Alcohols, Phenols and Ethers

Alcohols

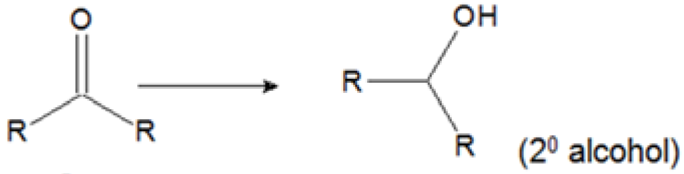
Preparation of Alcohols:

- **By hydrolysis of haloalkanes** : R-X + aq. KOH →ROH +KX
- **By reduction of Carbonyl compounds**

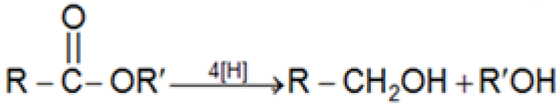
$4RCOOH + 3LiAlH_4 \rightarrow 4RCH_2OH$ (1°alcohol)

$CH_3(CH_2)_{14}COOC_2H_5 \xrightarrow{LiAlH_4} CH_3(CH_2)_{14}CH_2OH$

$R-CHO \longrightarrow RCH_2OH(1^{0}$ alcohol)



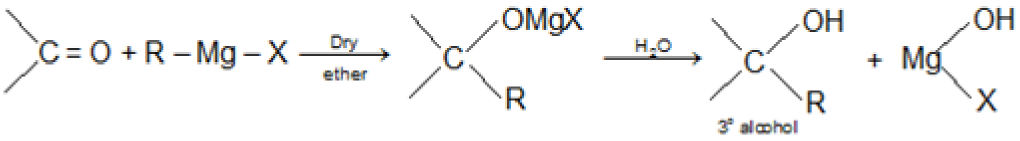
(2⁰ alcohol)



$R-\overset{\overset{O}{||}}{C}-OR' \xrightarrow{4[H]} R-CH_2OH + R'OH$

$CH_3CH_2COOCH_3 \xrightarrow{Cr_2O_4} CH_3CH_2CH_2OH + CH_3OH$

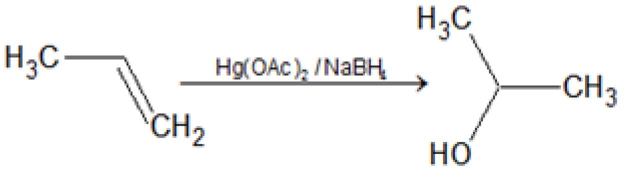
- **By the action of Grignard's Reagent on aldehydes, ketones and esters**



- **By Aliphatic Primary Amines:** $RCH_2NH_2 + HNO_2 \rightarrow RCH_2OH + N_2 + H_2O$
- **Hydration of alkenes:**

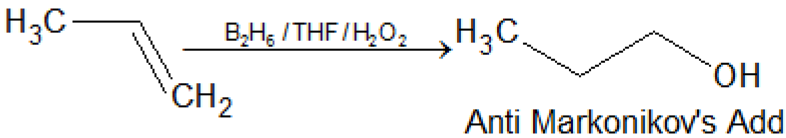
$$CH_2 = CHR + \underset{\text{Concentrated}}{H_2SO_4} \xrightarrow[H_2O]{\text{Boil}} CH_3 - CH(R)OH$$

- **Oxymercuration-demercuration:**



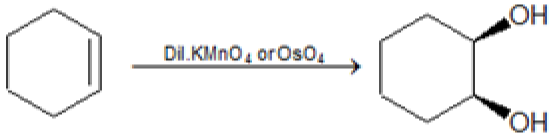
Markonikov's Addition

- **Hydroboration-oxidation:**

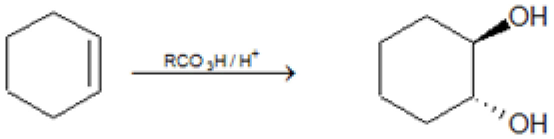


Anti Markonikov's Addition

- **Hydroxylation of alkenes:**



syn-Hydroxylation



anti-Hydroxylation

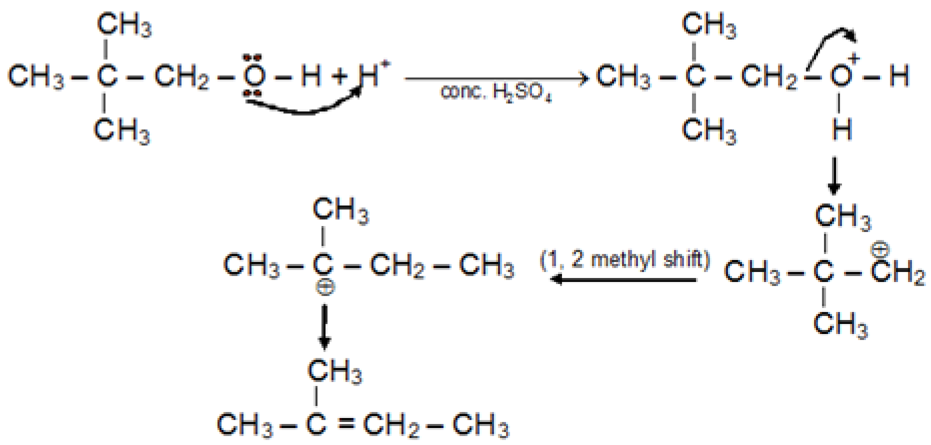
Physical Properties of Alcohol:

- Lower alcohols are liquid at room temperature while higher ones are solid.
- High boiling point due to presence of intermolecular hydrogen bonding. Order of Boiling Point: primary > secondary > tertiary
- Solubility in water decreases with increase in molecular mass due to decrease in extent of intermolecular hydrogen bonding.

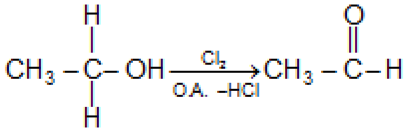
Chemical Properties of Alcohol:

- **Alcohol's reaction with metal:** $ROH + Na \rightarrow 2RO^{+}Na^{-} + H_2$
- **Formation of Halides:**
  - $3ROH + P+I2 \rightarrow 3RI + H_3PO_3$
  - $ROH + SOCl_2/PCl_3/PCl_5 \rightarrow RCl$
  - $ROH+HX \rightarrow RX$
  - $ROH+ NaBr,H_2SO_4 \rightarrow R\text{-}Br$
  - $ROH+ Zn+HCl \rightarrow R\text{-}Cl$
  - $R_2C\text{-}OH$ alcohol + $HCl \rightarrow R_2CCl$
- **Reaction with HNO_3:** $R\text{-}OH + HO\text{-}NO_2 \rightarrow R\text{-}O\text{-}NO_2$
- **Reaction with carboxylic acid (Esterification) :** $R\text{-}OH + R'\text{-}COOH + H^{+} \leftrightarrow R'\text{-}COOR$
- **Reaction with Grignard reagent:** $R'OH + RMgX \rightarrow RH + R'OMgX$
- **Reduction of alcohol :** $ROH + 2HI + \text{Red } P \rightarrow RH + I_2 + H_2O$
- **Dehydration of Alcohol:** Dehydration of alcohols takes place in acidic medium. Intra-molecular dehydration leads to the formation of alkene while inter molecular dehydration which forms ether. Ease of dehydration: 3° > 2° > 1

- **Satyzeff's Rule :** Elimination through b carbon containing minimum b hydrogen



- **Oxidation of Alcohol**:
  $RCH_2\text{-}OH + [O] \rightarrow RCHO \rightarrow RCOOH$
  $RCH_2\text{-}OH + [O] + PCC \rightarrow RCHO$
- **Haloform Reaction:** Compound containing CH_3CO- group (or compound on oxidation gives CH_3CO – group) which is attached with a C or H, in presence of halogen and mild alkali gives haloform.$CH_3\text{-}CH_2\text{-}COCH_2\text{-}CH_3$, $CH_3\text{-}CO\text{-}Cl$, CH_3COOH will not respond to haloform reaction wile CH_3CH_2OH will respond to haloform Reaction.



$$CH_3-CH_2-OH \xrightarrow[O.A.\ -HCl]{Cl_2} CH_3-\overset{O}{\overset{\|}{C}}-H$$

$$CH_3CH_2OH \xrightarrow{Cl_2+NaOH} CHCl_3$$

?

