitution mechanism.

Note : The mixture of HCl and anhydrous $ZnCl_2$ at room temperature is called *Lucas reagent* and the reaction is referred to as LUCAS TEST (appearance of a white *turbid* solution). 3° alcohols give Lucas Test instantly ; 2° alcohols give it after sometime and 1° alcohols do not give this test.

Note : Mechanism : Secondary, tertiary, allylic, and benzylic alcohols appear to react by S_N1 mechanism.

Step 1 : $(CH_3)_3C - \overset{\delta+}{O}H + H - \overset{\delta-}{Cl} \longrightarrow (CH_3)_3C - \overset{+}{O}H_2 + Cl^-$

Step 2 : $(CH_3)_3C - \overset{+}{O}H_2 \longrightarrow (CH_3)_3C^+ + H_2O$

Step 3 : $(CH_3)_3C^+ + Cl^- \longrightarrow (CH_3)_3C - Cl$

tert - Butyl chloride

Most of the primary alcohols and methyl alcohol react by S_N2 mechanism.

$$X^- + R - \overset{+}{O}H_2 \longrightarrow \left[X^{\delta-} \cdots\cdots R \cdots\cdots {}^{\delta+}OH_2\right] \longrightarrow X - R + H_2O$$

Why CH_3OH reacts faster than other primary alcohols ?

Actually, methyl substrate is least capable of heterolysis and thus reacts only by S_N2 reaction. Although most of the primary substrates also react by S_N2 mechanism, but because of increased steric hinderance they react less rapidly than the methyl.

(b) Reaction with Phosphorus halides :

$$3ROH + PCl_3 \xrightarrow{\Delta} 3RCl + H_3PO_3 \quad ; \quad ROH + PCl_5 \xrightarrow{\Delta} RCl + POCl_3 + HCl$$

Generally, in place of PBr_3, red P and Br_2 can be used. Similarly for PI_3, red P and I_2 is used.

(c) Reaction with Thionyl chloride :

$$ROH + SOCl_2 \xrightarrow[S_Ni]{\text{Pyridine}} R-Cl + SO_2\uparrow + HCl\uparrow$$

$$R-OH + SOCl_2 \xrightarrow[S_Ni]{} R-Cl + SO_2\uparrow + HCl\uparrow$$

If reaction takes place on chiral carbon atom then product is formed with retention in configuration because reaction proceed by intramolecular nucleophilic substitution (S_Ni) reaction mechanism.

Note : The reaction of alcohols with phosphorus and sulphur halides involves no rearrangement unlike with HX.

4. Dehydration to Alkenes : Alcohols on reaction with conc. H_2SO_4/Δ, H_3PO_4 or catalysts such as anhydrous zinc chloride or alumina, loose the water molecule and form alkenes.

$$C_2H_5OH \xrightarrow[170^\circ C]{\text{conc. } H_2SO_4 \text{ (excess)}} CH_2 = CH_2$$

$$CH_3CH_2\underset{\underset{OH}{|}}{C}H - CH_3 \xrightarrow[\Delta]{\text{conc. } H_2SO_4 \text{ (excess)}} \underset{\text{Major}}{CH_3CH = CHCH_3} + \underset{\text{Minor}}{CH_3CH_2CH = CH_2}$$

- The ease of dehydration is $3^\circ > 2^\circ > 1^\circ$ alcohols.
- The Dehydration always follow Saytzeff rule.
- In gas phase, alcohols are heated with alumina to give alkene $C_2H_5OH \xrightarrow[350^\circ C]{Al_2O_3} CH_2 = CH_2$

Note : **(i)** If alcohols are in excess, then ethers are formed.

$$\underset{\text{(Excess)}}{C_2H_5OH} + \underset{\text{(conc.)}}{H_2SO_4} \xrightarrow{140^\circ C} \underset{\text{Diethyl ether}}{C_2H_5 - O - C_2H_5} + H_2O$$

$$\underset{\text{(Excess)}}{C_2H_5OH} + Al_2O_3 \xrightarrow{200^\circ C} C_2H_5 - O - C_2H_5$$

(ii) Note that , at 170°C or above dehydration occurs and at around 140°C, ethers are formed when conc. H_2SO_4 is used.

(iii) When conc. H_2SO_4 is in excess, alkenes are formed and when alcohols are in excess, then ethers are formed.

