Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 1

Introduction of hydroxy compounds.

Hydroxy compounds are compounds in which the hydroxy group, $-OH$ is directly linked with the aliphatic or aromatic carbon. Hydroxy compounds can be classified into following three categories.

(1) **Aliphatic hydroxy compounds** (alcohols) **:** Alcohols are regarded as hydroxy derivatives of hydrocarbons.

$$\underset{\text{Hydrocarbon}}{R-H} \xrightarrow[+OH]{-H} \underset{\text{Alcohol}}{R-OH} \quad (R = \text{alkyl group})$$

They can be mono, di or tri-hydric alcohols depending upon whether they contain one, two or three hydroxy groups.

Monohydric alcohols	***Dihydric alcohol***	***Trihydric alcohol***	***Polyhydric alcohol***
CH_3OH Methanol C_2H_5OH Ethanol	CH_2OH $\vert$ CH_2OH Glycol	CH_2OH $\vert$ $CHOH$ $\vert$ CH_2OH Glycerol	CH_2OH $\vert$ $(CHOH)_4$ $\vert$ CH_2OH sorbital or Mannitol

(2) **Aromatic hydroxy compounds** (Phenols) **:** Phenols are regarded as hydroxy derivatives of aromatic hydrocarbons (arenes).

$$\underset{\text{Arene}}{Ar-H} \xrightarrow[+OH]{-H} \underset{\text{Phenol}}{Ar-OH}$$

They can be mono, di or tri-hydric phenols depending upon whether they contain one, two or three hydroxy groups.

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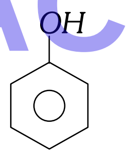
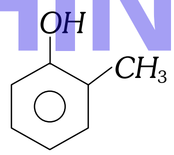
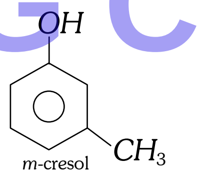
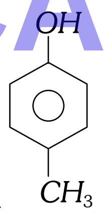
Monohydric phenols :

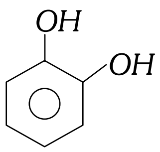

Phenol

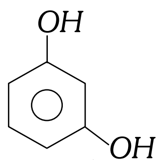

o-cresol

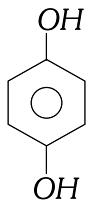

m-cresol


p-cresol

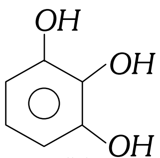
Dihydric phenols :

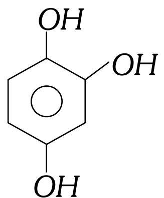

Catechol

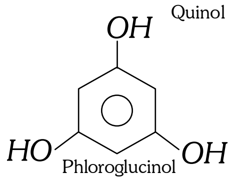

Resorcinol


Quinol

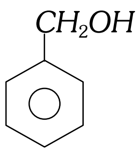
Trihydric phenols :

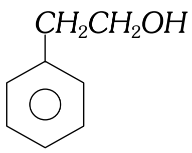

Pyrogallol


Hydroxy quinol


Phloroglucinol

(3) **Aromatic alcohols :** Compounds in which the hydroxy group is present in the side chain are termed aromatic alcohols.


Benzyl alcohol


2 phenyl ethanol

Monohydric alcohols.

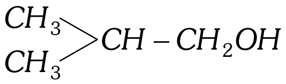
Alcohols containing one hydroxyl group are known as monohydric alcohols. These alcohols may be saturated or unsaturated depending on the nature of hydrocarbon groups. Saturated monohydric alcohols form a homologous series of the general formula $C_nH_{2n+1}OH$. They are also represented as $R-OH$ where R represents an alkyl group. They may be regarded as derivatives of water, *i.e.*, one hydrogen atom of the water molecule is replaced by an alkyl group.

$$\underset{\text{Water}}{HOH}\xrightarrow[+R]{-H}\underset{\text{Alcohol}}{R-OH}$$

(1) Classification : Monohydric alcohols are subdivided into three classes

(i) ***Primary alcohols*** **:** In these alcohols, the hydroxyl group is attached with primary (1^o) carbon atom. They possess a characteristic group $-CH_2OH$ and their general formula is RCH_2OH. R may be H in the first member and alkyl group in the rest of the members.

Examples : $\underset{\text{Methyl alcohol}}{HCH_2OH}$; $\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$; $\underset{n\text{-propyl alcohol}}{CH_3CH_2CH_2OH}$;

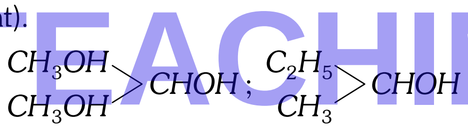


$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-CH_2OH$$

isobutyl alcohol

(ii) ***Secondary alcohols*** **:** In these monohydric alcohols, the hydroxyl group is attached with secondary (2°) carbon atom. They possess a characteristic group $>CHOH$ and the general formula $\begin{matrix}R\\R'\end{matrix}\!\!>CHOH$ (R and R' may be same or different).

Example :

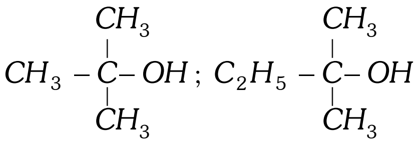


$$\begin{matrix}CH_3OH\\CH_3OH\end{matrix}\!\!>CHOH\ ;\quad \begin{matrix}C_2H_5\\CH_3\end{matrix}\!\!>CHOH$$

Isopropyl alcohol sec. butyl alcohol

(iii) ***Tertiary alcohols*** **:** In these monohydric alcohols, the hydroxyl group is attached with tertiary (3°) carbon atom. They contain a characteristic group $\gt COH$ and have the general formula $\begin{matrix}R''\\R'\\R\end{matrix}\!\!>OH$ (R, R' and R'' may be same or different).

Examples :



$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-OH\ ;\quad C_2H_5-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-OH$$

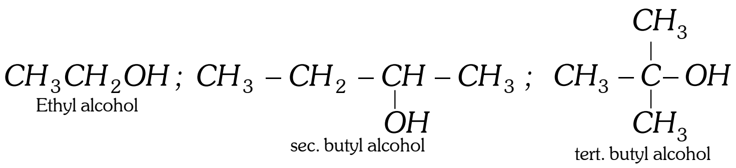
tert. Butyl alcohol tert. Amyl alcohol

(2) Nomenclature

(i) ***Common system*** **:** Named as alkyl alcohol.

Note : ✹ *In higher members, it is always indicated whether the – OH group is attached to primary, secondary and tertiary carbon. By prefixing n for primary sec. for secondary and tert. for tertiary.*

Example :



$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}\ ;\quad CH_3-CH_2-\underset{\underset{\large OH}{|}}{CH}-CH_3\ ;\quad CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-OH$$

sec. butyl alcohol tert. butyl alcohol

(ii) ***Carbinol system*** **:** CH_3OH is called carbinol. All other members are considered its alkyl derivatives.

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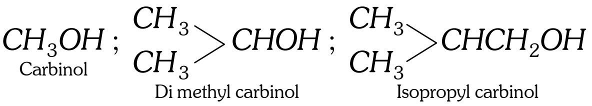
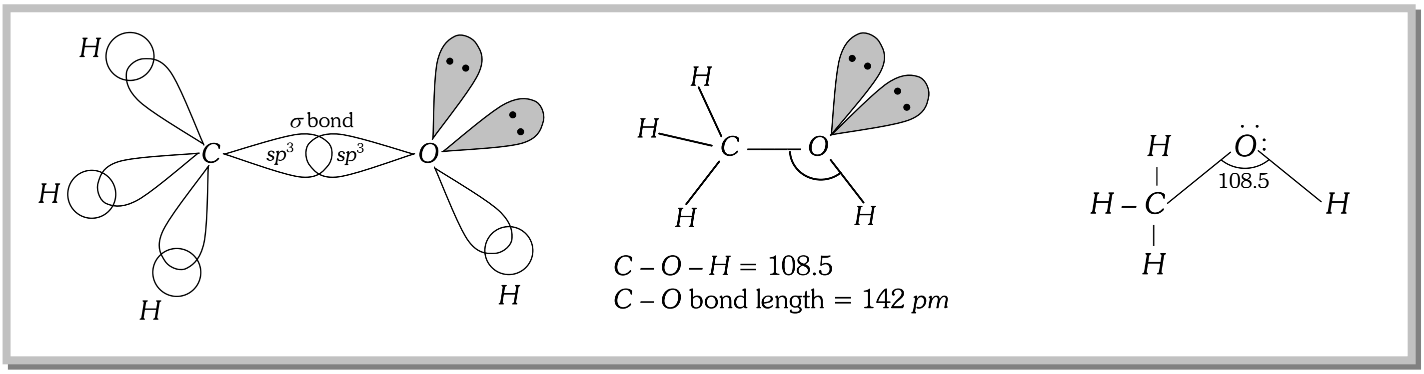
Example :


$\underset{\text{Carbinol}}{CH_3OH}$; $\underset{\text{Di methyl carbinol}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH}$; $\underset{\text{Isopropyl carbinol}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHCH_2OH}$

(iii) ***IUPAC system*** **:** Named as alkanol.

Example : $\underset{\text{Methanol}}{CH_3OH}$; $\underset{\text{Propanol-1}}{CH_3CH_2CH_2OH}$; $\underset{\text{Butanol-1}}{CH_3CH_2CH_2CH_2OH}$

(3) **Structure :** Oxygen of $-OH$ group is bonded to sp^3 hybrid carbon by a sigma bond.



$C-O-H = 108.5$

$C-O$ bond length $= 142\ pm$

(4) Isomerism

(i) ***Chain isomerism*** **:**

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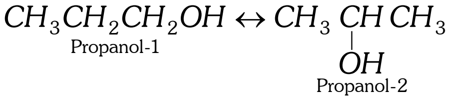
$\underset{\text{Butanol-1}}{CH_3CH_2CH_2CH_2OH} \leftrightarrow \underset{\text{2 Methyl propanol-1}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2OH}$

(ii) ***Positional isomerism*** **:**


$\underset{\text{Propanol-1}}{CH_3CH_2CH_2OH} \leftrightarrow \underset{\text{Propanol-2}}{CH_3\underset{\underset{\displaystyle OH}{|}}{CH}CH_3}$

(iii) ***Functional isomerism*** **:** $\underset{\text{Ethanol}}{CH_3CH_2OH} \leftrightarrow \underset{\text{Methoxy methane}}{CH_3OCH_3}$

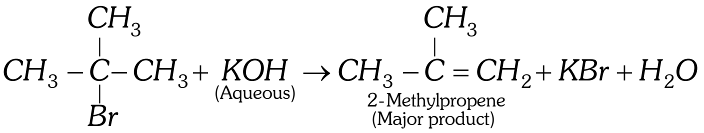
(5) General methods of preparation of monohydric alcohols

(i) ***From alkyl halide*** **:** $\underset{\text{Bromoethane}}{C_2H_5Br} + \underset{\text{(Aqueous)}}{KOH} \rightarrow \underset{\text{Ethanol}}{C_2H_5OH} + KBr$; $\underset{\text{Bromoethane}}{C_2H_5Br} + \underset{\text{Moist silver oxide}}{AgOH} \rightarrow \underset{\text{Ethanol}}{C_2H_5OH} + AgBr$

Note : ✹ *1° alkyl halide gives good yield of alcohols.*

✹ *2° alkyl halide gives mixture of alcohol and alkene.*

✹ *3° alkyl halide gives alkenes due to dehydrohalogenation.*



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_3 + \underset{\text{(Aqueous)}}{KOH} \rightarrow \underset{\substack{\text{2-Methylpropene}\\\text{(Major product)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2} + KBr + H_2O$$

✹ *Oxidation number of carbon in different organic compounds are given below in increasing order,*

Alkane, alkene, alkyne, alkyl halide, alcohol, carbonyl compounds, acids and acid derivatives

$\xrightarrow{\hspace{12cm}}$

Oxidation number of carbon in increasing order

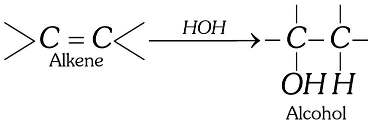
✹ *Alkanes and alkenes can be converted into alcohols by oxidation method while carbonyl compounds, acid and their derivatives can be converted into alcohol by reduction.*

✹ *Oxidation no. of carbon in RX and ROH is same hence RX converts into R–OH by displacement reaction.*

(ii) **From alkenes**

(a) *Hydration*

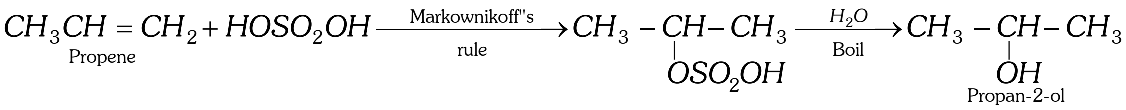
Direct process :



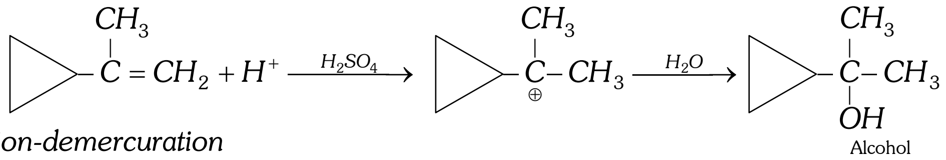
$$\underset{\text{Alkene}}{>C=C<} \xrightarrow{HOH} \underset{\text{Alcohol}}{\underset{OH\quad H}{-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-}}$$

Indirect process : $\underset{\text{Ethene}}{CH_2=CH_2} + \underset{\text{Sulphuric acid}}{HOSO_2OH} \to \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2OSO_2OH} \xrightarrow[\text{Boil}]{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH} + H_2SO_4$

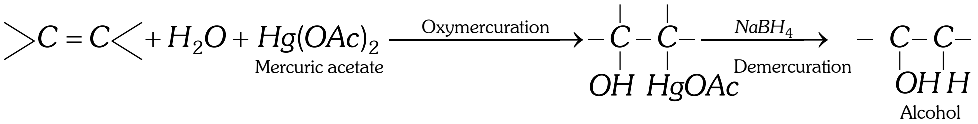
In case of unsymmetrical alkenes



$$\underset{\text{Propene}}{CH_3CH=CH_2} + HOSO_2OH \xrightarrow[\text{rule}]{\text{Markownikoff"s}} CH_3-\underset{OSO_2OH}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{Boil}]{H_2O} \underset{\text{Propan-2-ol}}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_3}$$



(b) *Oxymercuration-demercuration*



$$>C=C< + H_2O + \underset{\text{Mercuric acetate}}{Hg(OAc)_2} \xrightarrow{\text{Oxymercuration}} \underset{OH\quad HgOAc}{-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-} \xrightarrow[\text{Demercuration}]{NaBH_4} \underset{\text{Alcohol}}{\underset{OH\quad H}{-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-}}$$

This reaction is very fast and produces the alcohol in high yield. The alcohol obtained corresponds to Markownikoff's addition of water to alkene.