Test for Alcohols:

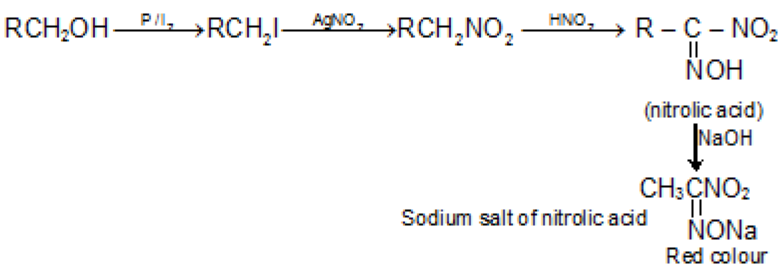
1. **Lucas Test:**

Alcohols + $ZnCl_2$ + HCl

- 1^o Alcohol: $RCH_2OH + ZnCl_2 + HCl \rightarrow$ No reaction at room temperature
- 2^0 Alcohol: $R_2CHOH + ZnCl_2 + HCl \rightarrow R_2CHCl$ White turbidity after 5-10 min.
- 3^0 Alcohol: $R_3CHOH + ZnCl_2 + HCl \rightarrow R_3CHCl$ white turbidity instantaneously.

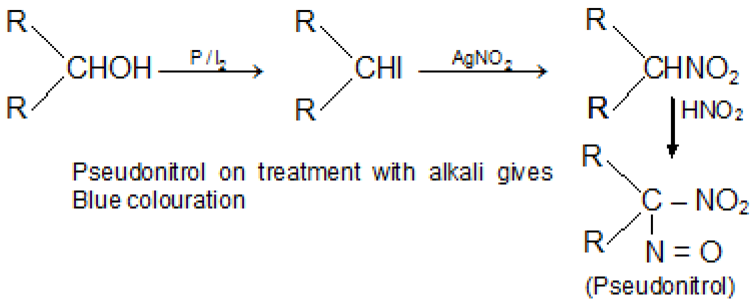
2. **Victor Meyer Test**

1° alcohol:



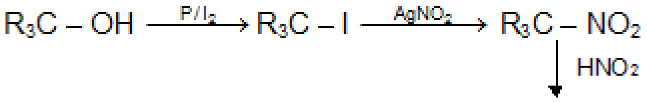
Nitrolic acid on treatment with alkali gives colouration

2° alcohol:



Pseudonitrol on treatment with alkali gives Blue colouration

3° alcohol:



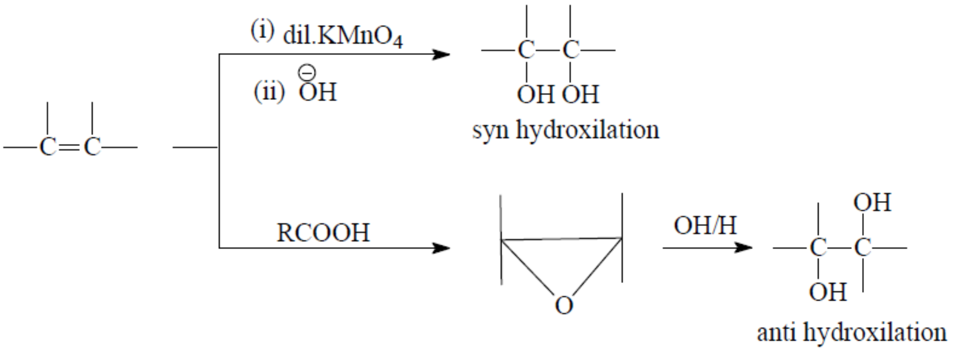
No reaction

(colour less)

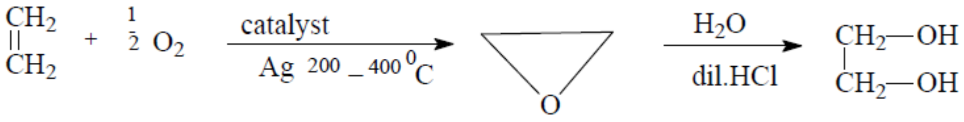
Dihydric alcohol

Dihydric alcohols are prepared by following different methods:

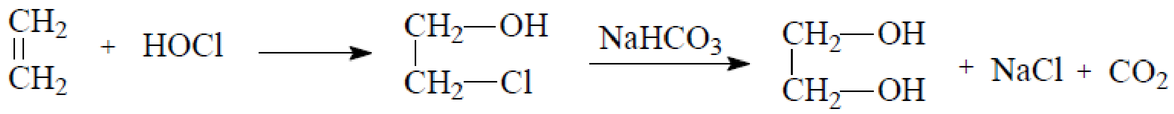
From ethylene: (a) through icy dilute alkaline solution of Bayer's reagent.



(b) With O2 in presence of Ag **:**

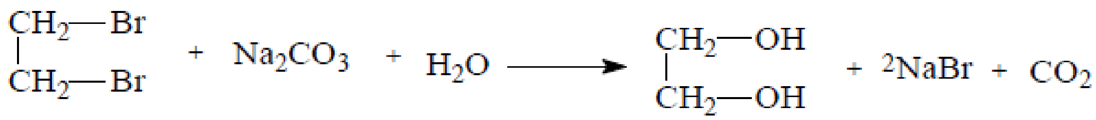


(c) With HOCl followed by hydrolysis:



$$\begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + HOCl \longrightarrow \begin{array}{l}CH_2-OH\\ |\\ CH_2-Cl\end{array} \xrightarrow{NaHCO_3} \begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + NaCl + CO_2$$

From 1, 2 dibromo ethane :



$$\begin{array}{l}CH_2-Br\\ |\\ CH_2-Br\end{array} + Na_2CO_3 + H_2O \longrightarrow \begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + {}^2NaBr + CO_2$$

Physical properties of dihydric alcohol

(i) It is a colourless, syrupy liquid and sweet in taste. Its boiling point is 197°*C*. melting point -11.50C

(ii) It is miscible in water and ethanol in all proportions but is insoluble in ether.

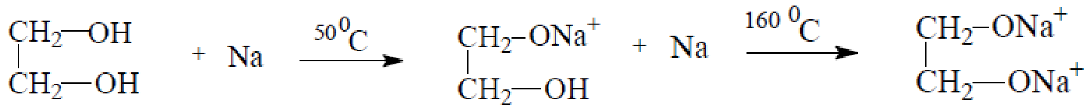
(iii) It is toxic as methanol when taken orally.

(iv) It is widely used as a solvent and as an antifreeze agent.