5. Reaction with Ammonia : When a mixture of the vapours of an alcohol and ammonia are passed over heated alumina or thoria catalyst at 360°C, a mixture of primary, secondary and tertiary amines is produced.

$$ROH + NH_3 \xrightarrow[360^\circ C]{Al_2O_3} \underset{1^\circ\text{amine}}{RNH_2} \xrightarrow[Al_2O_3]{ROH} \underset{2^\circ\text{amine}}{R_2NH} \xrightarrow[Al_2O_3]{ROH} \underset{3^\circ\text{amine}}{R_3N}$$

6. Reaction with Grignard Reagent : $ROH + R'MgX \longrightarrow \underset{\text{(an alkane)}}{R'-H} + Mg\begin{matrix}OR\\X\end{matrix}$

7. Reduction : $ROH + 2HI \xrightarrow[\Delta]{\text{Red P}} RH + I_2 + H_2O$

8. Oxidation : The oxidation of alcohols is used to distinguish between 1°, 2°, 3° alcohols.

1° alcohols : $RCH_2OH \xrightarrow[25°C]{[O]} \underset{\text{aldehyde}}{RCHO} \xrightarrow{[O]} \underset{\text{acids}}{RCOOH}$

2° alcohols : $\begin{matrix}R\\R\end{matrix}\!\!>\!CHOH \xrightarrow{[O]} R-\overset{\overset{O}{\|}}{C}-R$ (Ketones)

Secondary alcohols are oxidised to ketones by chromic anhydride (CrO_3).

$$R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow{CrO_3} R-\overset{\overset{O}{\|}}{C}-R'$$

3° alcohols : $R_3C-OH \xrightarrow{[O]}$ do not oxidise

Tertiary alcohols do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidising agents ($KMnO_4$) and elevated temperatures, cleavage of various C–C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

The important oxidising agents are : $KMnO_4/H^+$, $Na_2Cr_2O_7/H^+$, Chromic acid (H_2CrO_4). Some examples are :

$$CH_3CH_2OH \xrightarrow{H_2CrO_4} CH_3CHO \xrightarrow{H_2CrO_4} CH_3COOH \quad ; \quad \underset{\text{Cyclohexanol}}{\bigcirc\!-OH} \xrightarrow{H_2CrO_4} \underset{\text{Cyclohexanone}}{\bigcirc\!=O}$$

***Note* : (i)** H_2CrO_4 does not oxidise double or triple bond in alcohols unlike $KMnO_4$ and $K_2Cr_2O_7$.

$$H_2C=CH-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{H_2CrO_4} H_2C=CH-\overset{\overset{O}{\|}}{C}-CH_3$$

(ii) Cycloalkanols in presence of 50% HNO_3 at 55°C undergo cleavage forming dioic acids.

$$\bigcirc\!-OH \xrightarrow[55-60°C]{HNO_3(50\%)} \underset{\text{1, 6 - Hexandioic acid}}{HOOC-(CH_2)_4-COOH}$$

(iii) It is difficult to stop oxidation at aldehydic stage in aqueous solution. Hence a special oxidising agent, Pyridinium chlorochromate (PCC) in CH_2Cl_2, is used to convert alcohols to aldehydes.

$$CH_2=CH-CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_2=CH-CH_2CHO$$

PCC only oxidises 1° and 2° alcohols, not unsaturated bonds. PCC does not oxidise 3° alcohols. It is however mainly used for 1° alcohols.

(iv) Manganese dioxide selectively oxidises the alcoholic group of allylic and benzylic 1° and 2° alcohols to give aldehydes and ketones respectively.

$$CH_3-CH=CH-CH_2-OH \xrightarrow{MnO_2} CH_3-CH=CH-CHO$$

$$C_6H_5-CH_2-OH \xrightarrow{MnO_2} C_6H_5-CHO$$

(v) Jones Reagent : H_2CrO_4 in acetone at 35°C oxidises 1° and 2° alcohols to aldehydes and ketones respectively. It, however does not oxidise double bond. It is mainly used for 2° alcohols.

9. Dehydrogenation : (With hot Copper)

This reaction also serves as a test for 1°, 2°, 3° alcohols.

1° alcohols : $CH_3CH_2OH \xrightarrow[300°C]{Cu} \underset{\text{Aldehyde}}{CH_3CHO} + H_2$

2° alcohols : $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - OH \xrightarrow[573\ K]{Cu} (CH_3)_2C = O + H_2$

3° alcohols : $(CH_3)_3C - OH \xrightarrow[573\ K]{Cu} (CH_3)_2 - C = CH_2 + H_2O$ (Alkenes are formed)

10. Lucas Test : Lucas reagent (a mixture of conc. HCl and $ZnCl_2$) reacts with alcohols to form corresponding alkyl chlorides which are insoluble in Lucas reagent.