(c) *Hydroboration oxidation* (HBO) **:** (Antimarkownikoff's orientation)

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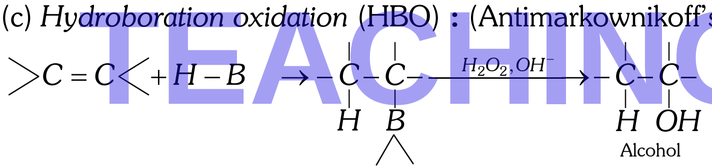
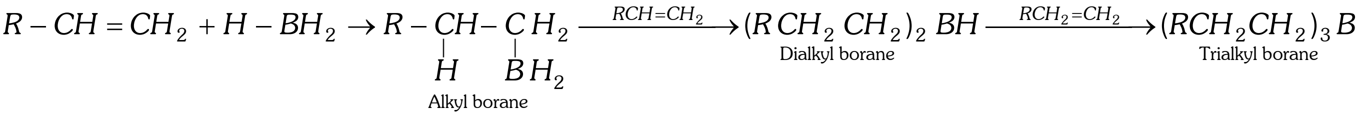


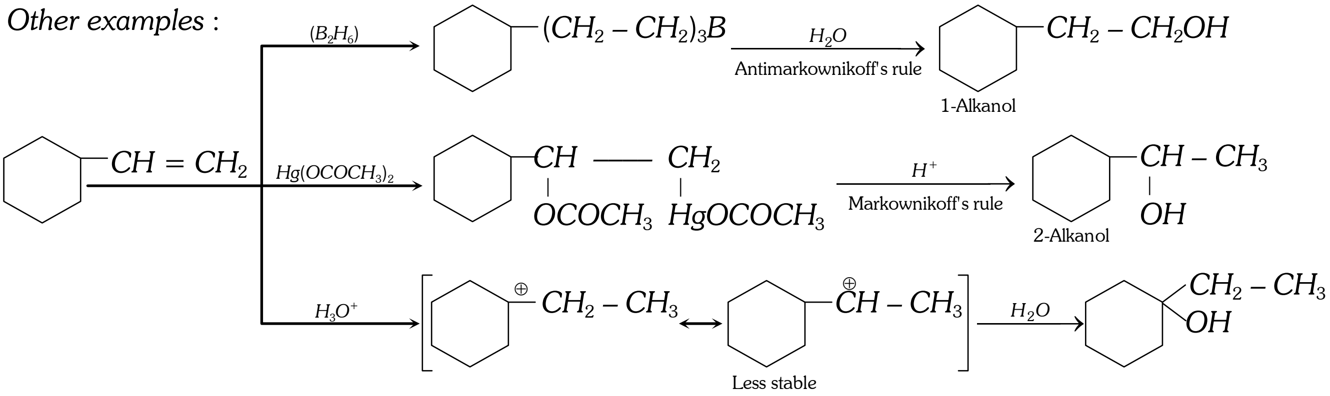
$$>C=C< + H-B \to \underset{H\quad B}{-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-} \xrightarrow{H_2O_2,OH^-} \underset{\text{Alcohol}}{\underset{H\quad OH}{-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-}}$$

Diborane is an electron defficient molecule. It acts as an electrophile reacting with alkenes to form alkyl boranes R_3B.



$$R-CH=CH_2+H-BH_2 \to \underset{\text{Alkyl borane}}{R-\underset{H}{\underset{|}{CH}}-\underset{BH_2}{\underset{|}{CH_2}}} \xrightarrow{RCH=CH_2} \underset{\text{Dialkyl borane}}{(RCH_2CH_2)_2BH} \xrightarrow{RCH_2=CH_2} \underset{\text{Trialkyl borane}}{(RCH_2CH_2)_3B}$$

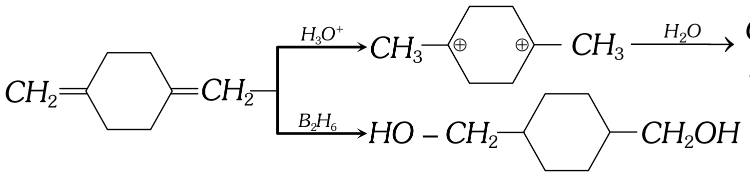
Other examples :



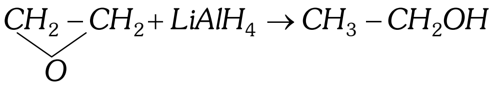
Note : ✹ *Carbocation are not the intermediate in HBO hence no rearrangement take place.*

(iii) ***By reduction of carbonyl compounds*** **:** Bouveault Blanc

$$\underset{\text{Aldehyde}}{RCHO} + H_2 \xrightarrow[LiAlH_4]{Pd} \underset{\text{Primary alcohol}}{RCH_2OH}; \qquad \underset{\text{Ketone}}{RCOR'} + H_2 \xrightarrow[\text{or } Ni/Pt]{NaBH_4} \underset{\text{Secondary alcohol}}{R-\underset{\underset{OH}{|}}{CH}-R'}$$

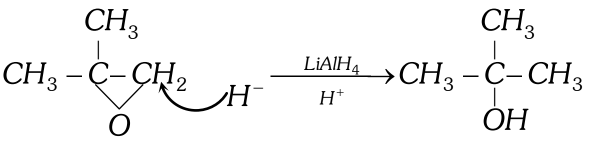


$LiAlH_4$ also reduces epoxides into alcohol :



$$\underset{\diagdown\,O\,\diagup}{CH_2-CH_2} + LiAlH_4 \rightarrow CH_3-CH_2OH$$

Hydride selectively attacks the less alkylated carbon of the epoxide.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\diagdown\,O\,\diagup}{C-CH_2}}\quad H^- \xrightarrow[H^+]{LiAlH_4} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$$

(iv) ***By reduction of carboxylic acids and their derivatives***

$$\underset{\text{Carboxylic acid}}{R-COOH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} \underset{\text{primary alcohol}}{RCH_2OH}; \quad \underset{\text{Carboxylic acid}}{RCOOH} \rightarrow \underset{\text{Ester}}{RCOOR'} \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

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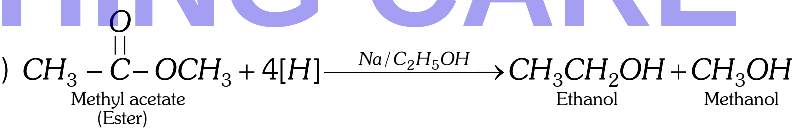
Esters are also reduced to alcohols

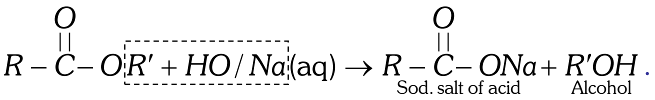


$$\text{(Bouveault Blanc reaction)}\ \underset{\substack{\text{Methyl acetate}\\ \text{(Ester)}}}{CH_3-\overset{\overset{O}{||}}{C}-OCH_3} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Methanol}}{CH_3OH}$$

Note : ✹ *Reduction with aluminium isopropoxide is known as Meerwein-Ponndorff verley reduction (MPV) reduction.*

$$Me_2C=O + \underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \xrightarrow{Al(OCHMe_2)} Me_2CHOH + \begin{matrix}CH_3\\ CH_3\end{matrix} \quad C=O$$

(v) ***By hydrolysis of ester :***



$$R-\overset{\overset{O}{||}}{C}-O\boxed{R' + HO/Na}(aq) \rightarrow \underset{\text{Sod. salt of acid}}{R-\overset{\overset{O}{||}}{C}-ONa} + \underset{\text{Alcohol}}{R'OH}.$$

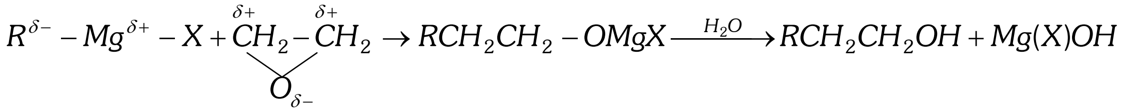
(vi) ***From primary amines :*** $\underset{\text{Aminoethane}}{CH_3CH_2NH_2} + HONO \xrightarrow{NaNO_2/HCl} \underset{\text{Ethanol}}{CH_3CH_2OH} + N_2 + H_2O$

Note : ✹ *It is not a good method of preparation of alcohols because number of by product are formed like alkyl chloride alkenes and ethers.*

(vii) ***From Grignard reagent***

(a) *With oxygen* : $2R-Mg-X+O_2 \xrightarrow[Al_2O_3]{\Delta} 2R-O-Mg-X \xrightarrow{2HOH} 2ROH + 2Mg(X)OH$

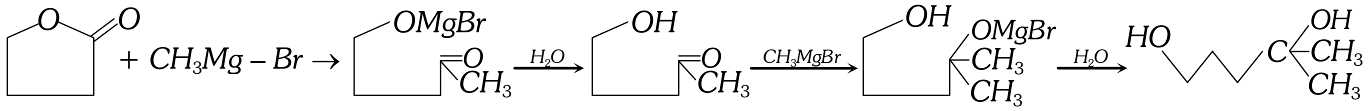
(b) *With ethylene oxide*

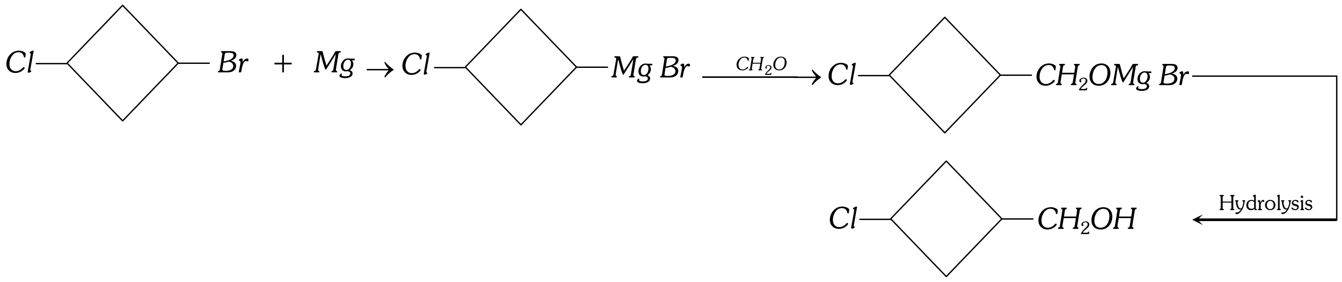


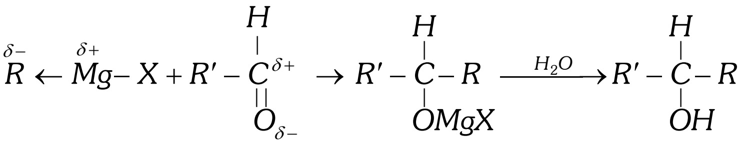
$$R^{\delta-}-Mg^{\delta+}-X+\underset{\underset{O_{\delta-}}{\diagdown\diagup}}{\overset{\delta+}{CH_2}-\overset{\delta+}{CH_2}} \rightarrow RCH_2CH_2-OMgX \xrightarrow{H_2O} RCH_2CH_2OH+Mg(X)OH$$

Other examples

With cyclic ester





(c) *With carbonyl compounds* **:** 

$$\overset{\delta-}{R}\leftarrow\overset{\delta+}{Mg}-X+R'-\overset{\overset{H}{|}}{\underset{\underset{O_{\delta-}}{||}}{C^{\delta+}}} \rightarrow R'-\overset{\overset{H}{|}}{\underset{\underset{OMgX}{|}}{C}}-R \xrightarrow{H_2O} R'-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-R$$

Note :
- *If R′ = H, product will be 1°alcohol.*
- *If R′ = R, product will be 2°alcohol.*
- *If carbonyl compound is ketone, product will be 3° alcohol.*
- *It is the best method for preparation of alcohol because we can prepare every type of alcohols.*

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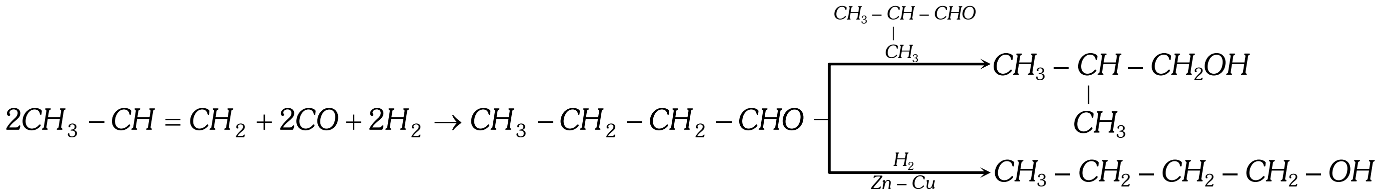
(viii) ***The oxo process*** **:** It is also called carbonylation or hydroformylation reaction. A mixture of alkene carbon monoxides and hydrogen. Under pressure and elevated temperature in the presence of catalyst forms aldehyde.