Chemical reactions of glycerol

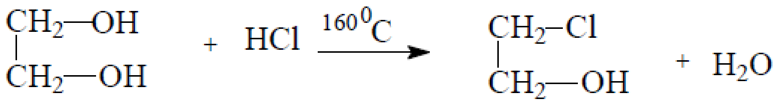
Glycerol molecule is made up of two 10 alcohol groups joined together its chemical reactions are, therefore twice over those of 1^0 alcohols

1. Action of Sodium: It reacts with Na at 50^0 c to form to form mono and dialkoxide at elevated temperature.



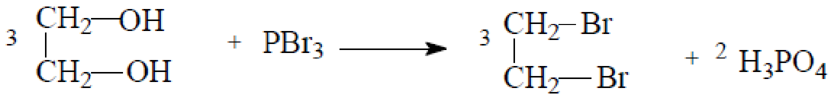
$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + Na \xrightarrow{50^0C} \begin{array}{l}CH_2-ONa^+\\ |\\ CH_2-OH\end{array} + Na \xrightarrow{160\ ^0C} \begin{array}{l}CH_2-ONa^+\\ |\\ CH_2-ONa^+\end{array}$$

2. Reaction with HC: Ethylene dichloride is formed in two successive steps at elevated Temperature



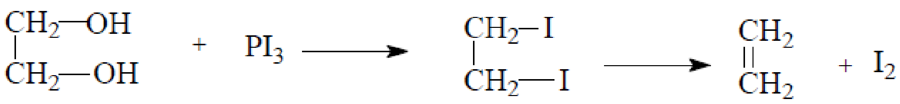
$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + HCl \xrightarrow{160^0C} \begin{array}{l}CH_2-Cl\\ |\\ CH_2-OH\end{array} + H_2O$$

3. Action with phosphorus halides : ethylene dihalides are formed as follow:



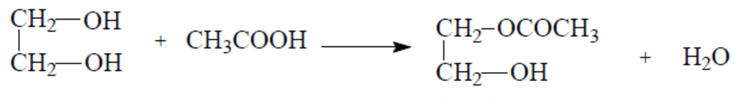
$$3\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + PBr_3 \longrightarrow 3\begin{array}{l}CH_2-Br\\ |\\ CH_2-Br\end{array} + {}^2\ H_3PO_4$$

PI3 produce ethylene diodide which is unstable and split into I2= and ethylene



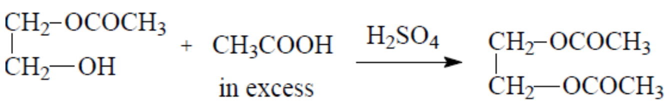
$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + PI_3 \longrightarrow \begin{array}{l}CH_2-I\\ |\\ CH_2-I\end{array} \longrightarrow \begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + I_2$$

4. Reaction with carboxylic acid: Gives diester depending upon the amount of glycol and acid taken:



$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} + CH_3COOH \longrightarrow \begin{array}{l}CH_2-OCOCH_3\\ |\\ CH_2-OH\end{array} + H_2O$$

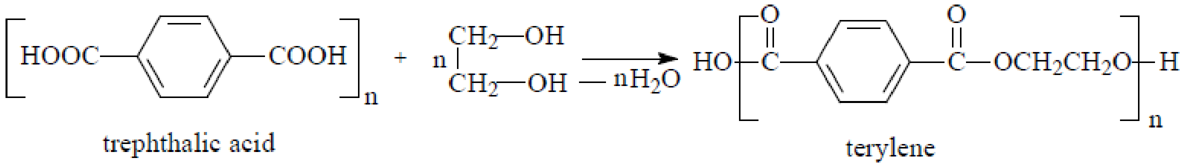
glycol monoacetate



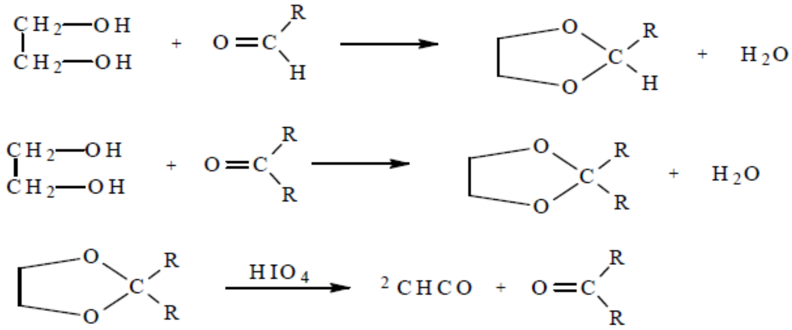
$$\begin{array}{l}CH_2-OCOCH_3\\ |\\ CH_2-OH\end{array} + \underset{\text{in excess}}{CH_3COOH} \xrightarrow{H_2SO_4} \begin{array}{l}CH_2-OCOCH_3\\ |\\ CH_2-OCOCH_3\end{array}$$

glycol diacetate

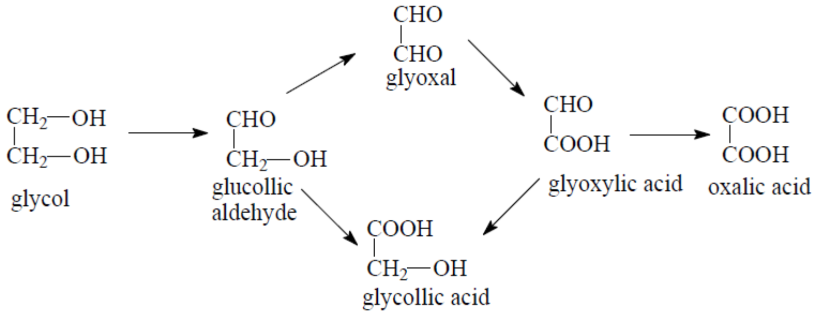
With dibasic acid it form polymer:



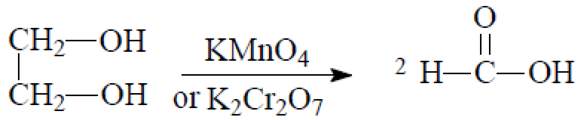
5. Reaction with aldehyde and ketones: Glycol reacts with aldehyde and ketones in presence of p- toluene sulphonic acid to give cyclic acetals/ketals which further may give ketone/aldehyde while treating with HIO4. This reaction thus can be useful to protect carbonyl group.



6. (i) The oxidation of ethylene glycol with HNO3 to yields a number of substance as

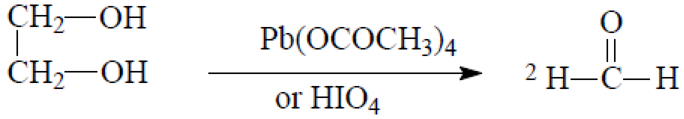


(ii) Oxidation with KMnO4 or K2Cr2O7 to form formic acid:



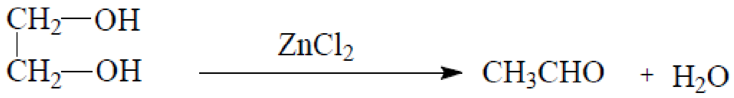
$$\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} \xrightarrow[\text{or } K_2Cr_2O_7]{KMnO_4} 2\ H-\overset{\overset{O}{||}}{C}-OH$$

(iii) Oxidation with Pb (OCOCH3)4 or HIO4 glycol gives formaldehyde.



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

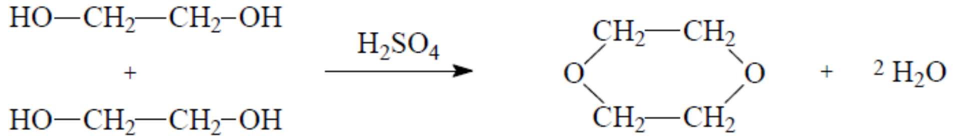
7. Dehydration: (i) Heating wih ZnCl2 glycol gives acetaldehyde



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

(ii) When heated alone at 5000C, it gives ethylene oxide.

(iii) Dioxane is obtained when glycol is heated with conc. H2SO4.

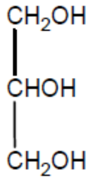


Uses of ethylene glycol:-

1. It is used as antifreeze substance which prevents the freezing of water in car radiators in cold countries.
2. Due it has a high viscosity, so it is used in the hydrolic break , printing ink ball, pen inks, organic solvents .
3. Used in the manufacture of Dacron, dioxane etc.
4. As a solvent and as a preservatives.
5. As a cooling agent in aeroplanes.
6. As an explosives in the form of dinitrate.
7. Large amounts of ethylene glycol are converted to polymers (such as polyethylene glycol) used in The manufacture of dacron fibers ,photographic films and cassette tapes.