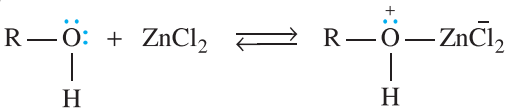
1° alcohols : $RCH_2OH \xrightarrow[HCl]{ZnCl_2}$ No reaction at room temperature.

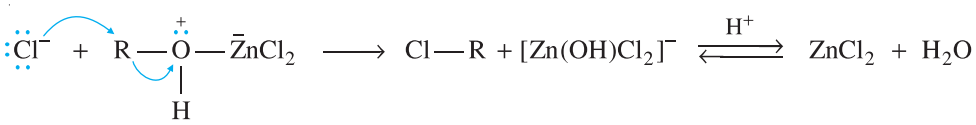
2° alcohols : $R_2CH - OH \xrightarrow[HCl]{ZnCl_2} R_2CH - Cl$ White turbidity after 5 – 10 minutes.

3° alcohols : $R_3C - OH \xrightarrow[HCl]{ZnCl_2} R_3C - Cl$ White turbidity instantaneously.

Note : Allyl and Benzyl alcohols react as rapidly as 3° alcohols to form soluble chlorides with Lucas reagent.

Function of $ZnCl_2$ in Lucas reagent : Since chloride ion is a weaker nucleophilie than bromide or iodide ions, HCl does not react with less reactive 1° and 2° alcohols unless some good Lewis acid like $ZnCl_2$ is added to the reaction mixture. Zinc chloride, a good Lewis acid, forms a complex with the alcohol. The complex provides a better leaving group for the reaction than H_2O.





(i) In case of 2° and 3° alcohols, the function of acid is to help in the formation of carbocations.

(ii) In case of methyl and 1° alcohols, the function of acid is to produce a substrate in which the leaving group is a weakly basic species ; H_2O or $[Zn(OH)Cl_2]^-$ rather than a strongly basic hydroxide ion.

(iii) 3° and Benzyl alcohols are more reactive due to formation of more stable corresponding carbocations.

11. Victor Meyer Test : This test is based upon the fact that three types (1°, 2° and 3°) of nitroalkanes (formed by alcohols) react differently with nitrous acids followed by the action of Sodium hydroxide(alkali).

1° Alcohols : $RCH_2OH \xrightarrow[\text{or HI}]{P/I_2} RCH_2I \xrightarrow{AgNO_2} RCH_2NO_2 \xrightarrow{HNO_2} R-\underset{\underset{NOH}{\|}}{C}-NO_2$ Nitrolic acid

➤ Nitrolic acid on treatment with alkali dissolve in it to give a red colouration.

$R-\underset{\underset{NOH}{\|}}{C}-NO_2 \xrightarrow{\text{Alkali}} R-\underset{\underset{\bar{N}O\overset{+}{N}a}{\|}}{C}-NO_2$

Nitrolic acid — Red colouration

2° Alcohols : $\begin{matrix}R\\R\end{matrix}\!\!>\!CH-OH \xrightarrow{P/I_2} \begin{matrix}R\\R\end{matrix}\!\!>\!CHI \xrightarrow{AgNO_2} \begin{matrix}R\\R\end{matrix}\!\!>\!CHNO_2 \xrightarrow{HNO_2} \begin{matrix}R\\R\end{matrix}\!\!>\!\underset{\underset{N=O}{|}}{C}-NO_2$ Pseudonitrol

➤ Pseudonitrol on treatment with alkali does not dissolve but gives blue colour.

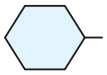
$\begin{matrix}R\\R\end{matrix}\!\!>\!\underset{\underset{N=O}{|}}{C}-NO_2 \xrightarrow{\text{Alkali}}$ Blue colouration

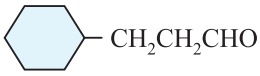
Pseudonitrol

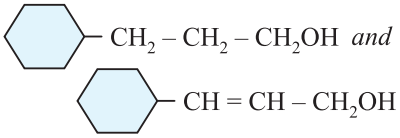
3° Alcohol : $R_3C-OH \xrightarrow{P/I_2} R_3C-I \xrightarrow{AgNO_2} R_3C-NO_2 \xrightarrow{HNO_2}$ No reaction.

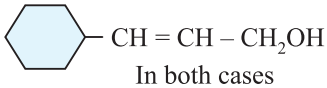
IN-CHAPTER EXERCISE - A

Choose the correct alternative. Only One Choice is correct. Questions marked with '*' may have More than One Correct Option.