Catalyst is cobalt carbonyl hydride $[CoH(CO)_4]$ product is a mixture of isomeric straight chain (major) and branched chain (minor) aldehydes. Aldehydes are reduced catalytically to the corresponding alcohols.



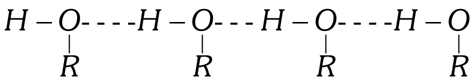
$$2CH_3-CH=CH_2+2CO+2H_2 \rightarrow CH_3-CH_2-CH_2-CHO - \begin{cases} \xrightarrow{\underset{CH_3}{\overset{|}{CH_3-CH-CHO}}} \underset{\underset{CH_3}{|}}{CH_3-CH-CH_2OH} \\ \xrightarrow[Zn-Cu]{H_2} CH_3-CH_2-CH_2-CH_2-OH \end{cases}$$

(6) **Physical properties of monohydric alcohols**

(i) ***Character*** **:** Alcohols are neutral substances. These have no effect on litmus paper. This is analytical test for alcohols.

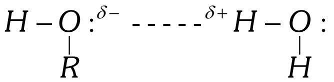
(ii) ***Physical state*** **:** The lower alcohols (upto C_{12}) are colourless alcohol with characteristic smell and burning taste. The higher members with more than 12-carbon atoms are colourless and odourless solids.

(iii) ***Polar character*** **:** Oxygen atom of the – *OH* group is more electronegative than both carbon and hydrogen. Thus the electron density near oxygen atom is slightly higher. Hydrogen bonding shown below



$\underset{R}{\underset{|}{H-O}}\text{----}\underset{R}{\underset{|}{H-O}}\text{---}\underset{R}{\underset{|}{H-O}}\text{----}\underset{R}{\underset{|}{H-O}}$. This gives polar character to OH bond.

(iv) ***Solubility* :** The lower alcohols are miscible in water.



$\underset{R}{\underset{|}{H-O}}:^{\delta-}\text{-----}{}^{\delta+}\underset{H}{\underset{|}{H-O}}:$

$$\text{Solubility} \propto \frac{1}{\text{Size of alkyl groups}}$$

Increase in carbon-chain increases organic part hence solubility in water decreases.

Isomeric 1°, 2°, 3° alcohols have solubility in order 1° > 2° > 3°.

(v) ***Boiling points* :** Due to intermolecular hydrogen bonding boiling points of alcohols are higher than hydrocarbon and ethers.

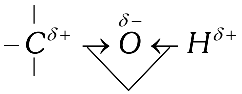
$$\text{B.P.} \propto \frac{1}{\text{No. of branches}};\ \text{B.P. follows the trends : } 1^\circ \text{ alcohols} > 2^\circ > 3^\circ \text{ alcohol}$$

(vi) ***Density* :** Alcohols are lighter than water. Density ∝ Molecular masses.

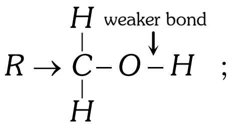
(vii) ***Intoxicating effects* :** Methanal is poisonous and is not good for drinking purposes. It may cause blindness and even death. Ethanal is used for drinking purposes.

TEACHING CARE

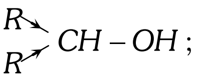
(7) Chemical properties : Characteristic reaction of alcohol are the reaction of the $-OH$ group. The reactions of the hydroxyl group consists of either cleavage of $C-O$ bond or the cleavage of $O-H$ bond.



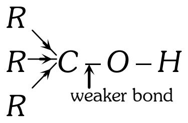
$C-O$ bond is weaker in the case of tertiary alcohols due to $+I$ effect of alkyl groups while $-OH$ bond is weaker in primary alcohols as electron density increase between $O-H$ bond and hydrogen tends to separates as a proton.



Primary



Secondary



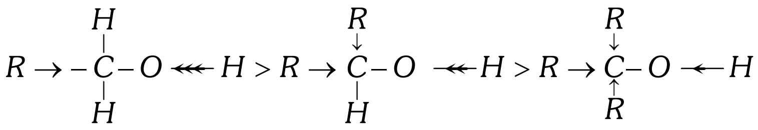
Tertiary

Thus primary alcohols give the most of reaction by cleavage of $O-H$ bond while tertiary alcohols are most reactive because of cleavage of $C-O$ bond. Hence $-O-H$ cleavage reactivity order : Primary > Secondary > Tertiary and $C-O-$ cleavage reactivity order : Tertiary > Secondary > Primary alcohol

(i) ***Reaction involving cleavage of* with removal of '*H*' as proton**

Alcohols are stronger acids than terminal acetylene but are not acidic enough to react with aqueous $NaOH$ or KOH. Acidic nature is in the order $HOH > ROH > CH \equiv CH > NH_3 > RH$.

Acidic nature of alcohol decrease with increase of alkyl groups on $-OH$ bonded carbon due to $+I$ (inductive) effect of alkyl group.



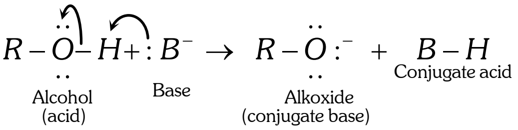
$$R \rightarrow -\overset{H}{\underset{H}{C}}-O \lll H > R \rightarrow \overset{R\downarrow}{\underset{H}{C}}-O \twoheadleftarrow H > R \rightarrow \overset{R\downarrow}{\underset{R\uparrow}{C}}-O \leftarrow H$$

(a) *Reaction with Na* **:** (Active metals)

$2RO-H+2M \rightarrow 2ROM+H_2\,(M = Na, K, Mg, Al,$ etc.)

Evolution of H_2 shows the presence of $-OH$ and reaction show that alcohols are acidic in nature. Alcohols acts as Bronsted acids because they donate a proton to a strong base $(:B^-)$.

Example :



$$R-\underset{\text{(acid)}}{\underset{\text{Alcohol}}{\ddot{\underset{\cdot\cdot}{O}}}}-H+\underset{\text{Base}}{:B^-} \rightarrow \underset{\text{(conjugate base)}}{\underset{\text{Alkoxide}}{R-\ddot{\underset{\cdot\cdot}{O}}:^-}} + \underset{\text{Conjugate acid}}{B-H}$$

On reaction of alkoxide with water, starting alcohol is obtained.

$$\underset{\text{Acid}}{H-\ddot{\underset{\cdot\cdot}{O}}-H}+\underset{\text{Base}}{R\ddot{\underset{\cdot\cdot}{O}}:} \rightarrow \underset{\text{Conjugate acid}}{R-O-H} + \underset{\text{Conjugate base}}{OH^-}$$

This is the analytical test for alcohols.

(b) *Reaction with carboxylic acid* [Esterification] **:** $\underset{\text{acid}}{RCO\boxed{-OH+H}}\underset{\text{Alcohol}}{-OR'} \xrightleftharpoons{\text{Conc. } H_2SO_4} \underset{\text{Ester}}{RCOOR'}+H_2O$

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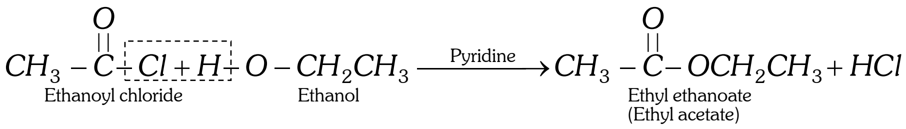
When HCl gas is used as catalyst, the reaction is called fischer-speier esterification.

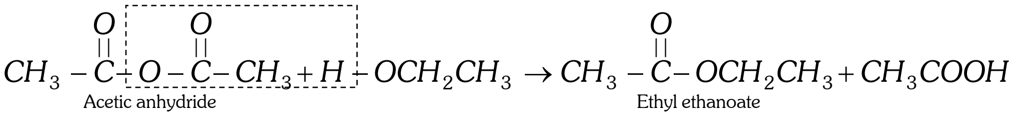
Presence of bulky group in alcohol or in acid decreases the rate of esterification. This is due to steric hinderence of bulky group. Reactivity of alcohol in this reaction is $1^o > 2^o > 3^o$.

(c) *Reaction with acid derivatives* **:** (Analytical test of alcohol)



$$\underset{\text{Ethanoyl chloride}}{CH_3-\overset{\overset{O}{||}}{C}\boxed{-Cl+H}}\underset{\text{Ethanol}}{-O-CH_2CH_3} \xrightarrow{\text{Pyridine}} \underset{\text{(Ethyl acetate)}}{\underset{\text{Ethyl ethanoate}}{CH_3-\overset{\overset{O}{||}}{C}-OCH_2CH_3}}+HCl$$

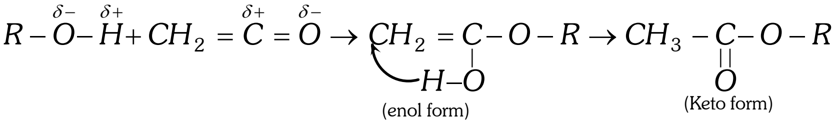
Acylation :



$$\underset{\text{Acetic anhydride}}{CH_3-\overset{\overset{O}{||}}{C}\boxed{-O-\overset{\overset{O}{||}}{C}-CH_3+H}}-OCH_2CH_3 \rightarrow \underset{\text{Ethyl ethanoate}}{CH_3-\overset{\overset{O}{||}}{C}-OCH_2CH_3}+CH_3COOH$$

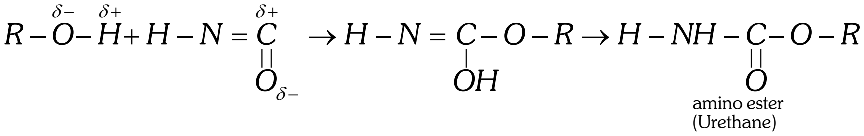
(d) *Reaction with grignard reagents* **:** $\underset{\text{alcohol}}{\underset{\text{Methyl}}{CH_3OH}}+\underset{\text{bromide}}{\underset{\text{Ethyl magnesium}}{C_2H_5MgBr}} \rightarrow \underset{\text{Ethane}}{C_2H_6}+CH_3OMgBr$

(e) *Reaction with ketene* **:**



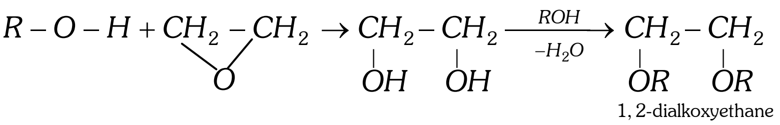
$$R-\overset{\delta-}{O}-\overset{\delta+}{H}+CH_2=\overset{\delta+}{C}=\overset{\delta-}{O} \rightarrow \underset{\text{(enol form)}}{CH_2=\underset{H-O}{\underset{|}{C}}-O-R} \rightarrow \underset{\text{(Keto form)}}{CH_3-\underset{O}{\underset{||}{C}}-O-R}$$

(f) *Reaction with isocyanic acid* **:**



$$R-\overset{\delta-}{O}-\overset{\delta+}{H}+H-N=\underset{O_{\delta-}}{\underset{||}{\overset{\delta+}{C}}} \rightarrow H-N=\underset{OH}{\underset{|}{C}}-O-R \rightarrow \underset{\text{(Urethane)}}{\underset{\text{amino ester}}{H-NH-\underset{O}{\underset{||}{C}}-O-R}}$$

(g) *Reaction with ethylene oxide* **:**



$$R-O-H+\underset{\diagdown O \diagup}{CH_2-CH_2} \rightarrow \underset{OH\quad OH}{CH_2-CH_2} \xrightarrow[-H_2O]{ROH} \underset{\substack{OR\quad OR \\ \text{1, 2-dialkoxyethane}}}{CH_2-CH_2}$$

(h) *Reaction with diazomethane* **:** $R-OH+CH_2N_2 \rightarrow \underset{\text{(Ether)}}{R-O-CH_3}+N_2$

(i) ***Alkylation :*** $ROH+R_2'SO_4 \rightarrow ROR'+R'HSO_4$

(ii) *Reaction involving cleavage of* $-\overset{|}{\underset{|}{C}}-OH$ *with removal or substitution of –OH group*

(a) *Reaction with hydrogen halides* **:** Alcohols give alkyl halide. The reactivity of *HX* is in the order of *HI* > *HBr* > *HCl* and the reactivity of *ROH* is in the order of allyl, benzyl > 3° > 2°> 1°. The reaction follows a nucleophilic substitution mechanism.