TRIHYDRIC ALCOHOL

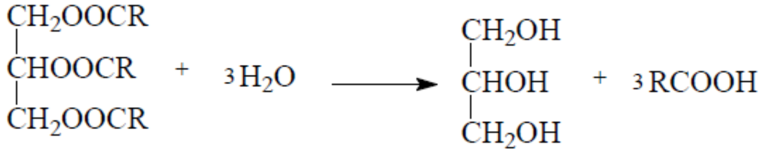
It is a triol. The introduction of third –OH group in diol molecule raises the b.p. about 1000C, increase viscosity and make the alcohol more sweet. Viz; glycerol



$$\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

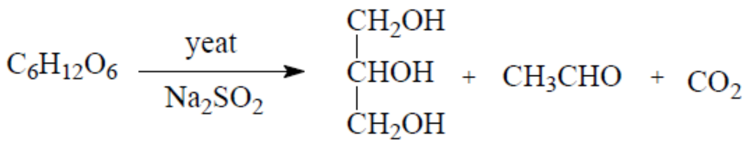
Glycerol can be synthesized by following different methods:

1. **From fats and oil:** On hydrolysis of fats and oils, glycerol and higher fatty acids are formed.



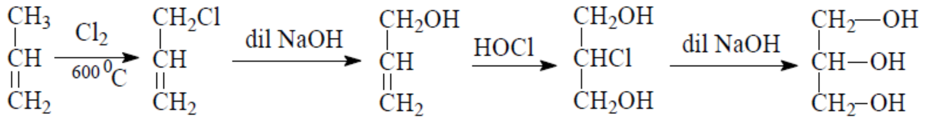
$$\begin{array}{l}CH_2OOCR\\ |\\ CHOOCR\\ |\\ CH_2OOCR\end{array} + 3H_2O \longrightarrow \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + 3RCOOH$$

2. **By fermentation of sugars:** Alcoholic fermentation of sugar in the presence of sodium sulphite gives good yield of glycerol.



$$C_6H_{12}O_6 \xrightarrow[Na_2SO_2]{yeat} \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + CH_3CHO + CO_2$$

3. **Synthesis (from propene):** Today much of glycerol is obtained from propene.



$$\begin{array}{l}CH_3\\ |\\ CH\\ ||\\ CH_2\end{array} \xrightarrow[600^0C]{Cl_2} \begin{array}{l}CH_2Cl\\ |\\ CH\\ ||\\ CH_2\end{array} \xrightarrow{dil\ NaOH} \begin{array}{l}CH_2OH\\ |\\ CH\\ ||\\ CH_2\end{array} \xrightarrow{HOCl} \begin{array}{l}CH_2OH\\ |\\ CHCl\\ |\\ CH_2OH\end{array} \xrightarrow{dil\ NaOH} \begin{array}{l}CH_2-OH\\ |\\ CH-OH\\ |\\ CH_2-OH\end{array}$$

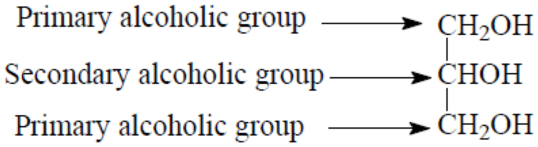
Physical properties: Glycerol is a colourless, odourless, viscous and hygroscopic liquid, sweet in taste and non-oxic in nature.

It is soluble in water and ethyl alcohol but insoluble in ether.

It has high boiling point, i.e., 290°C. The high viscosity and high boiling point of glycerol are due to association through hydrogen bonding purified in the lab by reduced pressure distillation or vacuum distillation.

Chemical reactions

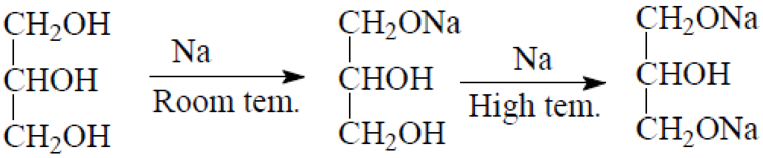
Glycerol molecule contains two 1^0 – OH groups and one 2^0 – OH group. Thus, it shows characteristics of both primary and secondary alcohols.



$$\begin{array}{l}\text{Primary alcoholic group}\longrightarrow CH_2OH\\ \qquad\qquad\qquad\qquad\qquad\quad |\\ \text{Secondary alcoholic group}\longrightarrow CHOH\\ \qquad\qquad\qquad\qquad\qquad\quad |\\ \text{Primary alcoholic group}\longrightarrow CH_2OH\end{array}$$

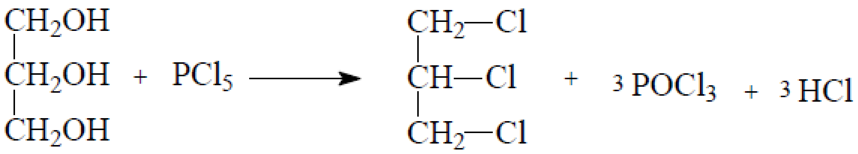
In general, 10 – OH groups are more reactive than 20 – OH group.

1. Reaction with sodium: Only primary alcoholic groups are attacked one by one and secondary alcoholic group is not attacked, Sodium forms monosodium glycerolate at room temperature and disodium glycerolate at higher temperature.



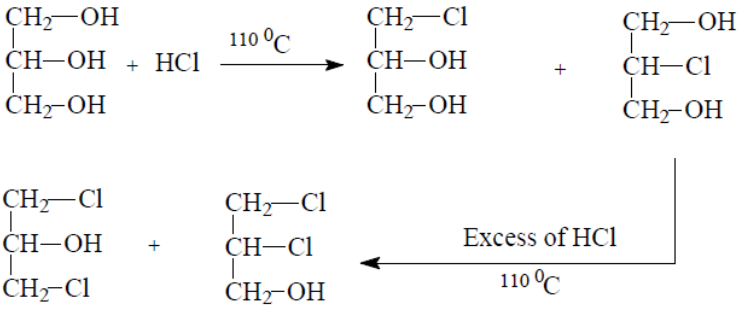
$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}\xrightarrow[\text{Room tem.}]{Na}\begin{array}{l}CH_2ONa\\|\\CHOH\\|\\CH_2OH\end{array}\xrightarrow[\text{High tem.}]{Na}\begin{array}{l}CH_2ONa\\|\\CHOH\\|\\CH_2ONa\end{array}$$

2. Reaction with PCI5**:** All three OH groups are replaced by Cl atoms.



$$\begin{array}{l}CH_2OH\\|\\CH_2OH\\|\\CH_2OH\end{array} + PCl_5 \longrightarrow \begin{array}{l}CH_2{-}Cl\\|\\CH{-}Cl\\|\\CH_2{-}Cl\end{array} + 3\,POCl_3 + 3\,HCl$$

3. Reaction with HCI or HBr: When HCI is passed into glycerol at 110°C, both , _ or _ glycerol monochlorohydrins are formed. If the HCI gas is passed for sufficient time, glycerol _, _' dichlorohydrin and glycerol, _,_- dichlorohydrin are formed.



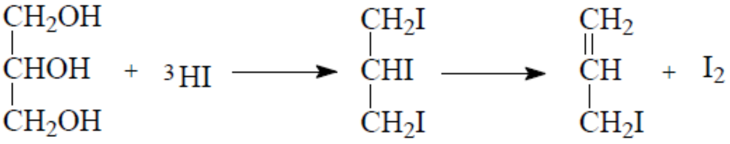
$$\begin{array}{l}CH_2{-}OH\\|\\CH{-}OH\\|\\CH_2{-}OH\end{array} + HCl \xrightarrow{110\,^0C} \begin{array}{l}CH_2{-}Cl\\|\\CH{-}OH\\|\\CH_2{-}OH\end{array} + \begin{array}{l}CH_2{-}OH\\|\\CH{-}Cl\\|\\CH_2{-}OH\end{array}$$

$$\xrightarrow[110\,^0C]{\text{Excess of HCl}} \begin{array}{l}CH_2{-}Cl\\|\\CH{-}OH\\|\\CH_2{-}Cl\end{array} + \begin{array}{l}CH_2{-}Cl\\|\\CH{-}Cl\\|\\CH_2{-}OH\end{array}$$

Same reactions occur with HBr.