1. B $\xleftarrow{NaBH_4}$  $\xrightarrow{H_2/Pt}$ A. *A and B respectively are* :

(A) 

(B) 

(C) 

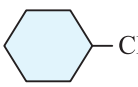
In both cases

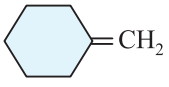
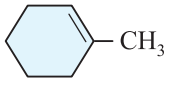
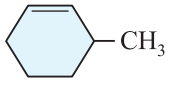
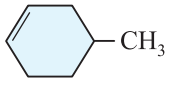
(D)

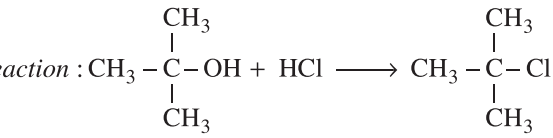
2. *Oxo process* :

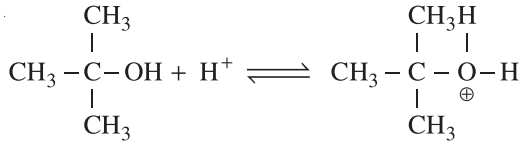
(A) *is simply carbonylation or hydroformylation reaction* **(B)** *use cobalt carbonyl hydride* $[CoH(CO)_4]$

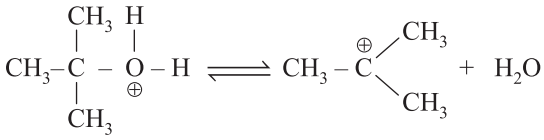
(C) *both statements are correct* **(D)** *both statements are incorrect*

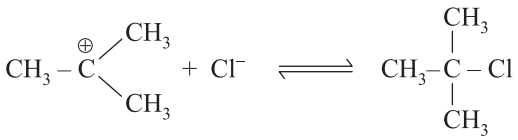
3.  *on dehydration with conc.* H_2SO_4 *forms predominantly* :

(A)  **(B)**  **(C)**  **(D)** 

4. *In the reaction :*  *the rate-determining step is :*

(A) 

(B) 

(C) 

(D) *all steps take place with equal ease*

***5.** *The reduction of R–COOH to R – CH_2OH can be effected by :*

(A) *sodium/alcohol* **(B)** *Zn/HCl* **(C)** *$LiAlH_4$ in ether* **(D)** *aluminium isopropoxide*

6. *The boiling points of isomeric alcohols follows the order decreasing :*

(A) *primary > secondary > tertiary* **(B)** *tertiary > secondary > primary*

(C) *secondary > tertiary > primary* **(D)** *They do not follow any order*

7. *The acidic character of* 1°, 2°, 3° alcohols and H_2O *is of the order*

(A) $H_2O > 1^\circ > 2^\circ > 3^\circ$ **(B)** $3^\circ > 2^\circ > 1^\circ > H_2O$

(C) $1^\circ > 2^\circ > 3^\circ > H_2O$ **(D)** *None of these*

8. *In the following reaction sequence :*

$$R-OH \xrightarrow{P + I_2} R-I \xrightarrow{AgNO_2} RNO_2 \xrightarrow{HNO_2} \text{no reaction}$$

The alcohol is a :

(A) *primary alcohol* **(B)** *secondary alcohol*

(C) *tertiary alcohol* **(D)** *phenol*

9. *Which of the following is the most reactive with HCl in the presence of $ZnCl_2$?*

(A) $(CH_3)_3COH$ **(B)** $(CH_3)_2CHCH_2CH_2OH$

(C) $(CH_3)_2CHOH$ **(D)** C_6H_5OH

10. *Methanol is manufactured by passing (under pressure) a mixture of water gas and excess hydrogen over heated :*

(A) *platinized asbestos* **(B)** *cobalt chloride*

(C) *Zn and Cr oxides* **(D)** *finely divided metal*

11. CH_3CHCH_3 (Br) $\xrightarrow[KOH]{\text{alc.}} A \xrightarrow[\text{peroxide}]{HBr} B \xrightarrow{CH_3ONa} C$

In the above reaction sequence, the final product is :

(A) *diethyl ether* **(B)** 1-*methoxypropane*

(C) *isopropyl alcohol* **(D)** *propylene glycol*

12. *The compound which reacts fastest with Lucas reagent at room temperature is :*

(A) 1-*Cyclopentylmethanol* **(B)** *butan-2-ol*

(C) 2-*methylpropan-1-ol* **(D)** 2-*methylpropan-2-ol*