Grove's process : $ROH+HX \xrightarrow[\text{anhydrous }\Delta]{ZnCl_2} R-X+H_2O$

If alcohols react with *HI* and red phosphorus, alkane will be formed.

$$C_2H_5OH+2HI \xrightarrow[\text{heat}]{\text{Red }P} C_2H_6+I_2+H_2O$$

Primary alcohols follow SN^2 mechanism . $\underset{\substack{\text{Protonated} \\ 1^\circ \text{ alcohol}}}{R-OH_2^+}+X^- \rightarrow {}^{\delta-}X---R---\mathrm{OH}_2^{\delta+} \rightarrow R-X+H_2O$

In secondary and tertiary alcohols, the SN^1 mechanism operates

$$R-OH \overset{H^+}{\rightleftharpoons} R-OH_2^+ \overset{-H_2O}{\rightleftharpoons} R^+ \xrightarrow{X^-} R-X$$

TEACHING CARE

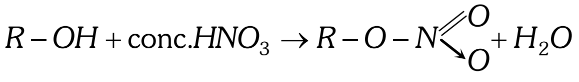
(b) *Reaction with* PCl_5 **:** $ROH+PX_5 \rightarrow RX+POX_3+HX\ ;\ X=Cl$ (Analytical test for alcohols)

(c) *Reaction with* PCl_3 **:** $\underset{\text{Alcohol}}{3ROH}+\underset{\substack{\text{Phosphorus} \\ \text{trichloride}}}{PCl_3} \rightarrow \underset{\substack{\text{Alkyl} \\ \text{chloride}}}{3RCl}+\underset{\substack{\text{Phosphorus} \\ \text{acid}}}{H_3PO_3}$

(d) *Reaction with thionyl chloride* $[SOCl_2]$ **:** $ROH+SOCl_2 \xrightarrow{\text{Pyridine}} RCl+SO_2+HCl$

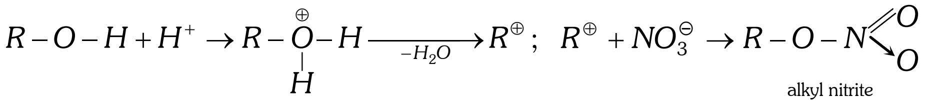
(e) *Reaction with ammonia* **:** $ROH+NH_3 \xrightarrow[360^\circ C]{Al_2O_3} \underset{\substack{\text{Primary} \\ \text{amine}}}{RNH_2} \xrightarrow[Al_2O_3]{ROH} \underset{\substack{\text{Secondary} \\ \text{amine}}}{R_2NH} \xrightarrow[Al_2O_3]{ROH} \underset{\substack{\text{Tertiary} \\ \text{amine}}}{R_3N}$

(f) *Reaction with* HNO_3 **:**



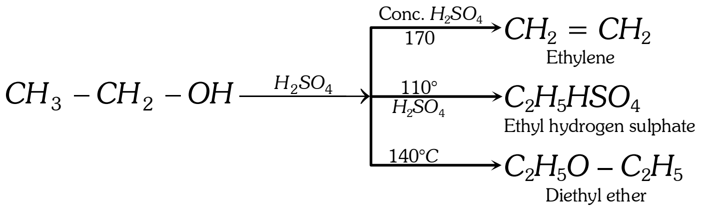
$$R-OH+\text{conc.}HNO_3 \rightarrow \underset{\text{alkyl nitrite}}{R-O-N \lt^{O}_{O}}+H_2O$$

Mechanism : $HNO_3 \rightarrow H^+ + NO_3^-$

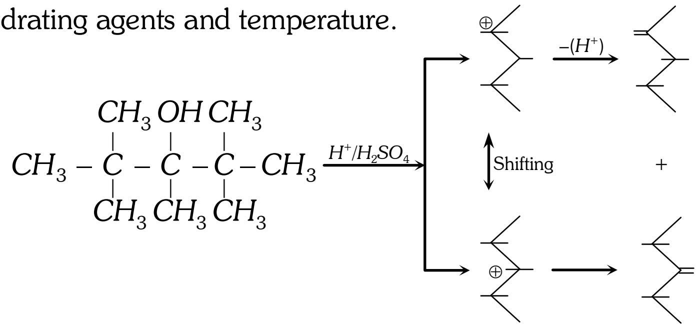


$$R-O-H+H^+ \rightarrow R-\underset{H}{\overset{\oplus}{O}}-H \xrightarrow[-H_2O]{} R^{\oplus}\ ;\ R^{\oplus}+NO_3^{\ominus} \rightarrow \underset{\text{alkyl nitrite}}{R-O-N \lt^{O}_{O}}$$

(g) *Reaction with* H_2SO_4 [Dehydration of alcohol] : The elimination of water from a compound is known as dehydration. The order of case dehydration is Tertiary > Secondary > primary alcohol. The products of dehydration of alcohols are depend upon the nature of dehydrating agents and temperature.

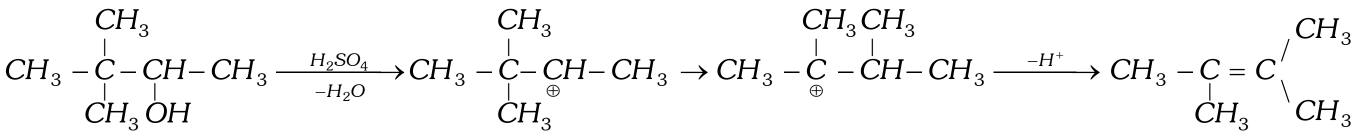


$$CH_3-CH_2-OH \xrightarrow{H_2SO_4} \begin{cases} \xrightarrow{\text{Conc. }H_2SO_4,\ 170} \underset{\text{Ethylene}}{CH_2=CH_2} \\ \xrightarrow{110^\circ,\ H_2SO_4} \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} \\ \xrightarrow{140^\circ C} \underset{\text{Diethyl ether}}{C_2H_5O-C_2H_5} \end{cases}$$



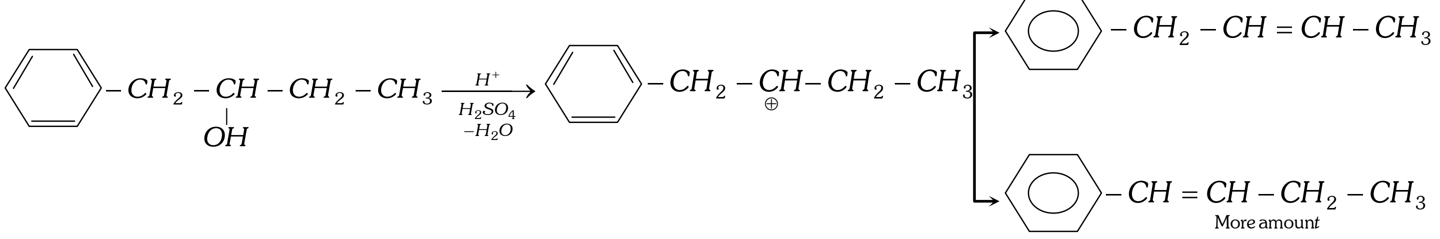
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{OH}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{H^+/H_2SO_4}$$

Alcohol leading to conjugated alkene are dehydrated to a greater extent than those of alcohols leading to nonconjugated alkene. Thus dehydration is in order $CH_2=CH-\underset{OH}{CH}-CH_3 > CH_3-CH_2-\underset{OH}{CH}-CH_3$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3 \xrightarrow[-H_2O]{H_2SO_4} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\oplus}{CH}-CH_3 \rightarrow CH_3-\underset{\oplus}{\overset{CH_3}{C}}-\overset{CH_3}{CH}-CH_3 \xrightarrow{-H^+} CH_3-\underset{CH_3}{C}=C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$$

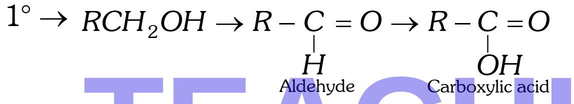
2-alkene



(iii) *General reaction of alcohols*

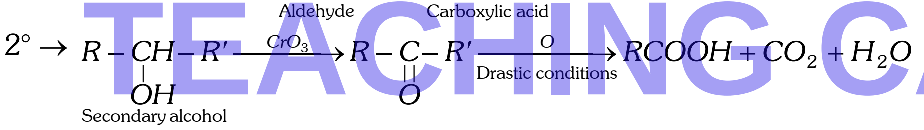
(a) *Reduction* **:** $R-OH+2HI\xrightarrow{\Delta}R-H$

(b) *Oxidation* **:** Difference between 1°, 2° and 3° alcohols.



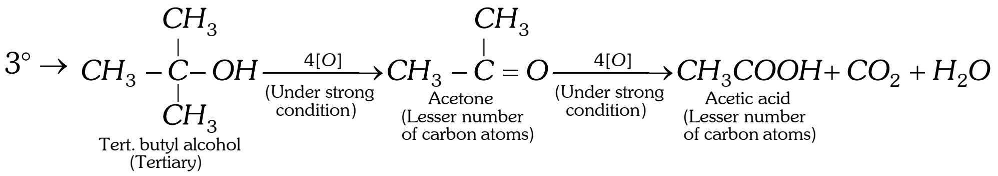
$$1^\circ \rightarrow RCH_2OH \rightarrow R-\underset{H}{C}=O \rightarrow R-\underset{OH}{C}=O$$

Aldehyde Carboxylic acid



$$2^\circ \rightarrow R-\underset{OH}{CH}-R' \xrightarrow{CrO_3} R-\underset{O}{\underset{\|}{C}}-R' \xrightarrow[\text{Drastic conditions}]{O} RCOOH+CO_2+H_2O$$

Secondary alcohol

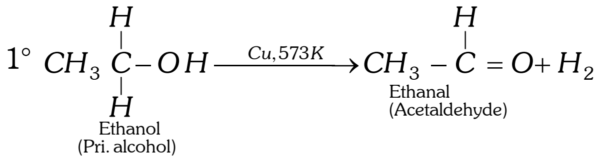


$$3^\circ \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[\text{(Under strong condition)}]{4[O]} CH_3-\overset{CH_3}{C}=O \xrightarrow[\text{(Under strong condition)}]{4[O]} CH_3COOH+CO_2+H_2O$$

Tert. butyl alcohol (Tertiary) Acetone (Lesser number of carbon atoms) Acetic acid (Lesser number of carbon atoms)

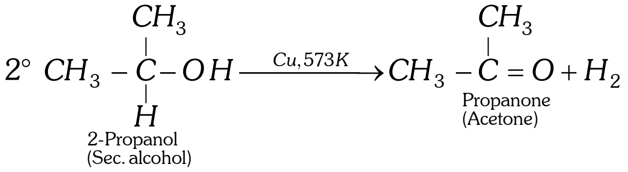
Note : ✹ *3° alcohols are resistant to oxidation, but on taking stronger oxidising agent they form ketone.*

(c) *Catalytic oxidation/dehydrogentaion*



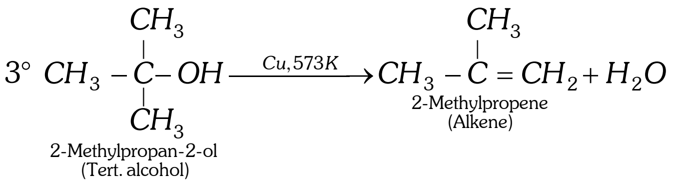
$$1^\circ\ CH_3\underset{H}{\overset{H}{C}}-OH \xrightarrow{Cu,573K} CH_3-\overset{H}{C}=O+H_2$$

Ethanol (Pri. alcohol) Ethanal (Acetaldehyde)



$$2^\circ\ CH_3-\underset{H}{\overset{CH_3}{C}}-OH \xrightarrow{Cu,573K} CH_3-\overset{CH_3}{C}=O+H_2$$

2-Propanol (Sec. alcohol) Propanone (Acetone)



$$3^\circ\ CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow{Cu,573K} CH_3-\overset{CH_3}{C}=CH_2+H_2O$$

2-Methylpropan-2-ol (Tert. alcohol) 2-Methylpropene (Alkene)

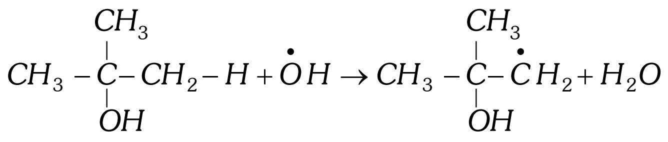
This is dehydration process and difference between 1°, 2° and 3°alcohols.

TEACHING CARE

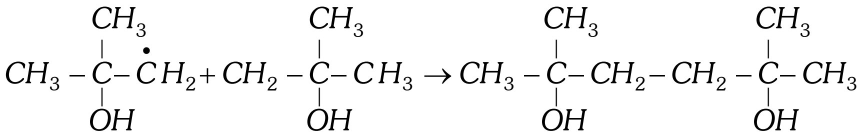
(d) *Oxidation through Fenton's reagent* : $[FeSO_4 + H_2O_2]$

Mechanism

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + \overset{\bullet}{O}H;$$



$$CH_3 - \underset{OH}{\overset{CH_3}{C}} - CH_2 - H + \overset{\bullet}{O}H \rightarrow CH_3 - \underset{OH}{\overset{CH_3}{C}} - \overset{\bullet}{C}H_2 + H_2O$$



$$CH_3 - \underset{OH}{\overset{CH_3}{C}} - \overset{\bullet}{C}H_2 + CH_2 - \underset{OH}{\overset{CH_3}{C}} - CH_3 \rightarrow CH_3 - \underset{OH}{\overset{CH_3}{C}} - CH_2 - CH_2 - \underset{OH}{\overset{CH_3}{C}} - CH_3$$

2, 5-dimethyl hexandiol-2, 5

Important reagents used for oxidation of alcohols

≅ PCC [Pyridinium chloro chromate $(C_6H_5\overset{\oplus}{N}HClCrO_3^-)$] to oxidise 1° alcohols to aldehydes and 2° alcohols to ketones.

≅PDC [Pyridinium di chromate $(C_5H_5.NH)_2^{2+}Cr_2O_7^{2-}$] to oxidise 1° alcohols to aldehyde and 2° alcohol to ketones.

≅H_2CrO_4 (chromic acid) to oxidise 1° alcohol to carboxylic acid.

≅$CrO_3 \cdot H_2SO_4$/ Acetone to oxidise 2°alcohol to ketones.