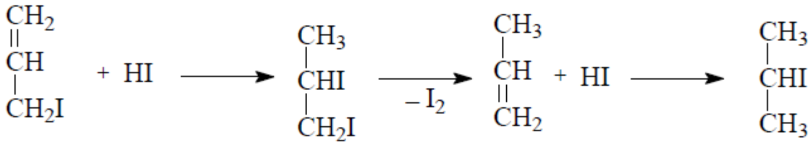
4. Reaction with HI: Glycerol reacts with HI in two ways:

(a) When glycerol is warmed with a small amount of hydrogen iodide, allyl iodide is formed. First tri iodide is formed but due to large size of iodine atom I2 comes out from product.

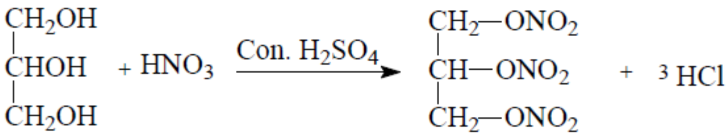


$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + 3\,HI \longrightarrow \begin{array}{l}CH_2I\\|\\CHI\\|\\CH_2I\end{array} \longrightarrow \begin{array}{l}CH_2\\||\\CH\\|\\CH_2I\end{array} + I_2$$

(b) When glycerol is heated with a large amount of HI, the allyl iodide first formed is reduced to propene, which in presence of excess of HI forms iso-propyl iodide.

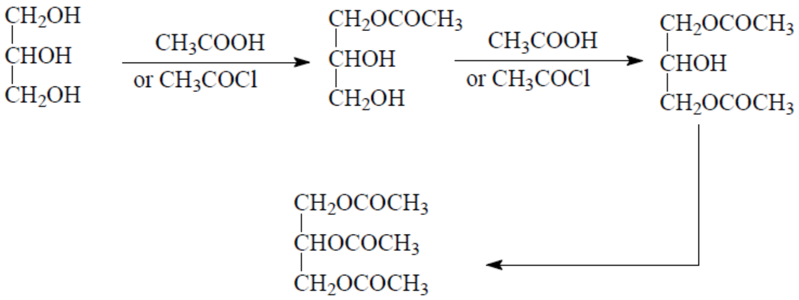


5. Reaction with HNO3: When one part of glycerol in a thin stream is added to three times conc. HNO3 and five parts of concentrated sulphuric acid, nitro-glycerine (glyceryl trinitrate) is formed.



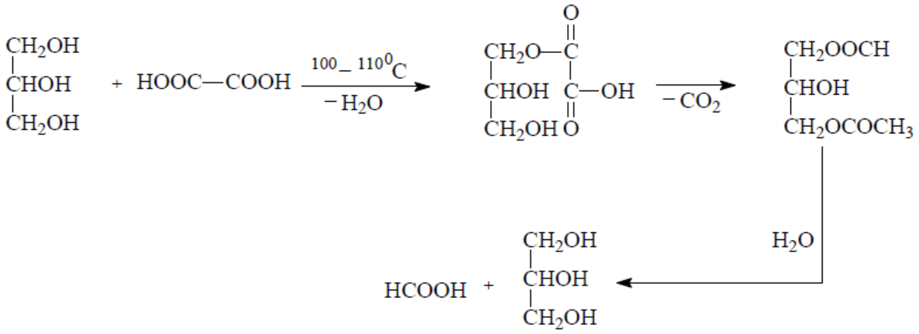
Glyceryl trinitrate is a yellow oily liquid. It is poisonous and causes headache. It explodes violently when heated rapidly or subjected to sudden shock. It becomes a safer explosive when absorbed on kieselguhr. In this form, it is known as **dynamite.** Dynamite was discovered by Alfred Nobel in 1867.

6. Reaction with acetic acid, acetic anhydride or acetyl chloride: Mono-, di- and triesters are formed.

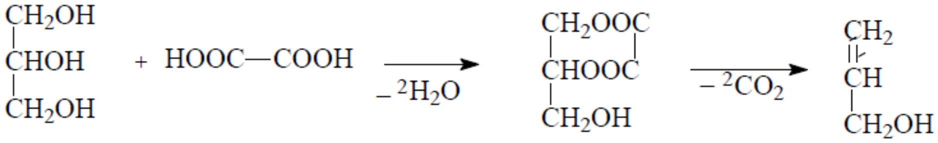


7. **Reaction with oxalic acid:** Different products are formed under different conditions.

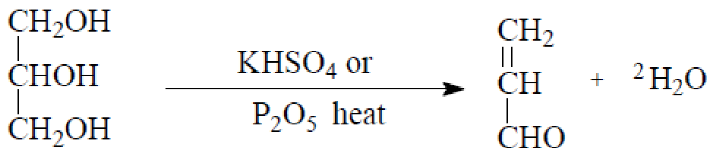
(a) At 1000C and with excess of oxalic acid, formic acid is formed



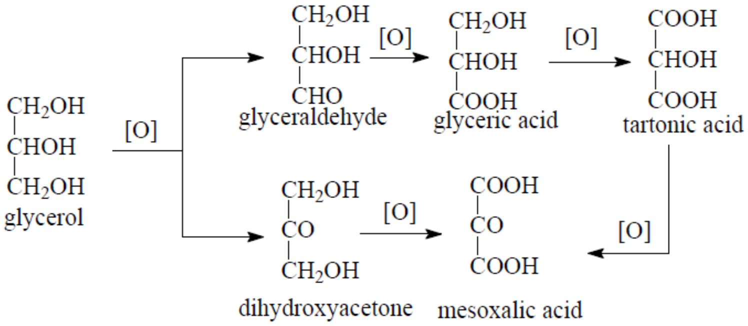
(b) At 2600C allyl alcohol is formed



8. Dehydration: Glycerol when heated alone or with dehydrating agents such as potassium hydrogen sulphate or phosphorus penta oxide or conc. sulphuric acid, acrolein or acrylaldehyde is formed which has a characteristic bad smell. This reaction can be used as a test of glycerol.



9. Oxidation: Glycerol gives different oxidation products depending on the nature of oxidizing agent. The following products may be obtained during oxidation of glycerol.



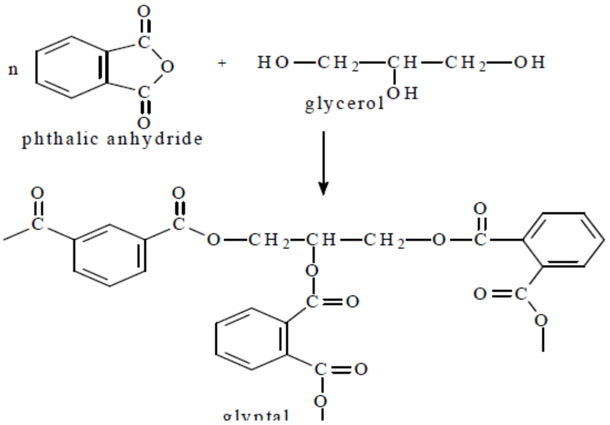
(a) Dilute HNO3 gives mainly glyceric acid.

(b) Conc. HNO3 oxidises glycerol into glyceric acid and tartronic acid.

(c) Bismuth nitrate gives mainly meso oxalic acid.

(d) Fenton’s reagent (H2O2 + FeSO4) or NaOBr or Br2- water in presence of Na2CO3 oxidises glycerol into a mixture of glyceraldehyde and dihydroxy acetone (or glycerose).

10. Formation of resin: 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.

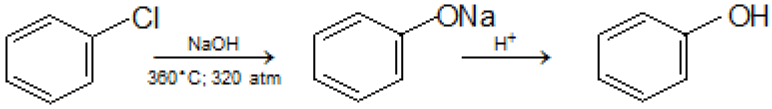


Uses: Glycerol is used: Glycerol is used as a sweetening agent in confectionery, beverages and medicines being non-toxic in nature. It is used as antifreeze in automobile radiators, in the preparation of good quality of soap, hand lotions, shaving creams, tooth pastes and cosmetics and as a lubricant in watches and preservative.