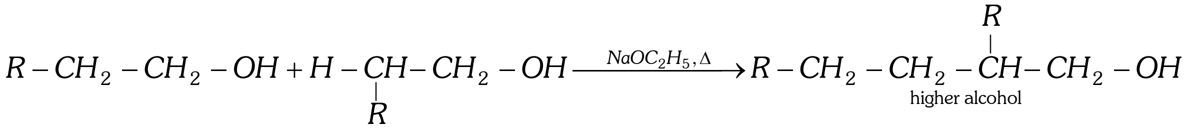
≅Jones reagents (chromic acid in aqueous acetone solution) oxidise 1° alcohol to aldehyde and 2° alcohol to ketone without affecting $(C = C)$ double bond.

≅MnO_2 selectively oxidises the –OH group of allylic and benzylic 1° and 2° alcohols to give aldehyde and ketone respectively.

≅N_2O_4 in $CHCl_3$ (field's) oxidises primary and secondary benzyl alcohol.

TEACHING CARE

(e) *Self condensation* : **Guerbet's reaction**



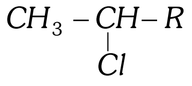
$$R - CH_2 - CH_2 - OH + H - \underset{R}{CH} - CH_2 - OH \xrightarrow{NaOC_2H_5,\Delta} \underset{\text{higher alcohol}}{R - CH_2 - CH_2 - \overset{R}{CH} - CH_2 - OH}$$

(f) *Reaction with cerric ammonium nitrate* : $\underset{\text{Yellow colour}}{\text{Cerric ammonium nitrate} + ROH} \rightarrow$ Red colour solution of complex. This is analytical test for alcohols.

(g) *Iodoform test* : When a few drops of alcohol are warmed with iodine and KOH yellow precipitate of iodoform with characteristic smell is obtained. Any alcohol consists CH_3CHOH group give iodoform test.

Example : CH_3CH_2OH, $CH_3 - CHOH - CH_3$, $C_6H_5 - CHOH - CH_3$

Since reaction takes place with alkali solution as one of the reagents hence alkyl halide like $CH_3 - CH_2Cl$ and



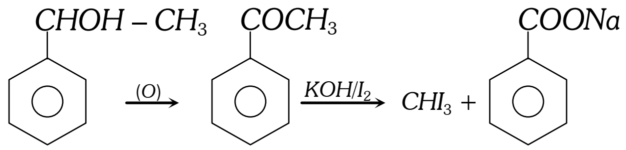
$CH_3 - \underset{Cl}{CH} - R$ will also give this test.

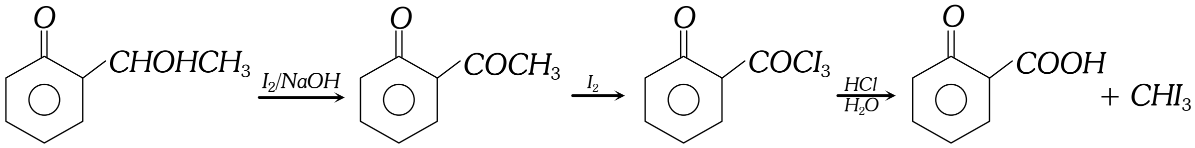
$$2NaOH + I_2 \rightarrow NaI + NaOI + H_2O; \quad CH_3CH_2OH + 2NaOI \rightarrow CH_3CHO + 2NaOH + 2HI$$

$$CH_3CHO + 3NaOH \rightarrow CI_3CHO + 3NaOH; \quad CI_3 - CHO + NaOH \rightarrow \underset{\text{Iodofiorm}}{CHI_3} + HCOONa$$

$$CI_3 - CHO + HCl \rightarrow CHI_3 + HCOOH$$

Other example





(8) Individual members of monohydric alcohols

Methanol

(i) Preparation

(a) By destructive distillation

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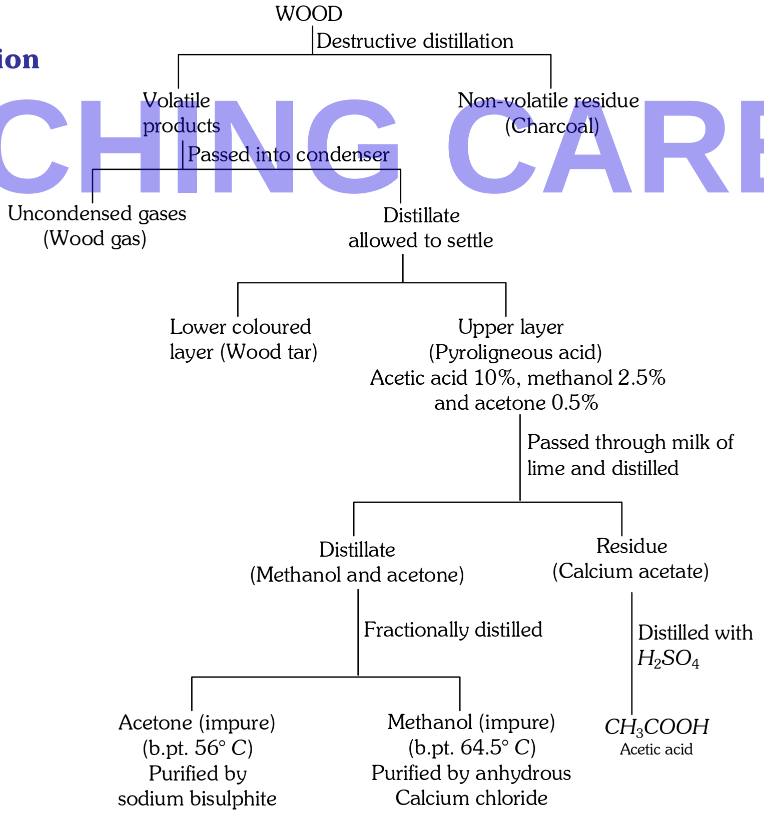

(b) *From water gas* : $C + H_2O \xrightarrow{1300^\circ C} \underset{\text{water gas}}{CO + H_2}$; $\underset{\text{Compressed gases}}{CO + 2H_2} \xrightarrow[300^\circ C]{ZnO+Cr_2O_3} \underset{\text{Methyl alcohol}}{CH_3OH}$

(c) *From natural gas* : $\underset{\text{(9:1) by volume}}{2CH_4 + O_2} \rightarrow 2CH_3OH$

(ii) *Physical properties*

(a) It is a colourless liquid and boils at 64.5° C.

(b) It is miscible in water, good solvent for fats and oils.

(c) It is inflammable and burns with a faint luminous flame.

(d) It has pleasant smell and burning taste.

(iii) Uses

(a) For the manufacture of formaldehyde and formaline. $CH_3OH \xrightarrow{K_2Cr_2O_7} CH_2O + H_2O$

(b) A 20% mixture of methyl alcohol and gasoline is a good motor fuel.

(c) Use as an antifreeze for automobile radiators.

(d) To denaturate ethyl alcohol, mixture is called methylated spirit.

(e) In the preparation of dyes, medicines and perfumes.

Ethanol

(i) Preparation

(a) *From Ethylene* : $C_2H_4 + H_2O \xrightarrow[300^\circ C,\,70atm]{H_3PO_4} C_2H_5OH$ Yield of ethyl alcohol is 95%.

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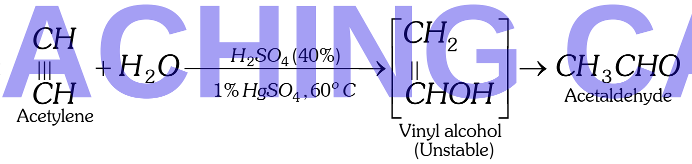
(b) *From acetylene* :



$$\underset{\text{Acetylene}}{\begin{matrix}CH\\ |||\\ CH\end{matrix}} + H_2O \xrightarrow[1\%\,HgSO_4,\,60^\circ C]{H_2SO_4\,(40\%)} \underset{\substack{\text{Vinyl alcohol}\\ \text{(Unstable)}}}{\left[\begin{matrix}CH_2\\ ||\\ CHOH\end{matrix}\right]} \rightarrow \underset{\text{Acetaldehyde}}{CH_3CHO}$$

$$CH_3CHO + H_2 \xrightarrow[110-140^\circ C]{Ni} \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(c) *Fermentation* : This word is given by Lebeig. Fermentation process is exothermic. Ethanol is prepared by molasses and invert sugar molasses is the waste product in sugar industry. It is a mixture of sugar (30%) and invert sugar (32-40%) combine form of glucose and fructose called invert sugar. Temperature should be 25-30°C. low concentration (8-10%) is favourable.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{invertase enzyme}]{\text{yeast cell}} \underset{\text{glucose}}{C_6H_{12}O_5} + \underset{\text{fructose}}{C_6H_{12}O_6}\ ;\ C_6H_{12}O_6 \xrightarrow[\text{zymase enzyme}]{\text{yeast cell}} C_2H_5OH + CO_2 + H_2O$$

Certain amounts of inorganic compound such as ammonium sulphate, phosphate should be added. Oxygen is necessary for the growth of ferments. Boric acid, mercury salts etc. should not be present in the solution as these retards the fermentation.

(d) *From starch :* $\underset{\text{starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{diastase}} \underset{\text{maltose (wort)}}{nC_{12}H_{22}O_{11}}\ ;\ \underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H2O \xrightarrow{\text{maltose}} \underset{\text{glucose}}{2C_6H_{12}O_6}$

$$2C_6H_{12}O_6 \xrightarrow{\text{zymase}} C_2H_6OH + CO_2 + H_2O + \text{energy}$$

By this method ethanol prepared is 10-12% called wash. Raw spirit $\xrightarrow[\text{distillation}]{\text{Fractional}} \underbrace{\underset{95.5\%}{C_2H_5OH} + \underset{4.5\%}{H_2O}}_{\text{rectified spirit}}$

Manufacturing of ethyl alcohol (absolute) from rectified spirit called Azeotrophic distillation.

- Absolute alcohol is prepared by distillating rectified spirit with benzene.
- The first fraction consists of constant boiling mixture of ethyl alcohol, water and benzene [18.5% + 7.4% + 74.1%] and distills over at 64.8°C.
- The second fraction consists of a boiling mixture of ethyl alcohol and benzene [32.4% + 67.6%] and distills at $68.2^\circ C$.
- Pure alcohol distills at $78.3^\circ C$ and known as absolute alcohol (100%).

(ii) ***Properties* :** Same as monohydric alcohols.

(iii) ***Uses***

(a) In the manufacture of alcoholic beverages.

(b) As a preservative for biological specimens.

(c) As a low freezing and mobile liquid in scientific apparatus such as thermometers and spirit levels.

(d) In hospitals as an antiseptic.

(e) As a petrol substitute (power alcohol).

(9) Interconversion of monohydric alcohols

(i) ***Primary alcohol into secondary alcohols***

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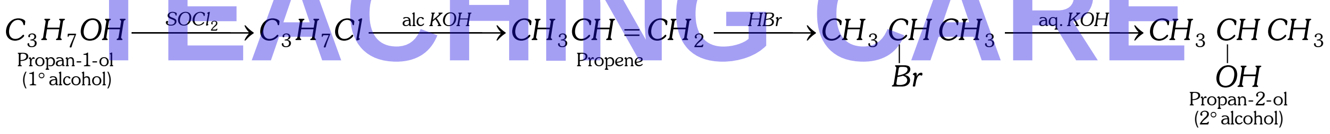
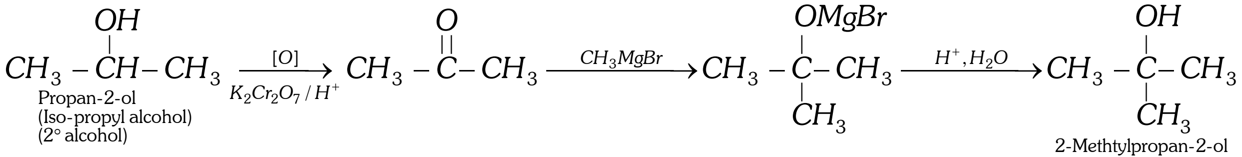


$$C_3H_7OH \xrightarrow{SOCl_2} C_3H_7Cl \xrightarrow{alc\ KOH} CH_3CH=CH_2 \xrightarrow{HBr} CH_3\underset{Br}{\underset{|}{C}H}CH_3 \xrightarrow{aq.\ KOH} CH_3\underset{OH}{\underset{|}{C}H}CH_3$$

Propan-1-ol (1° alcohol) Propene Propan-2-ol (2° alcohol)

(ii) ***Secondary alcohol into tertiary alcohol***

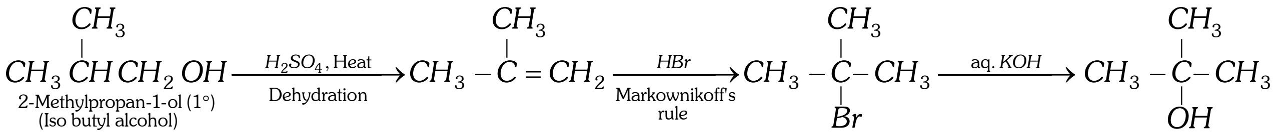


$$CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow[K_2Cr_2O_7/H^+]{[O]} CH_3-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{CH_3MgBr} CH_3-\overset{OMgBr}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3 \xrightarrow{H^+,H_2O} CH_3-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$$

Propan-2-ol (Iso-propyl alcohol) (2° alcohol)

2-Methtylpropan-2-ol (3°) (tert. butyl alcohol)

(iii) ***Primary alcohol into tertiary alcohol***



$$CH_3\overset{CH_3}{\overset{|}{C}H}CH_2OH \xrightarrow[Dehydration]{H_2SO_4,\ Heat} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[Markownikoff's\ rule]{HBr} CH_3-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_3 \xrightarrow{aq.\ KOH} CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$$

2-Methylpropan-1-ol (1°) (Iso butyl alcohol)

2-Methylpropan-2-ol (3°) (tert. butyl alcohol)

(iv) ***Lower alcohol into higher alcohol*** (ascent of series)

$$CH_3OH \xrightarrow{HI} CH_3I \xrightarrow{KCN} CH_3CN \xrightarrow[Reduction]{4(H)} CH_3CH_2NH_2 \xrightarrow{HONO} CH_3CH_2OH$$

Methanol (1 carbon atom) Ethanol (2 carbon atoms)

(v) ***Higher alcohol into lower alcohol*** [Descent series]

$$\underset{\substack{\text{Ethanol}\\\text{(2 carbon atoms)}}}{C_2H_5OH}\xrightarrow[{[O]}]{K_2Cr_2O_7,H^+}CH_3COOH\xrightarrow{NaOH}CH_3COONa\xrightarrow[\text{Heat}]{NaOH+CaO}CH_4\xrightarrow{Cl_2}CH_3Cl\xrightarrow{\text{aq. }KOH}\underset{\substack{\text{Methanol}\\\text{(one carbon atom)}}}{CH_3OH}$$

(10) **Alcoholic beverages :** Liquors used for drinking purposes containing ethyl alcohol as the principal constituent are called alcoholic beverages. Besides alcohol, these contain large amounts of water, colouring and flavouring materials. Alcoholic beverages are of two types :

(i) ***Undistilled beverages*** **:** These are prepared from fruit juices and grains. Those prepared from grapes and other fruit juices are known as wines. Wines contain 18-20% of ethyl alcohol and are used as such after fermentation, *i.e.*, with distillation. The natural wines when made stronger by the addition of rectified alcohol are known as fortified wines.

Name	*Undistilled Percentage of alcohol*	***Source***
Beer	3-6	**Barley**
Cider	2-6	**Apples**
Wine (Champagne)	8-10	**Grapes**
Claret	7-13	**Grape juice**
Port and Sherry (Fortified)	14-24	**Grape juice**

(ii) ***Distilled beverages*** **:** These are prepared by the fermentation of molasses, barley, maize, etc. The fermented liquor is then distilled. These contain a higher percentage of ethyl alcohol which may be as high as 50%.

Name	*Distilled Percentage of alcohol*	***Source***
Whisky	35-40	**Malt**
Rum	45-55	**Molasses**
Gin	40-45	**Maize**
Brandy	40-45	**Grape juice**
Cognac	40-50	**Grape juice**

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(11) **Alcoholometry :** The process of determining the percentage of alcohol in a given sample is known as alcoholometry. An alcohol water mixture having specific gravity 0.91976 at 15°C and containing 57.1% of ethyl alcohol by volume or 49.3% by mass is called proof-spirit. A sample having higher percentage of ethyl alcohol in comparison to proof-spirit is referred to as over-proof (O.P.) and the one having lower alcohol content than proof-spirit is known as under-proof (U.P.). Thus 15 U.P. means that 100 *ml* of the sample contains as much alcohol as 85 *ml* of proof spirit. Similarly, 15 O.P. means that 100 *ml* of the sample contains as much of alcohol as 115 *ml* of proof spirit.

(12) **Power alcohol :** Alcohol used for the generation of power is called power alcohol. Generally it is a mixture of 80% petrol and 20% absolute alcohol with cosolvent benzene. It is cheaply obtained from waste petrol.

(13) **Methylated spirit :** Ethyl alcohol containing 5 to 10% of methyl alcohol is known as methylated spirit or denatured spirit. Denaturing can also be done by adding 0.5% pyridine, petroleum naptha, rubber distillate (caoutchoucine) or $CuSO_4$.

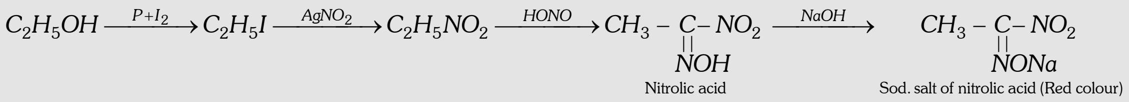
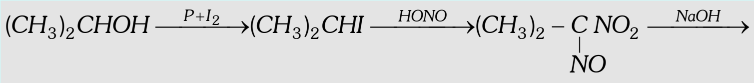
(14) **Toxicity of alcohols :** The toxicity of alcohols is mainly due to their biological to oxidation takes place in living organism. Methyl alcohol is highly toxic and its consumption causes, blindness and death. Ethyl alcohol is non toxic but produces physiological effect disturbing brain activity on drinking. The commercial alcohol is made unfit for drinking by mixing in it copper sulphate (which gives its colour) and pyridine (which makes it foul smelling liquid). It is known as denaturation of alcohol.

(15) Distinguish between primary, secondary and tertiary monohydric alcohols

(i) ***Lucas test* :** A mixture of anhydrous $ZnCl_2$ + conc. HCl is called as Lucas reagent.

Primary	$R-CH_2-OH \xrightarrow[-H_2O]{\text{conc. HC / ZnCl}_2\text{ anhy.}} R-CH_2-Cl \rightarrow$ ***ppt. appears after heating***
Secondary	$R_2CH-OH \xrightarrow[-H_2O]{\text{conc. HCl / ZnCl}_2\text{ anhy.}} R_2-CH-Cl \rightarrow$ **ppt. appears with in 5 minutes**
Tertiary	$R_3C-OH \xrightarrow{ZnCl_2 / HCl} R_3C-Cl \rightarrow$ **ppt. appears immediately**

(ii) ***Victor mayer test* :** Also known as RBW test. RBW → Red, Blue, White test.

Primary	 $C_2H_5OH \xrightarrow{P+I_2} C_2H_5I \xrightarrow{AgNO_2} C_2H_5NO_2 \xrightarrow{HONO} \underset{\text{Nitrolic acid}}{CH_3-\underset{\underset{NOH}{\Vert}}{C}-NO_2} \xrightarrow{NaOH} \underset{\text{Sod. salt of nitrolic acid (Red colour)}}{CH_3-\underset{\underset{NONa}{\Vert}}{C}-NO_2}$
Secondary	 $(CH_3)_2CHOH \xrightarrow{P+I_2} (CH_3)_2CHI \xrightarrow{HONO} (CH_3)_2-\underset{\underset{NO}{\vert}}{C}\,NO_2 \xrightarrow{NaOH}$ **No reaction (Blue colour)**
Tertiary	$(CH_3)_3COH \xrightarrow{P+I_2} (CH_3)_3Cl \xrightarrow{AgNO_2} (CH_3)_3CNO_2 \xrightarrow{HONO}$ **No reaction (colourless)**

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Difference between methanol and ethanol

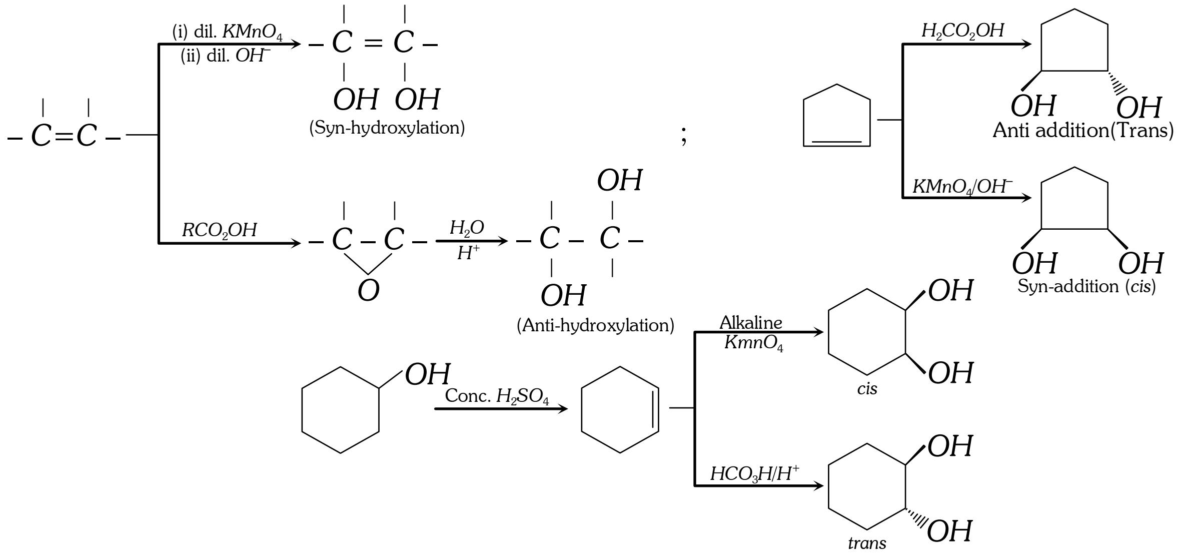
Methanol	***Ethanol***
(i) When CH_3OH is heated on Cu coil it gives formalin like smell.	**(i) It does not give formalin like smell.**
(ii) When CH_3OH is heated with salicylic acid in H_2SO_4 (conc.) then methyl salicylate is formed which has odour like winter green oil.	**(ii) No such odour is given.**
(iii) It does not give haloform or iodoform test.	**(iii) It gives haloform test**

Dihydric alcohols.

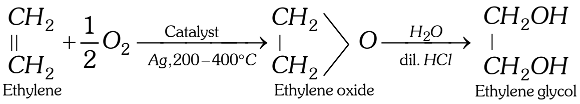
These are compound containing two hydroxyl groups. These are dihydroxy derivatives of alkanes. Their general formula is $C_nH_{2n+2}O_2$. The simplest and most important dihydric alcohol is ethylene glycol. They are classified as α, β, γ….. glycols, according to the relative position of two hydroxyl groups. α is 1, 2 glycol, β is 1, 3 glycol.

(1) **Preparation**

(i) ***From ethylene :*** (a) Through cold dilute alkaline solution of Bayer's reagent

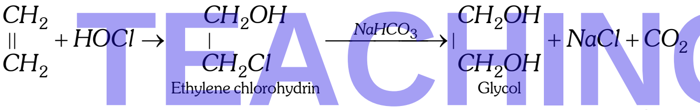


(b) *With O_2 in presence of Ag* :



$$\underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}} + \frac{1}{2}O_2 \xrightarrow[Ag,200-400^\circ C]{\text{Catalyst}} \underset{\text{Ethylene oxide}}{\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>O} \xrightarrow[\text{dil. }HCl]{H_2O} \underset{\text{Ethylene glycol}}{\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}}$$

(c) *With HOCl followed by hydrolysis* : (Industrial method)



$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + HOCl \rightarrow \underset{\text{Ethylene chlorohydrin}}{\begin{matrix}CH_2OH\\ |\\ CH_2Cl\end{matrix}} \xrightarrow{NaHCO_3} \underset{\text{Glycol}}{\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}} + NaCl + CO_2$$

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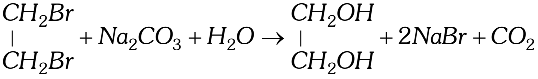
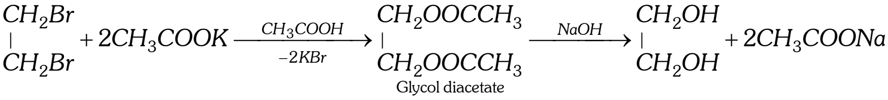
(ii) ***From 1, 2 dibromo ethane*** [Lab method]:



$$\begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix} + Na_2CO_3 + H_2O \rightarrow \begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + 2NaBr + CO_2$$



$$\begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix} + 2CH_3COOK \xrightarrow[-2KBr]{CH_3COOH} \underset{\text{Glycol diacetate}}{\begin{matrix}CH_2OOCCH_3\\ |\\ CH_2OOCCH_3\end{matrix}} \xrightarrow{NaOH} \begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + 2CH_3COONa$$

Note : ✸ *Vinyl bromide is formed as by product.*

✸*Best yield of glycol can be obtained by heating 1, 2-dibromo ethane with CH_3COOK in glacial acetic acid.*

(2) **Physical properties**

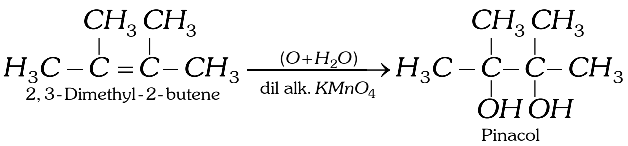
(i) It is a colourless, syrupy liquid and sweet in taste. Its boiling point is 197°C.

(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.

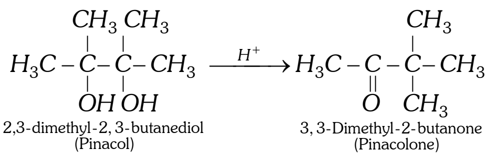
(iv) It is widely used as a solvent and as an antifreeze agent.