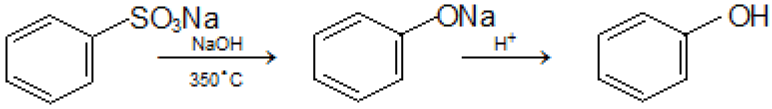
Phenols:

Preparation:

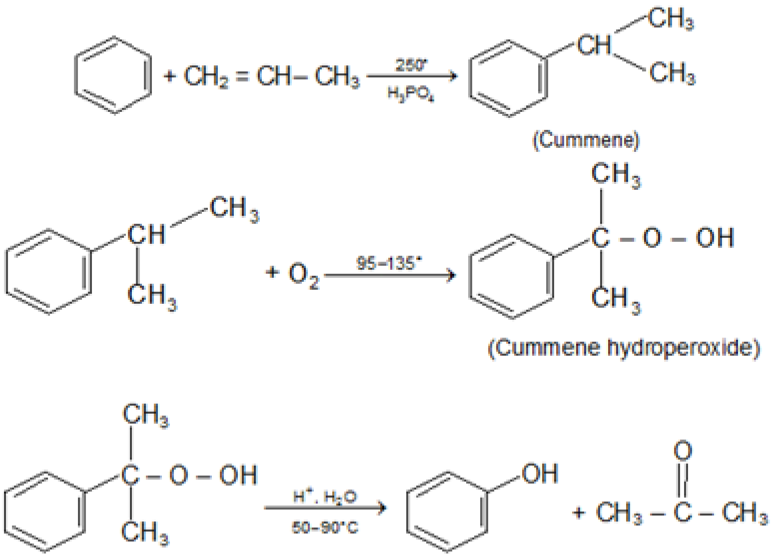
a. Hydrolysis of chlorobenzene: (Dow's process)



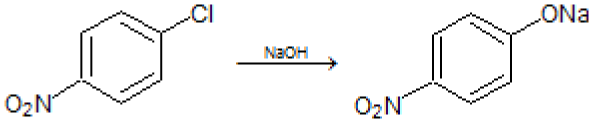
b. Alkali fusion of Sodium benzene sulfonate



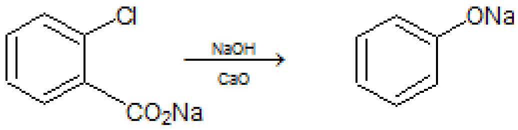
c. From Cummene Hydroperoxide



d. Aromatic Nucleophilic Substitution of Nitro Aryl Halides



e. Distillation of phenolic acids with soda-lime produces phenols, e.g. sodium salicylate gives phenol.



Physical Properties of Phenols

- Phenol is a colorless, toxic, corrosive, needle shaped solid.
- Phenol soon liquifies due to high hygroscopic nature.
- Phenol is less soluble in water, but readily soluble in organic solvents.
- Simplest phenols, because of hydrogen bonding have quite high boiling points.
- o-nitrophenol is, steam volatile and also is less soluble in water because of intramolecular hydrogen bonding

Chemical Properties of Phenols

a) Formation of Esters

Phenyl esters (RCOOAr) are not formed directly from RCOOH. Instead, acid chlorides or anhydrides are reacted with ArOH in the presence of strong base

$(CH_3CO)_2O + C_6H_5OH + NaOH \rightarrow CH_3COOC_6H_5 + CH_3COONa + H_2O$

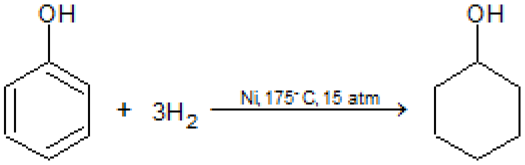
Phenyl acetate

$C_6H_5COCl + C_6H_5OH + NaOH \rightarrow C_6H_5COOC_6H_5 + Na^+Cl^- + H_2O$

Phenyl benzoate

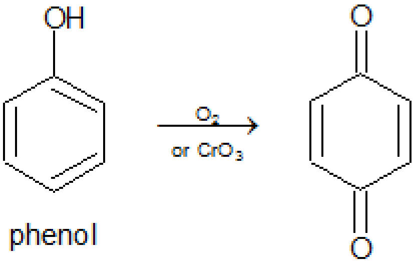
b) Displacement of OH group: $ArOH + Zn \xrightarrow{\Delta} ArH + ZnO$ (poor yields)

c) Hydrogenation



cyclohexanol

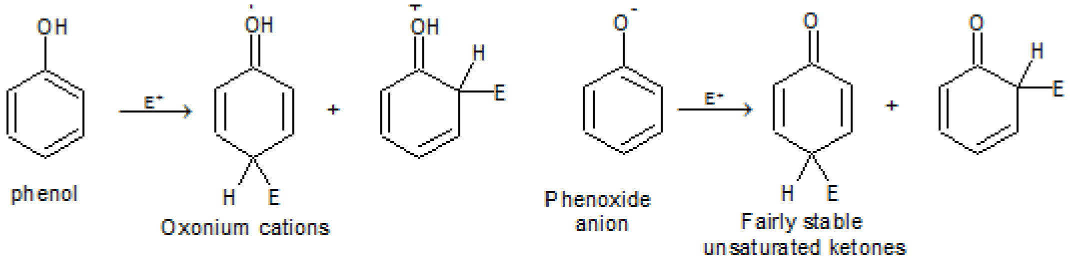
d) Oxidation to Quionones



phenol

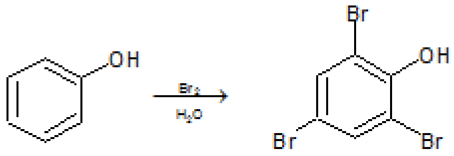
benzo-1,4-quinone

e) Electrophilic Substitution The —OH and even more so the —O(phenoxide) are strongly activating ortho ,para - directing

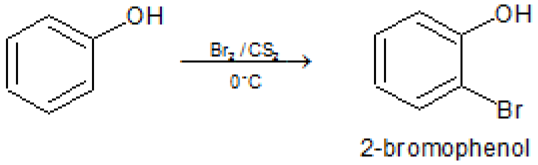


Special mild conditions are needed to achieve electrophilic monosubstituion in phenols because their high reactivity favors both polysubstitution and oxidation

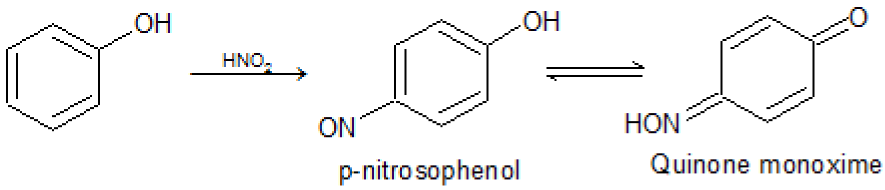
f) Halogenation



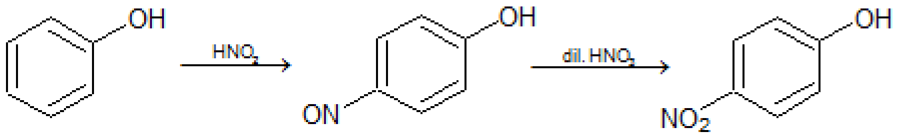
(goes via ArO; no monobromophenols)



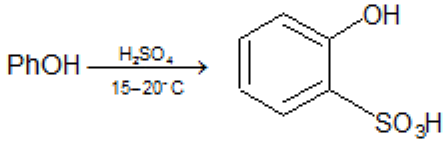
h) Nitrosation



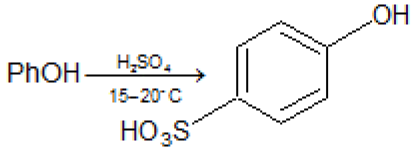
i) Nitration



j) Sulfonation



(rate-controlled)