Pinacol; 2-3-dimethyl-2, 3 butanediol :



$$\underset{\text{2, 3-Dimethyl-2-butene}}{H_3C-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3} \xrightarrow[\text{dil alk. }KMnO_4]{(O+H_2O)} \underset{\text{Pinacol}}{H_3C-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3}$$

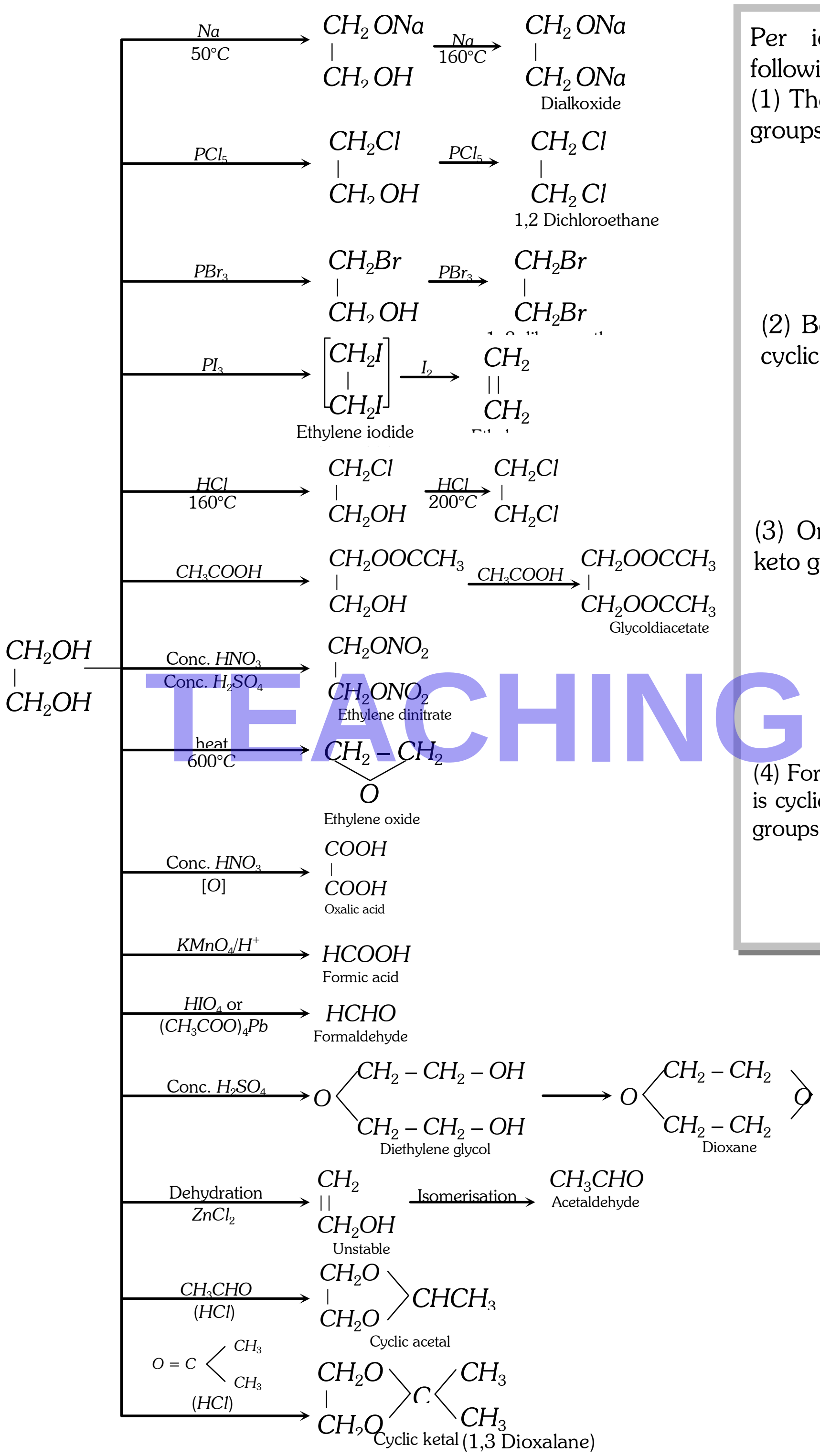
When pinacol react with mineral acid then pinacolone is formed.



$$\underset{\substack{\text{2,3-dimethyl-2, 3-butanediol}\\ \text{(Pinacol)}}}{H_3C-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3} \xrightarrow{H^+} \underset{\substack{\text{3, 3-Dimethyl-2-butanone}\\ \text{(Pinacolone)}}}{H_3C-\underset{O}{\underset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3}$$

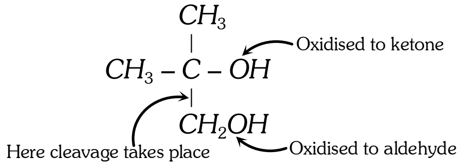
. This arrangement is called as Pinacol-pinacolon rearrangement

(3) **Chemical properties**

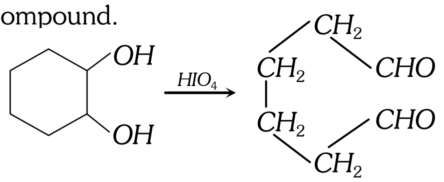


Per iodic oxidation of polyhdroxy alcohol gives following information,

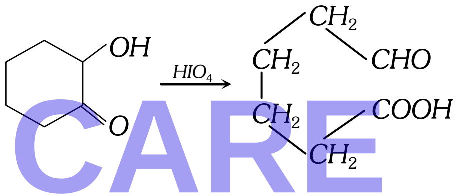
(1) There is cleavage of $(C-C)$ bond. When two $-OH-$ groups or oxo groups are on adjacent carbon positions.



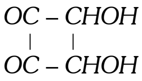
(2) Both CHO are present in one molecule indicating cyclic compound.



(3) On one side presence of $-COOH$ group indicates keto group adjacent to $(C-OH)$ group in (C).

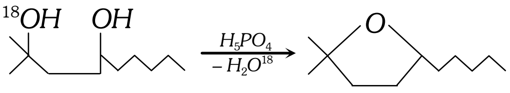


(4) Formation of two molecule of glyoxalic acid indicate that D is cyclic compound of four $C-$ atom with $C=O$ and $C-OH$ groups on both sides.



$$\begin{array}{l} OC-CHOH \\ \;|\qquad\;\; | \\ OC-CHOH \end{array}$$

Dehydration



Due to formation of stable carbocation

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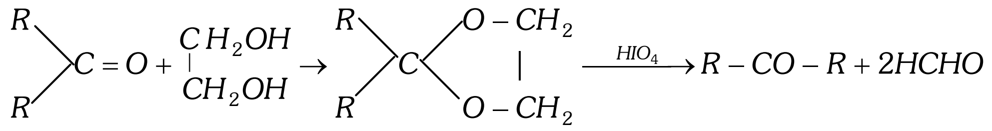
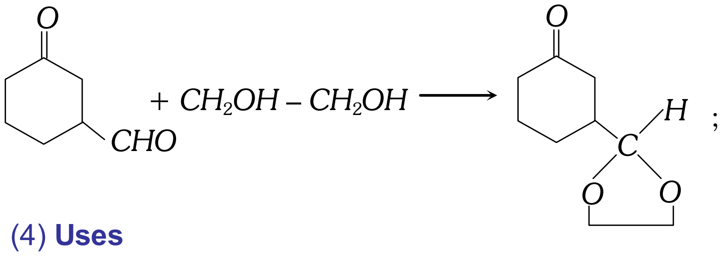
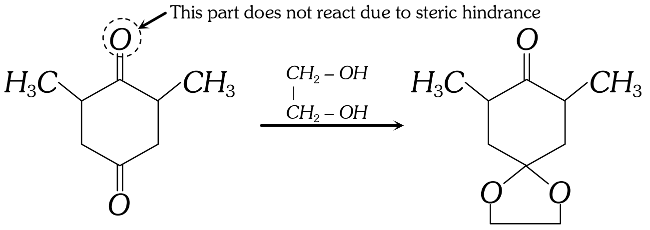
Dioxalane formation provides a path of protecting a carbonyl group in reaction studied in basic medium in which acetals are not affected. The carbonyl compound may be regenerated by the addition of periodic acid to aqueous solution of the dioxalane or by acidic hydrolysis.



Aldehyde is more reactive than ketone in dioxalane formation.




This part does not react due to steric hindrance

(4) Uses

(i) Used as an antifreeze in car radiators.

(ii) Used in the manufacture of dacron, dioxan etc.

(iii) As a solvent and as a preservatives.

(iv) As a cooling agent in aeroplanes.

(v) As an explosives in the form of dinitrate.

Trihydric alcohols.

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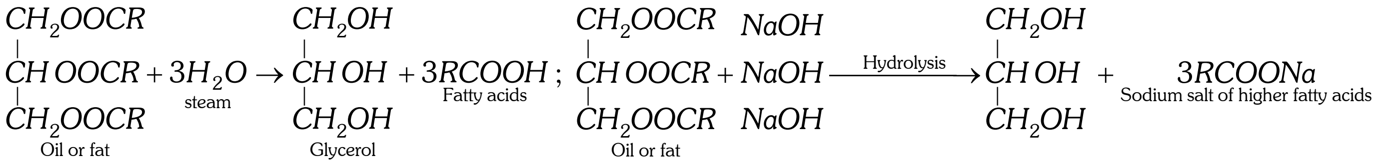
The only important trihydric alcohol is glycerol (propane-1, 2, 3-triol). It occurs as glycosides in almost all animal and vegetable oils and fats.

(1) Preparation

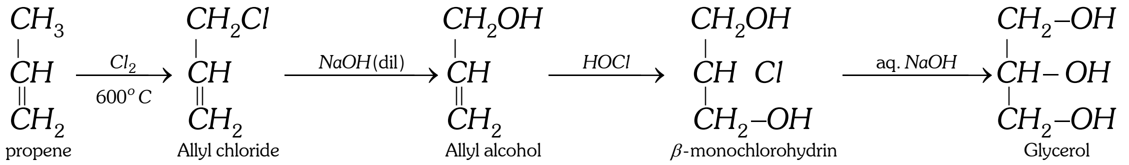
(i) *From oils and fats*



$$\underset{\text{Oil or fat}}{\begin{matrix}CH_2OOCR\\ |\\ CH\,OOCR\\ |\\ CH_2OOCR\end{matrix}} + \underset{\text{steam}}{3H_2O} \rightarrow \underset{\text{Glycerol}}{\begin{matrix}CH_2OH\\ |\\ CH\,OH\\ |\\ CH_2OH\end{matrix}} + \underset{\text{Fatty acids}}{3RCOOH}\;;\; \underset{\text{Oil or fat}}{\begin{matrix}CH_2OOCR & NaOH\\ | & \\ CH\,OOCR & +NaOH\\ | & \\ CH_2OOCR & NaOH\end{matrix}} \xrightarrow{\text{Hydrolysis}} \begin{matrix}CH_2OH\\ |\\ CH\,OH\\ |\\ CH_2OH\end{matrix} + \underset{\text{Sodium salt of higher fatty acids}}{3RCOONa}$$

(ii) *By fermentation of sugar* : $\underset{\text{Glucose}}{C_6H_{12}C_6} \xrightarrow[Na_2SO_3]{\text{Yeast}} \underset{\text{Glycerol}}{C_3H_8O_3} + \underset{\text{Acetaldehyde}}{CH_3CHO} + CO_2$

(iii) *From propene* [Modern method]



$$\underset{\text{propene}}{\begin{matrix}CH_3\\ |\\ CH\\ ||\\ CH_2\end{matrix}} \xrightarrow[600^\circ C]{Cl_2} \underset{\text{Allyl chloride}}{\begin{matrix}CH_2Cl\\ |\\ CH\\ ||\\ CH_2\end{matrix}} \xrightarrow{NaOH(\text{dil})} \underset{\text{Allyl alcohol}}{\begin{matrix}CH_2OH\\ |\\ CH\\ ||\\ CH_2\end{matrix}} \xrightarrow{HOCl} \underset{\beta\text{-monochlorohydrin}}{\begin{matrix}CH_2OH\\ |\\ CH\;\;Cl\\ |\\ CH_2{-}OH\end{matrix}} \xrightarrow{\text{aq. }NaOH} \underset{\text{Glycerol}}{\begin{matrix}CH_2{-}OH\\ |\\ CH{-}OH\\ |\\ CH_2{-}OH\end{matrix}}$$

(iv) *From propenal* : $CH_2 = CHCHO \xrightarrow[\text{catalyst}]{H_2} CH_2 = CHCH_2OH \xrightarrow{H_2O_2/\overset{\ominus}{O}H} \underset{\text{Glycerol}}{HOCH_2CHOHCH_2OH}$

(2) Physical properties

(i) It is a colourless, odourless, viscous and hygroscopic liquid.

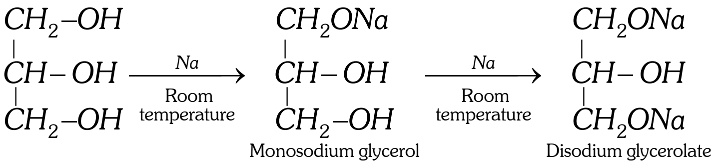
(ii) It has high boiling point *i.e.,* 290°C. The high viscosity and high boiling point of glycerol are due to association through hydrogen bonding.

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

(iv) It is sweet in taste and non toxic in nature.

(3) Chemical properties

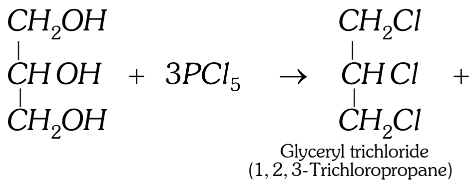
(i) ***Reaction with sodium :***



$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} \xrightarrow[\text{Room temperature}]{Na} \underset{\text{Monosodium glycerol}}{\begin{array}{l} CH_2ONa \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}} \xrightarrow[\text{Room temperature}]{Na} \underset{\text{Disodium glycerolate}}{\begin{array}{l} CH_2ONa \\ | \\ CH-OH \\ | \\ CH_2ONa \end{array}}$$

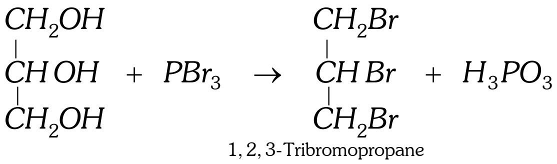
(ii) ***Reaction with PCl_5, PBr_3 and PI_3***

(a)



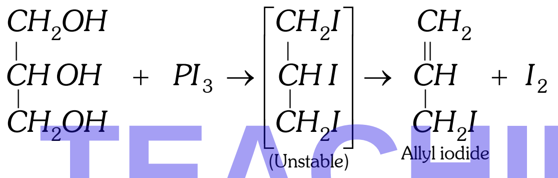
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3PCl_5 \rightarrow \underset{\substack{\text{Glyceryl trichloride} \\ \text{(1, 2, 3-Trichloropropane)}}}{\begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2Cl \end{array}} + 3POCl_3 + 3HCl$$

(b)



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + PBr_3 \rightarrow \underset{\text{1, 2, 3-Tribromopropane}}{\begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ CH_2Br \end{array}} + H_3PO_3$$

(c)



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + PI_3 \rightarrow \underset{\text{(Unstable)}}{\left[\begin{array}{l} CH_2I \\ | \\ CHI \\ | \\ CH_2I \end{array}\right]} \rightarrow \underset{\text{Allyl iodide}}{\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2I \end{array}} + I_2$$

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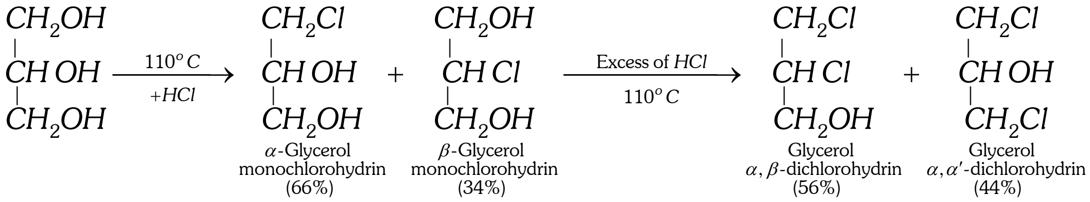
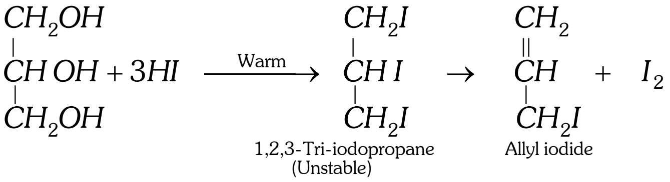
(iii) ***Reaction with HCl or HBr***



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[+HCl]{110^\circ C} \underset{\substack{\alpha\text{-Glycerol} \\ \text{monochlorohydrin} \\ (66\%)}}{\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\substack{\beta\text{-Glycerol} \\ \text{monochlorohydrin} \\ (34\%)}}{\begin{array}{l} CH_2OH \\ | \\ CHCl \\ | \\ CH_2OH \end{array}} \xrightarrow[110^\circ C]{\text{Excess of } HCl} \underset{\substack{\text{Glycerol} \\ \alpha,\beta\text{-dichlorohydrin} \\ (56\%)}}{\begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2OH \end{array}} + \underset{\substack{\text{Glycerol} \\ \alpha,\alpha'\text{-dichlorohydrin} \\ (44\%)}}{\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array}}$$

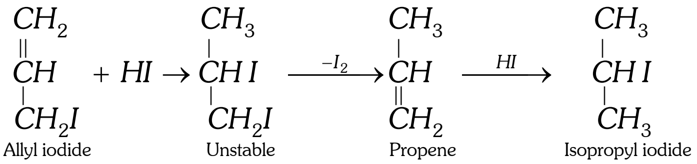
(iv) ***Reaction with HI***

(a)



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HI \xrightarrow{\text{Warm}} \underset{\substack{\text{1,2,3-Tri-iodopropane} \\ \text{(Unstable)}}}{\begin{array}{l} CH_2I \\ | \\ CHI \\ | \\ CH_2I \end{array}} \rightarrow \underset{\text{Allyl iodide}}{\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2I \end{array}} + I_2$$

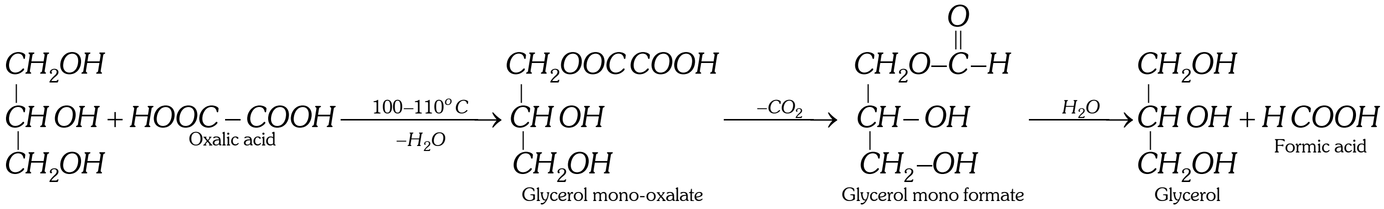
(b)



$$\underset{\text{Allyl iodide}}{\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2I \end{array}} + HI \rightarrow \underset{\text{Unstable}}{\begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CH_2I \end{array}} \xrightarrow{-I_2} \underset{\text{Propene}}{\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array}} \xrightarrow{HI} \underset{\text{Isopropyl iodide}}{\begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CH_3 \end{array}}$$

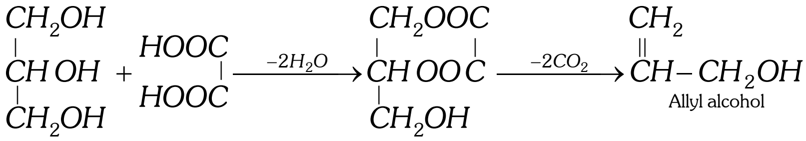
(v) ***Reaction with oxalic acid***

(a) At 110°C Glycerol is formed



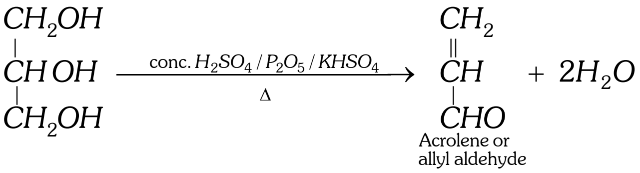
$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + \underset{\text{Oxalic acid}}{HOOC-COOH} \xrightarrow[-H_2O]{100-110^\circ C} \underset{\text{Glycerol mono-oxalate}}{\begin{array}{l}CH_2OOCCOOH\\|\\CHOH\\|\\CH_2OH\end{array}} \xrightarrow{-CO_2} \underset{\text{Glycerol mono formate}}{\begin{array}{l}CH_2O-\overset{\overset{O}{\|}}{C}-H\\|\\CH-OH\\|\\CH_2-OH\end{array}} \xrightarrow{H_2O} \underset{\text{Glycerol}}{\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}} + \underset{\text{Formic acid}}{HCOOH}$$

(b) At 260°C, allyl alcohol is formed



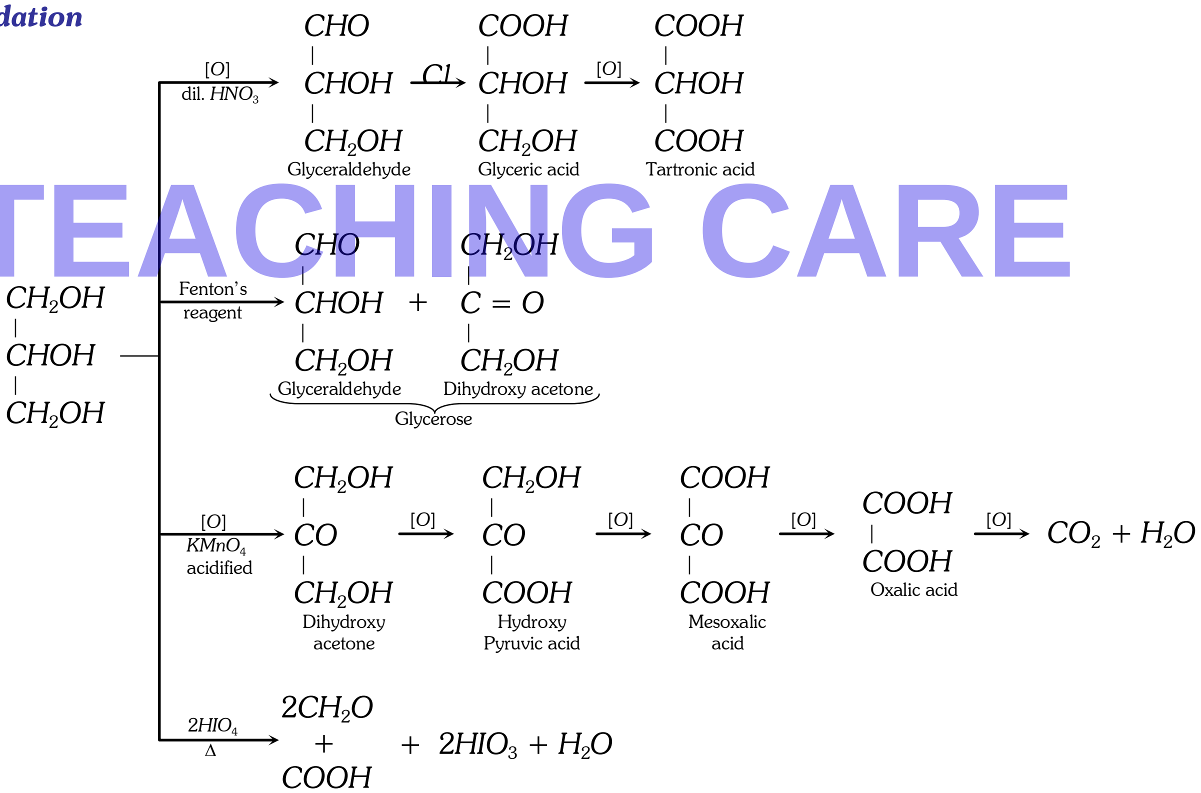
$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + \begin{array}{l}HOOC\\|\\HOOC\end{array} \xrightarrow{-2H_2O} \begin{array}{l}CH_2OOC\\|\qquad\quad|\\CHOOC\\|\\CH_2OH\end{array} \xrightarrow{-2CO_2} \underset{\text{Allyl alcohol}}{\begin{array}{l}CH_2\\\|\\CH-CH_2OH\end{array}}$$

(vi) **Dehydration :**



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow[\Delta]{\text{conc. }H_2SO_4/P_2O_5/KHSO_4} \underset{\text{Acrolene or allyl aldehyde}}{\begin{array}{l}CH_2\\\|\\CH\\|\\CHO\end{array}} + 2H_2O$$

(vii) **Oxidation**



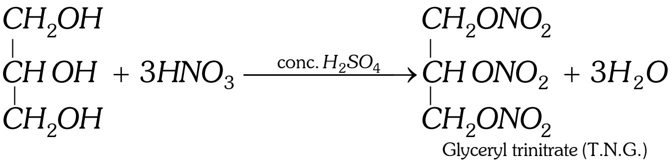
$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow[\text{dil. }HNO_3]{[O]} \underset{\text{Glyceraldehyde}}{\begin{array}{l}CHO\\|\\CHOH\\|\\CH_2OH\end{array}} \xrightarrow{Cl} \underset{\text{Glyceric acid}}{\begin{array}{l}COOH\\|\\CHOH\\|\\CH_2OH\end{array}} \xrightarrow{[O]} \underset{\text{Tartronic acid}}{\begin{array}{l}COOH\\|\\CHOH\\|\\COOH\end{array}}$$

$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow{\text{Fenton's reagent}} \underbrace{\underset{\text{Glyceraldehyde}}{\begin{array}{l}CHO\\|\\CHOH\\|\\CH_2OH\end{array}} + \underset{\text{Dihydroxy acetone}}{\begin{array}{l}CH_2OH\\|\\C=O\\|\\CH_2OH\end{array}}}_{\text{Glycerose}}$$

$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow[\text{acidified}]{[O]\ KMnO_4} \underset{\text{Dihydroxy acetone}}{\begin{array}{l}CH_2OH\\|\\CO\\|\\CH_2OH\end{array}} \xrightarrow{[O]} \underset{\text{Hydroxy Pyruvic acid}}{\begin{array}{l}CH_2OH\\|\\CO\\|\\COOH\end{array}} \xrightarrow{[O]} \underset{\text{Mesoxalic acid}}{\begin{array}{l}COOH\\|\\CO\\|\\COOH\end{array}} \xrightarrow{[O]} \underset{\text{Oxalic acid}}{\begin{array}{l}COOH\\|\\COOH\end{array}} \xrightarrow{[O]} CO_2 + H_2O$$

$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow[\Delta]{2HIO_4} \begin{array}{c}2CH_2O\\+\\COOH\end{array} + 2HIO_3 + H_2O$$

(viii) **Reaction with nitric acid :**



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + 3HNO_3 \xrightarrow{\text{conc. }H_2SO_4} \underset{\text{Glyceryl trinitrate (T.N.G.)}}{\begin{array}{l}CH_2ONO_2\\|\\CHONO_2\\|\\CH_2ONO_2\end{array}} + 3H_2O$$

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Dynamite is prepared from T.N.G.

Dynamite : A mixture of T.N.G. and glyceryl dinitrate absorbed in kieselguhr is called dynamite. It was discovered by Alfred. Nobel in 1867. It releases large volume of gases and occupy 10,900 times the volume of nitroglycerine.

$$C_3H_5(ONO)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$$

Blasting gelatin : A mixture of glyceryl trinitrate and cellulose nitrate (gun cotton).

Cordite : It is obtained by mixing glyceryl trinitrate with gun cotton and vaseline it is smokeless explosive.

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