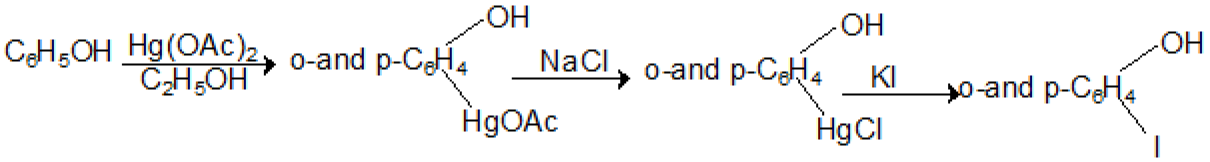
(eqbm-controlled)

k) Diazonium salt coupling to form azophenols

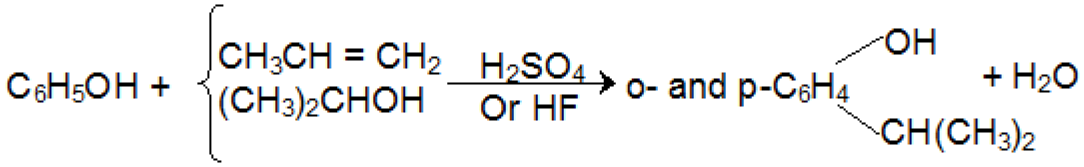
Coupling (G in ArG is an electron – releasing group)

$ArN_2^+ + C_6H_5G \longrightarrow$ p-G $— C_6H_4 — N = N —$ Ar (G = OH, NR_2, NHR, NH_2)

l) Mercuration



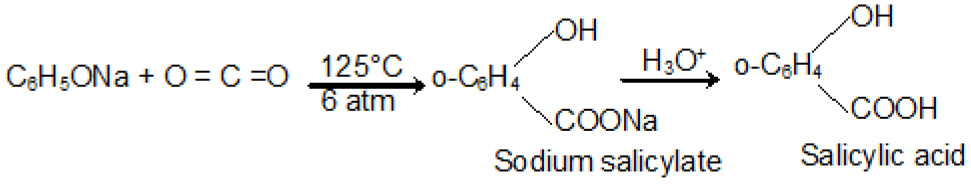
m) Ring alkylation



$$C_6H_5OH + \left\{\begin{matrix} CH_3CH=CH_2 \\ (CH_3)_2CHOH \end{matrix}\right. \xrightarrow[\text{Or HF}]{H_2SO_4} \text{o- and p-}C_6H_4\begin{matrix} OH \\ CH(CH_3)_2 \end{matrix} + H_2O$$

RX and $AlCl_3$ give poor yields because $AlCl_3$ coordinates with O.

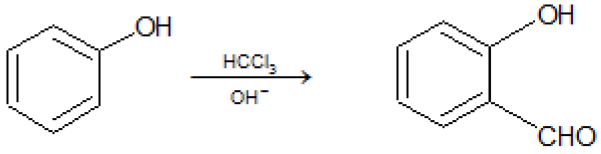
n) Kolbe synthesis of phenolic carboxylic acids



$$C_6H_5ONa + O=C=O \xrightarrow[\text{6 atm}]{125°C} \text{o-}C_6H_4\begin{matrix} OH \\ COONa \end{matrix} \xrightarrow{H_3O^+} \text{o-}C_6H_4\begin{matrix} OH \\ COOH \end{matrix}$$

Phenoxide carbanion adds at the electrophilic carbon of CO_2, para product is also possible.

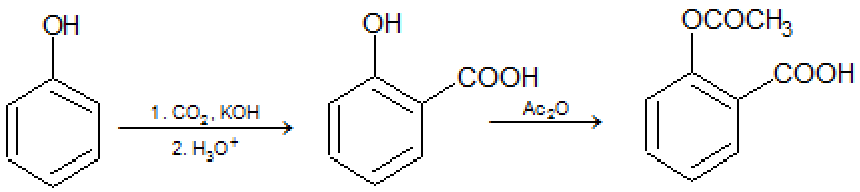
o) Reimer – Tiemann synthesis of phenolic aldehydes



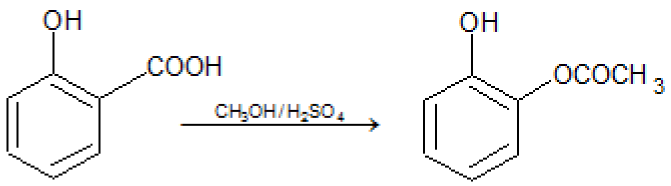
The electrophile is the dichlorocarbene, $:CCl_2$, formation of carbene is an example of α-elimination. $\bar{O}H + HCCl_3 \xrightarrow{-HCl} \ddot{C}Cl_2$

p) Synthesis of (a) aspirin (acetylsalicylic acid) (b) oil of wintergreen (methyl salicylate)

a)



b)

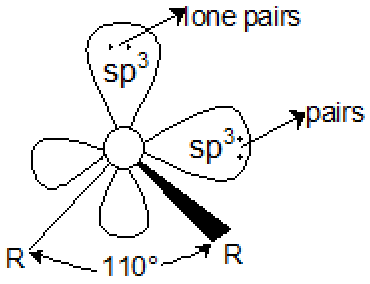


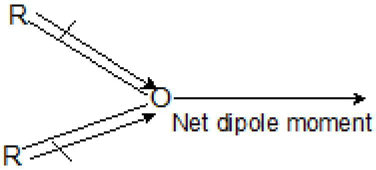
Ethers

Physical Properties of Ethers

- **Physical state, colour and odour:** Dimethyl ether and ethyl methyl ether is gas at ordinary temperature while the other lower homologues of ethers are colourless liquid with characteristic 'ether smell'.
- **Dipole nature:** Ethers have a tetrahedral geometry i.e., oxygen is sp^3 hybridized. The C—O—C angle in ethers is 110°. Because of the greater electronegativity of oxygen than

carbon, the C—O bonds are slightly polar and are inclined to each other at an angle of 110°, resulting in a net dipole moment.





Bond angle of ether is greater than that of tetrahedral bond angle of 109°28'.

- **Solubility and boiling point:** Due to the formation of less degree of hydrogen bonding, ethers have lower boiling point than their corresponding isomeric alcohols and are slightly soluble in water.

Preparation of Ethers:

a) From alcohols:

$$CH_3CH_2OH \xrightarrow[140^{o}C]{H_2SO_4} \underset{\text{Ether}}{CH_3CH_2-O-CH_2CH_3}$$

Order of dehydration of alcohol leading to formation of ethers: 1° > 2° > 3°

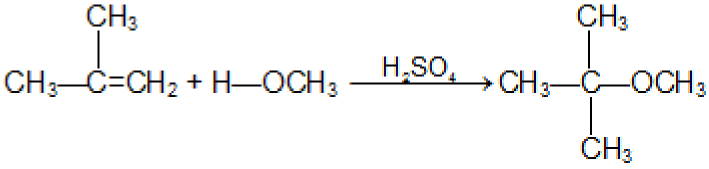
$$CH_3CH_2OH + CH_2N_2 \xrightarrow{HBF_4} CH_3CH_2—O—CH_3 + N_2$$

b) Williamson's synthesis:

R-X + Na^+ $^-$O-R' → R-O-R' + Na^+ X^-

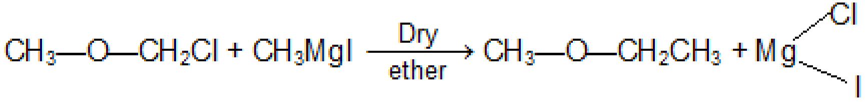
In case of tertiary substrate elimination occurs giving alkenes.

From alkenes:.



$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + H—OCH_3 \xrightarrow{H_2SO_4} CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OCH_3$$

From Grignard reagent: Treating a - halo ethers with suitable Grignard reagents.

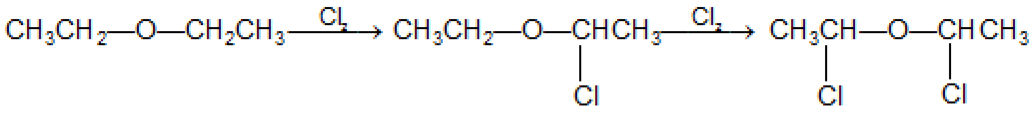


$$CH_3—O—CH_2Cl + CH_3MgI \xrightarrow[\text{ether}]{\text{Dry}} CH_3—O—CH_2CH_3 + Mg\begin{matrix}Cl\\ I\end{matrix}$$

On standing in contact with air, most aliphatic ethers are converted slowly into unstable peroxides. The presence of peroxides is indicated by formation of a red colour when the ether is shaken with an aqueous solution of ferrous ammonium sulfate and potassium thiocyanate

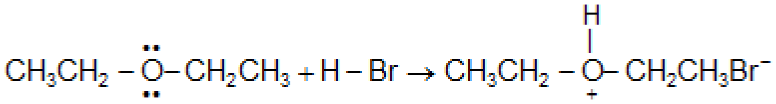
$$\text{Peroxide} + Fe^{2+} \rightarrow Fe^{3+} \xrightarrow{SCN^-} \underset{\text{Red}}{Fe(SCN)_n^{(3-n)-}} (n = 1 \text{ to } 6)$$

f) Halogenation of ethers:



$$CH_3CH_2{-}O{-}CH_2CH_3 \xrightarrow{Cl_2} CH_3CH_2{-}O{-}\underset{\underset{Cl}{|}}{C}HCH_3 \xrightarrow{Cl_2} CH_3\underset{\underset{Cl}{|}}{C}H{-}O{-}\underset{\underset{Cl}{|}}{C}HCH_3$$

g) Ethers as base:



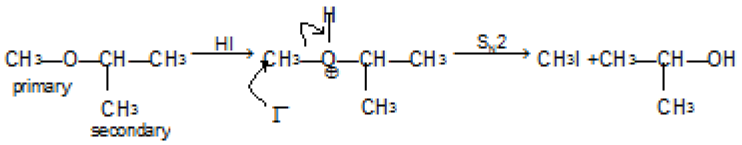
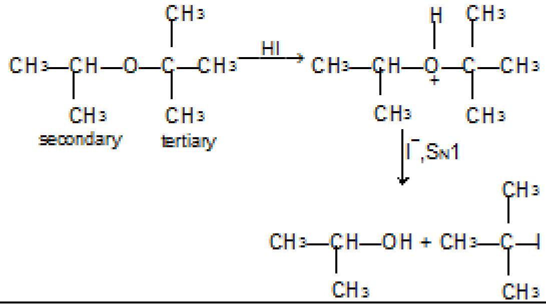
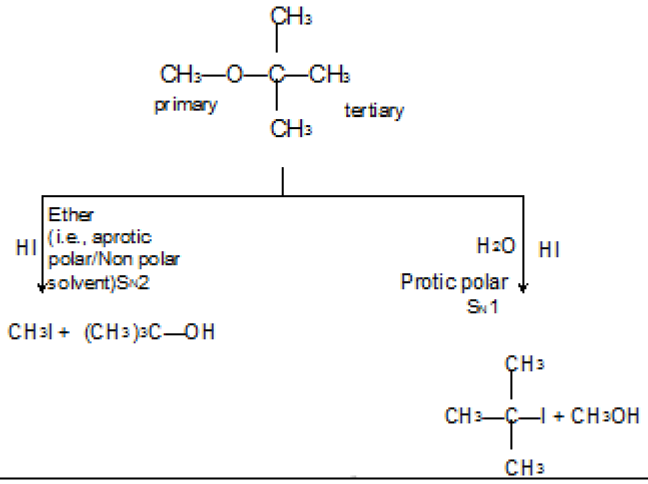
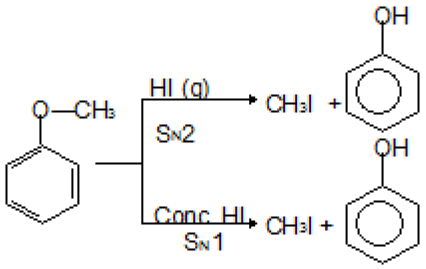
$$CH_3CH_2-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-CH_2CH_3 + H-Br \rightarrow CH_3CH_2-\overset{\overset{H}{|}}{\underset{+}{O}}-CH_2CH_3Br^-$$

h) Reaction With Cold conc. HI/HBr:

$$R{-}O{-}R' + \text{Cold HI} \longrightarrow R\text{-}OH + R'I\ (R' < R)$$

i) Hot conc. HI/HBr:

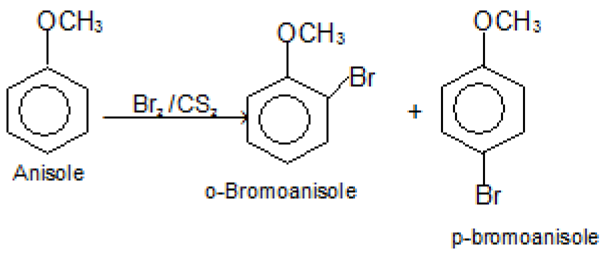
$$R{-}O{-}R' + \text{Hot HI} \longrightarrow RI + R'I + H_2O$$

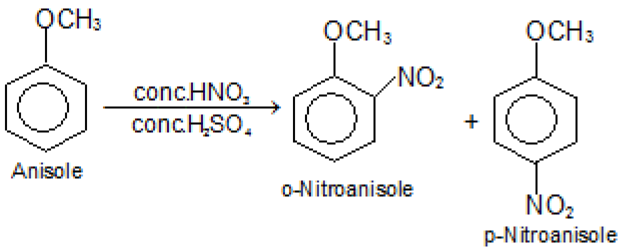
Case I:	
Case II:	
Case III:	
Case IV:	

i) Reaction with acid chlorides and anhydrides:

$$C_2H_5-O-C_2H_5 + CH_3COCl \xrightarrow[Anhy\ ZnCl_2]{\Delta} C_2H_5Cl + CH_3COOC_2H_5$$

j) Electrophilic substitution reactions

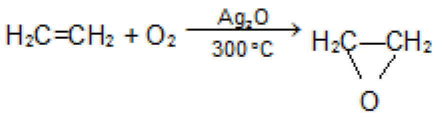




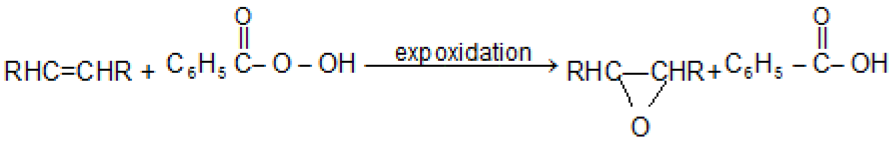
Epoxides or Oxiranes:

Preparation

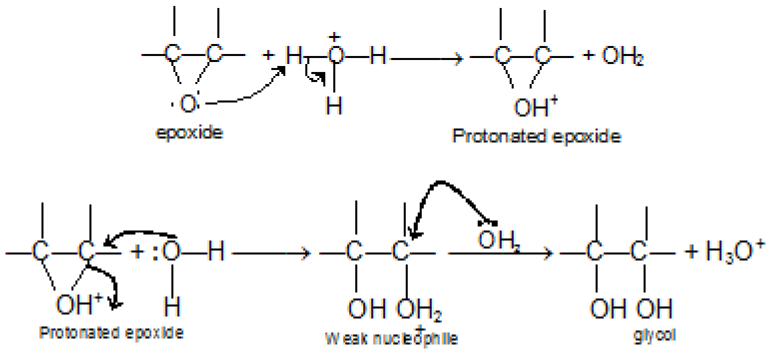
a) Oxidation of ethylene :



b) Expoxidation :



Acid catalysed ring opening



Base catalysed ring opening: