

CHAPTER-3

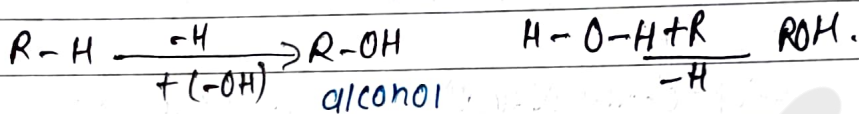
Alcohols

DATE

Introduction:-

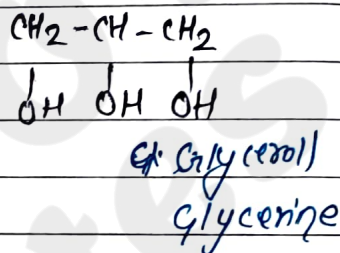
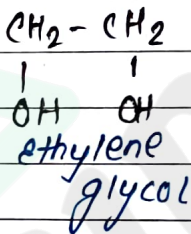
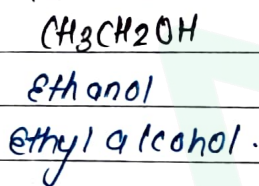
The hydroxy derivatives of aliphatic hydrocarbon obtained by the replacement of 1 or more hydrogen atoms of the aliphatic hydrocarbons by the same number of -OH (hydroxy group) from the different carbon atoms called alcohol.

General representation:- $C_nH_{2n+1}OH$



alkane

Example:-

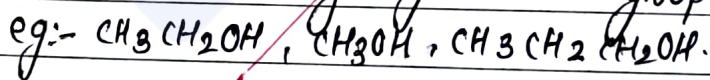


classification of alcohol:-

Alcohols are chemically classified into monohydric, dihydric, trihydric and polyhydric on the basis of number of -OH group present in molecule.

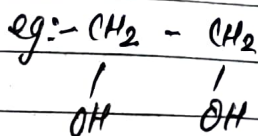
1. Monohydric alcohol \rightarrow

Containing only one -OH group in the molecule



2. Dihydric alcohol \rightarrow

Containing two OH-group in the molecule.



ethylene glycol
ethane-1,2-diol

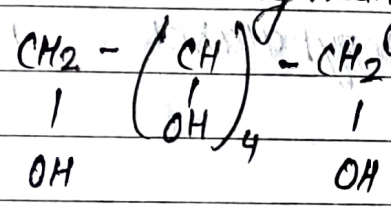
classmate

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3. Trihydric alcohol \rightarrow
 containing 3 - OH group in a molecule.
 eg:- $\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ | \quad | \quad | \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$

Glycerol / Glycerine

4. Polyhydric alcohol \rightarrow
 containing many - OH groups in a molecule.

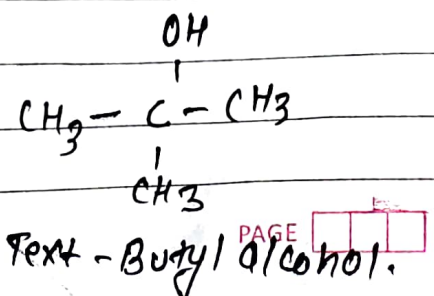
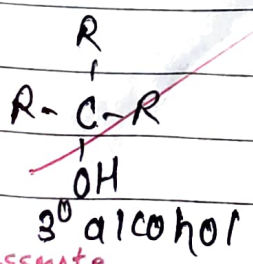
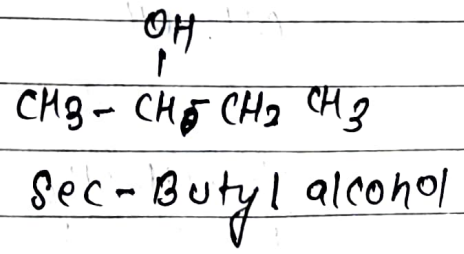
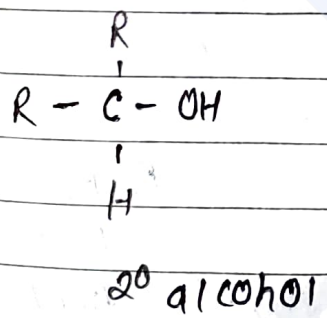
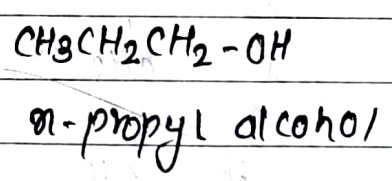
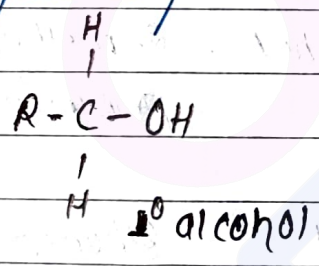


eg:- Mannitol / Sorbitol

Classification of Monohydric alcohol

General formula

Example.



Nomenclature:-

Prefix + suffix word root + suffix.

Alkanol + ol

General formula	Common name	IUPAC
CH_3OH	Methyl alcohol	Methanol
$\text{CH}_3\text{CH}_2\text{OH}$	Ethyl alcohol	Ethanol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	n-propyl alcohol	1-propanol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{OH} \end{array}$	ISO-propyl alcohol	Propan-2-ol
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_2\text{CH}_3 \end{array}$	Sec-butyl alcohol	Butan-2-ol.
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_2\text{OH} \end{array}$	ISO-butyl alcohol	2-methyl propan-1-ol.
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	Tert-butyl alcohol	2-methyl propan-2-ol
$\begin{array}{cc} \text{CH}_2 - \text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	Ethylene glycol	Ethane-1,2-diol
$\begin{array}{ccc} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	glycerol	Propane-1,2,3-triol

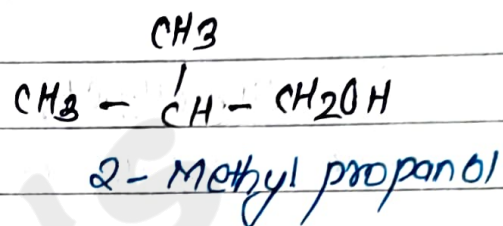
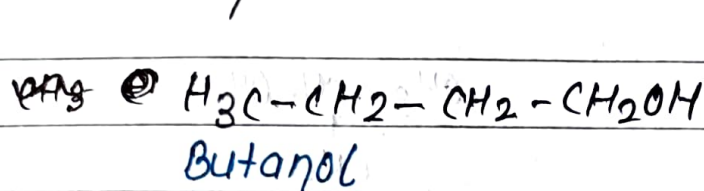
Isomerism in alcohol:-

Alcohol shows chain, positional and functional isomerism

→ Alcohol shows functional isomerism with ether.

1. Chain isomerism → Alcohols containing more than three carbon atoms exhibit chain isomerism.

Molecular formula: $C_4H_{10}O$ (possible isomer)

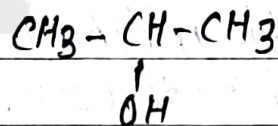
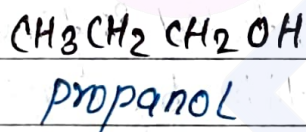


chain isomer

→ It differs in the length of carbon chain.

2. Position isomerism → Alcohols containing more than two carbon atoms exhibit position isomers

Molecular formula: C_3H_8O

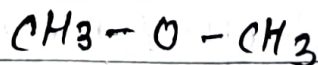
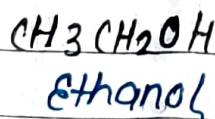


propan-2-ol

→ Differ in position of -OH group in the chain.

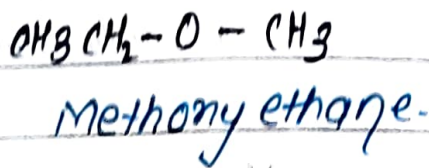
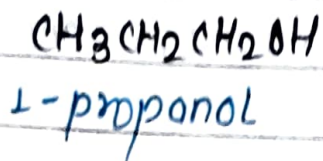
3. Functional isomerism → It differs in the functional group of two compounds. Alcohol shows functional isomerism with ether.

1) C_2H_6O

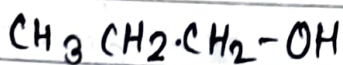
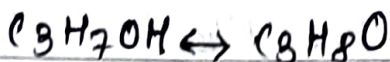
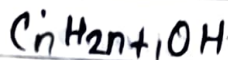


methoxymethane (dimethyl ether)

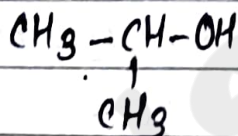
Q) C_3H_8O



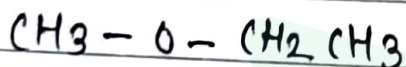
Q.N Write the possible isomer of C_3H_8O with their IUPAC name.



IUPAC: propan-1-ol



propan-2-ol



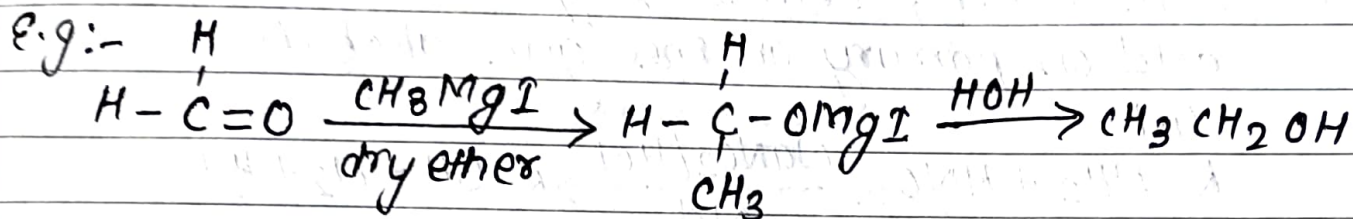
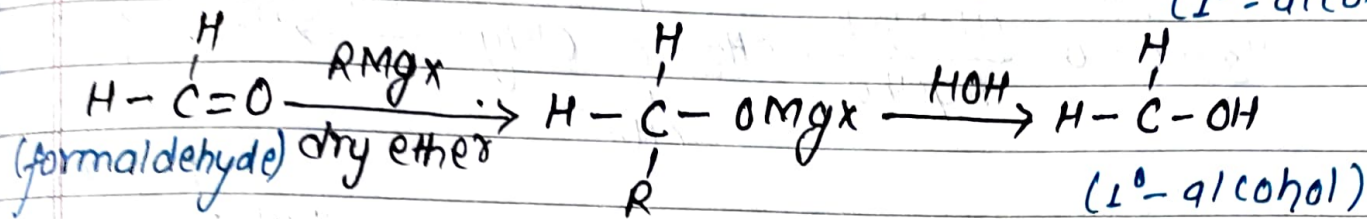
IUPAC: methoxy ethane

VI # Distinction of 1° , 2° and 3° alcohol by Victor Meyer's method.

→ Victor Meyer's method is one of the most convenient method for the distinction of 1° , 2° and 3° alcohol. In this method, the alcohol to be tested is first converted into corresponding alkyl iodide by reacting with red phosphorous and iodine or HI then it is reacted with silver nitrate ($AgNO_3$). Now the solution is allowed to react with nitrous acid (HNO_2) obtained by the action of $NaNO_2$ and HCl . Finally the solution is made alkaline by adding excess KOH solution.

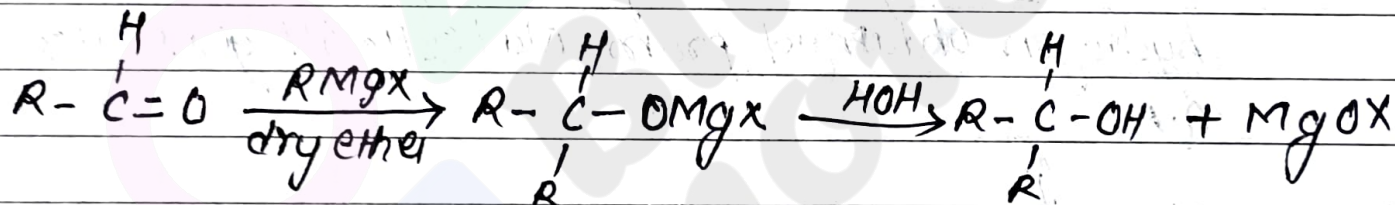
In doing so, if blood red colouration is observed it indicates primary alcohol, if blue colouration is observed it indicates 2° alcohol. If colourless solution is observed it indicates 3° alcohol. ✓

Imp
 (I) Formaldehyde with Grignard reagent gives primary alcohol:
 (1° -alcohol)

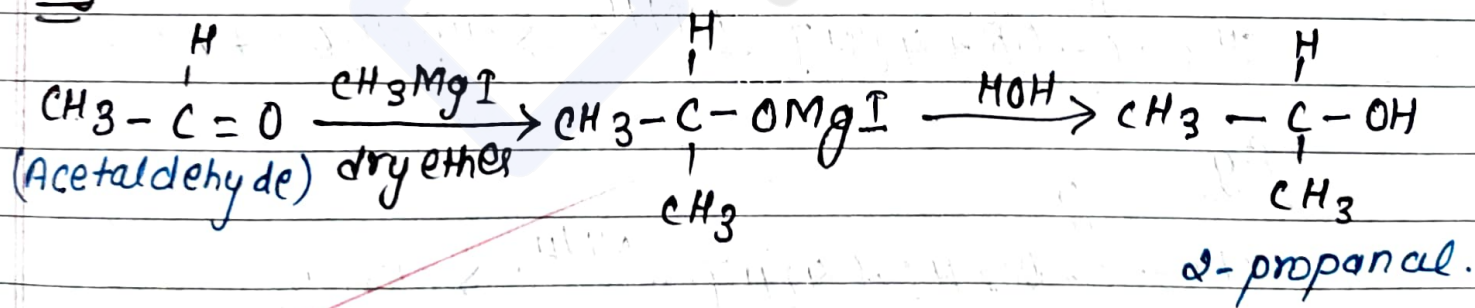


(II) Aldehydes other than formaldehyde gives with Grignard reagent gives secondary alcohol (2° -alcohol)

eg G.R

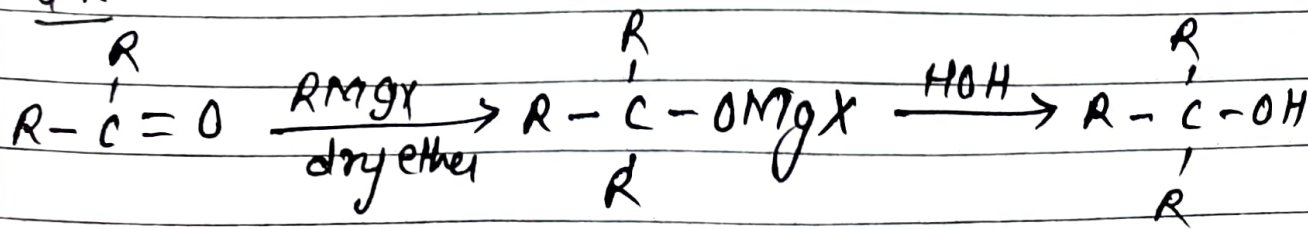


E.g

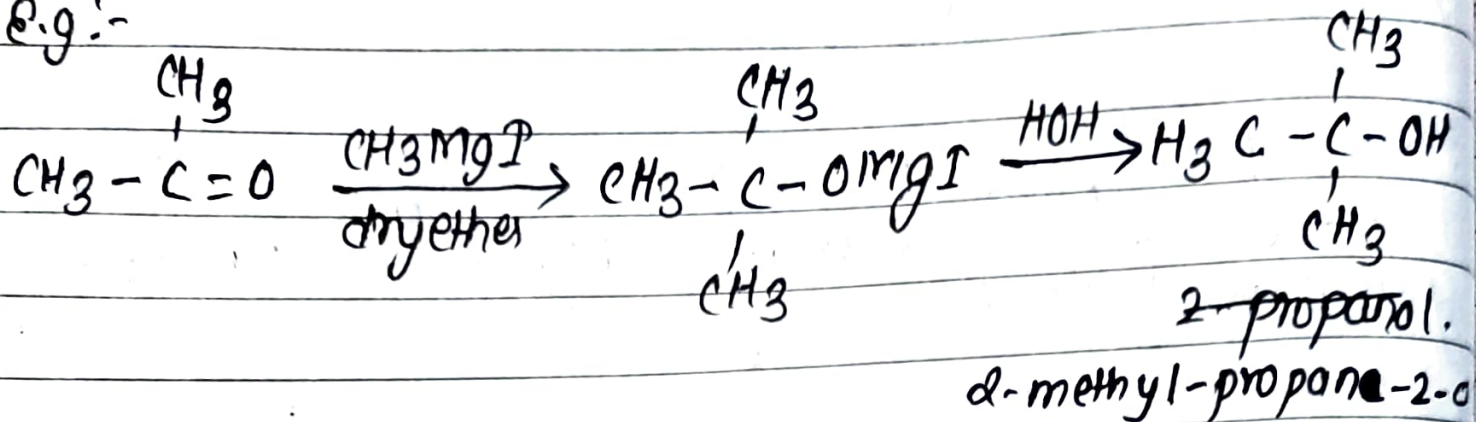


(III) Ketones with Grignard reagent give tertiary alcohol (3°)

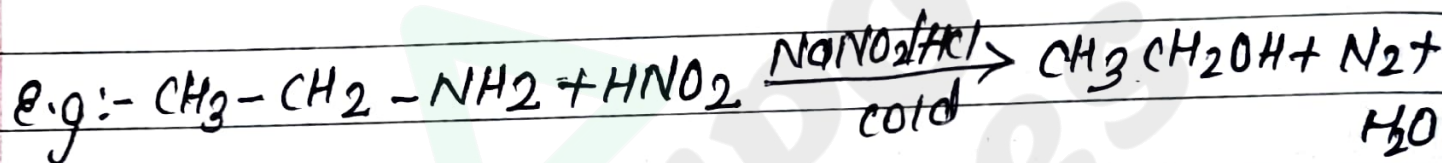
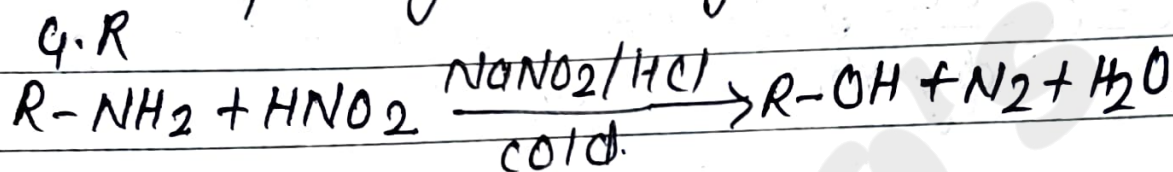
G.R



E.g.:-

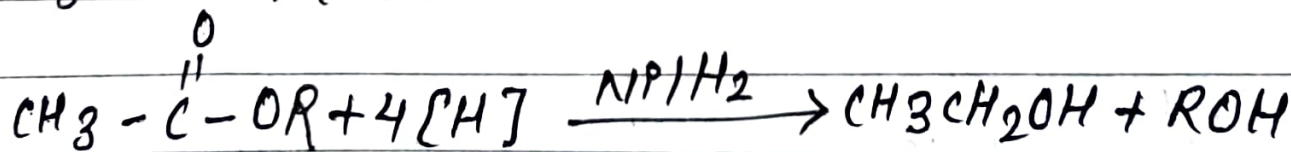
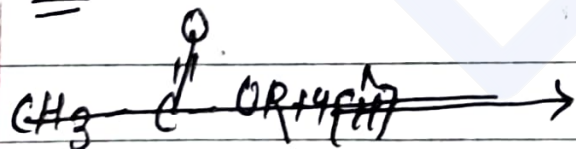


3) From primary amines \rightarrow By the action of nitrous acid on primary amines gives alcohol.

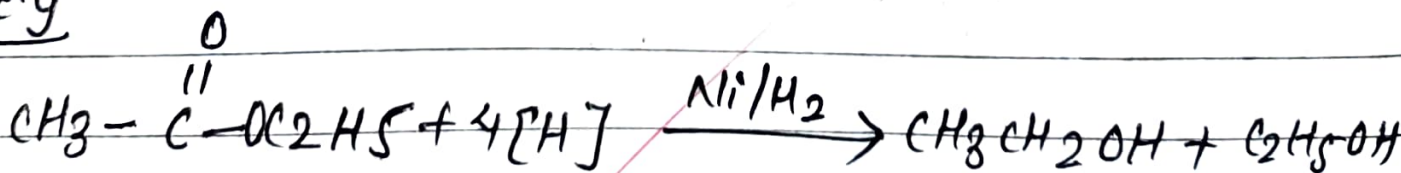


(4) From reduction of esters \rightarrow By reduction of ester with H_2 in presence of Ni or Pb or Pt or Pd as catalyst hydrogen obtained from $\text{Na/C}_2\text{H}_5\text{OH}$ gives alcohol

G.R:-



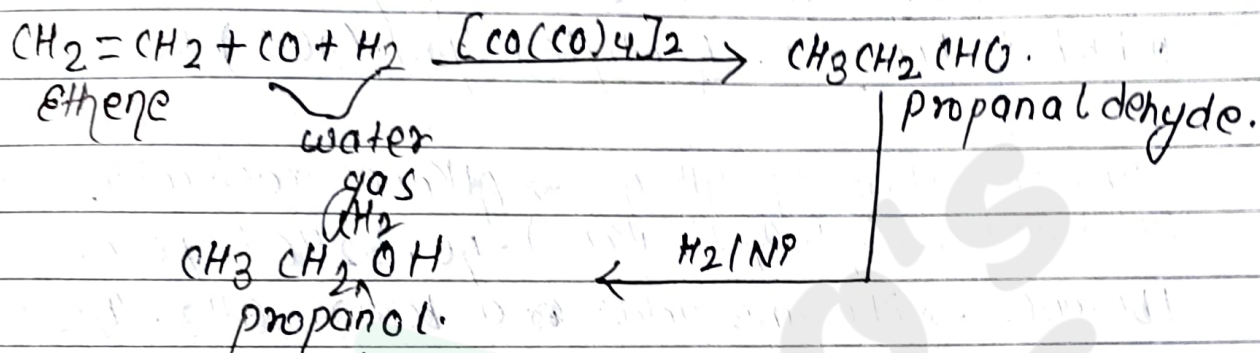
E.g



Industrial preparation of ethanol →

1) Oxo-process:

In this process alkene reacts with water gas ($\text{CO} + \text{H}_2$) in presence of cobalt carbonyl catalyst under high pressure to give aldehyde which on catalytic hydrogenation gives alcohol.



- Note: Methyl and ethyl alcohol cannot be prepared by this method.

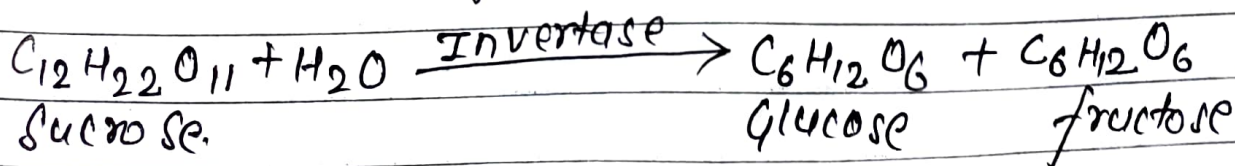
(2) Fermentation of sugar:-

Fermentation is a process in which complex compounds are broken into simpler compounds by the action of enzymes. Alcohols are obtained by fermentation of sugar and starch.

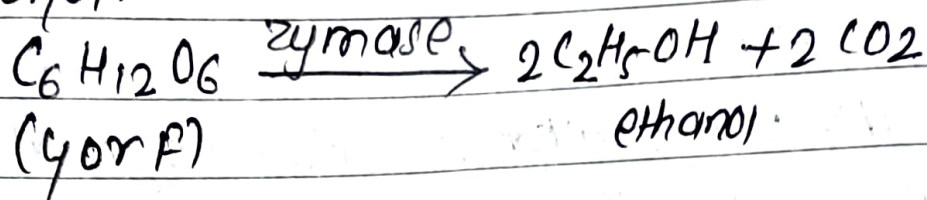
It is the oldest method for the preparation of alcohol.

The mother liquor left after crystallization of sugar is called molasses. It is a rich source of sugar like fructose, glucose and sucrose. It is diluted with water to about 10% sugar contents and yeast is added to it.

The enzyme invertase present in the yeast converts sucrose into glucose and fructose.

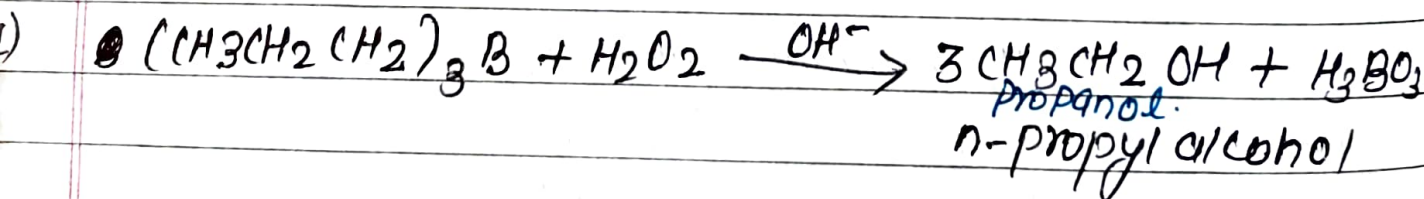
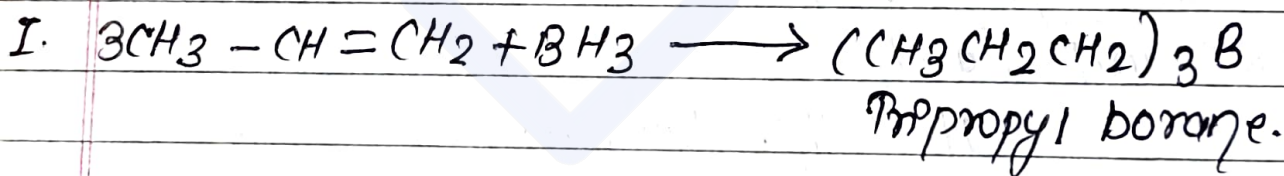


The enzymes zymase convert glucose and fructose to alcohol.



The fermentation completes in 5 days. The fermented liquor contains 8-10% ethanol is called wash. The wash on fractional distillation gives 96.5% ethanol, which is known as Rectified spirits (96.5) %.

(3) Hydroboration of Alkenes → Alkenes react with diborane (used for the prepⁿ of 1° alcohol) - i.e., B₂H₆ to form trialkyl boranes. Diborane adds as borane, BH₃. The positive part of BH₃ is the boron, the negative part is hydrogen. Trialkyl boranes are used for making primary alcohols by reaction with alkaline aqueous solution of hydrogen peroxide.

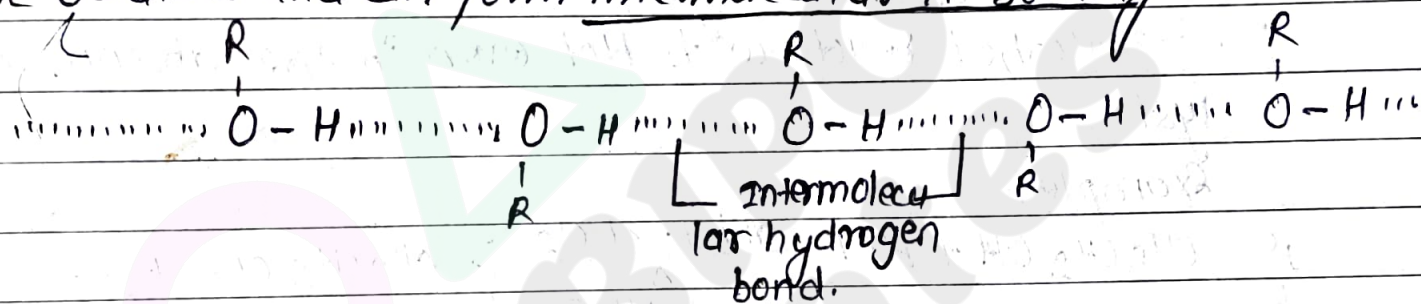


→ The overall result of the above reaction appears to be anti-Markovnikov addition of H₂O to a double bond.

Physical properties of Monohydric alcohols:-

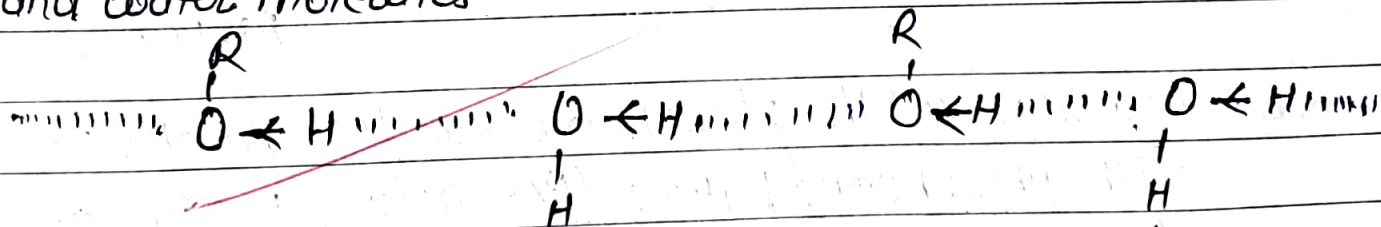
(1) Physical state: \rightarrow Lower alcohols are colorless, volatile and toxic liquid having alcoholic smell and burning nature. Higher members are colorless and odourless waxy solids.

(2) Boiling point \rightarrow Alcohols have higher bpt. than that of corresponding alkanes, alkyl halides and ethers. It is because in alcohols the H-atom is directly bonded to the highly electronegative O-atom and can form intermolecular H-bonding.



\Rightarrow Among isomeric alcohols, as branching increases bpt decreases.

(3) Solubility: \rightarrow Lower alcohols (C_1 to C_3) are completely soluble in water. It is due to formation of H-bonds between alcohol and water molecules.



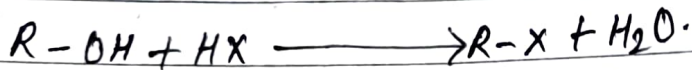
(4) Density: Alcohols are lighter than water.

Chemical properties

A. Cleavage of $R-OH \rightarrow R^+ + OH^-$

1a) Reaction with Hydrogen halide:- Alcohols react with hydrogen halides to give alkyl halides.

General reaction:

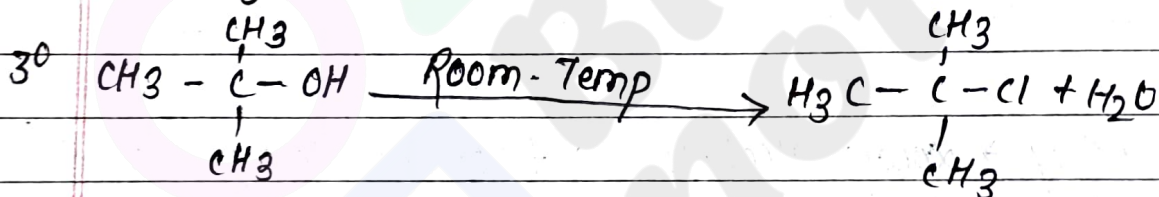
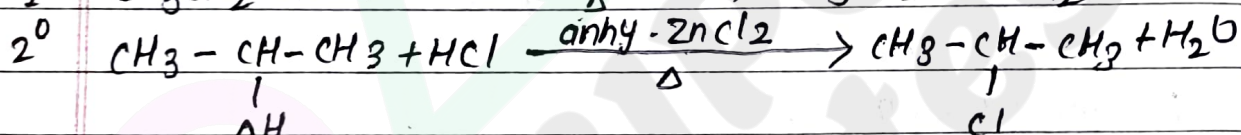
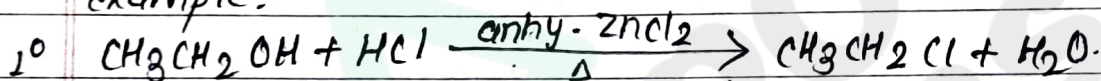


The order of reactivity is $3^\circ > 2^\circ > 1^\circ$ alcohol and $HI > HBr > HCl$ which increases with the size of halogen atom.

°- 1° and 2° alcohol react with HCl in the presence of anhydrous $ZnCl_2$ as catalyst.

°- 3° alcohol react with HCl even in the absence of catalyst.

Example:-

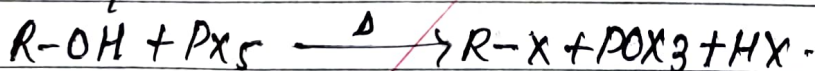


3° (2-methyl-2-propanol)

2-chloro-2-methylpropane

(b) Reaction with phosphorus halide:- Alcohol reacts with phosphorus halide (PX_5 or PX_3) to give alkyl halide.

General reaction:

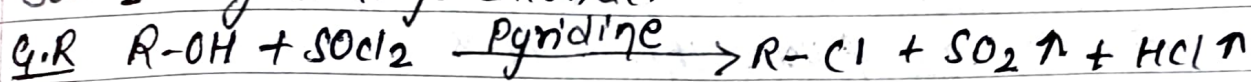


Example:

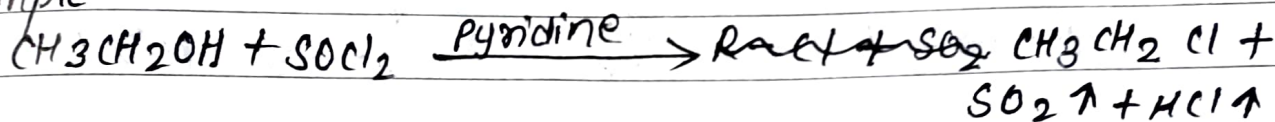


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① Reaction with (SOCl_2) thionyl chloride \rightarrow Alcohols react with SOCl_2 to give alkyl chloride.



Example



\rightarrow This is most suitable method to prepare alkyl halide because side products are gases easily escape out leaving alkyl halide in pure form.

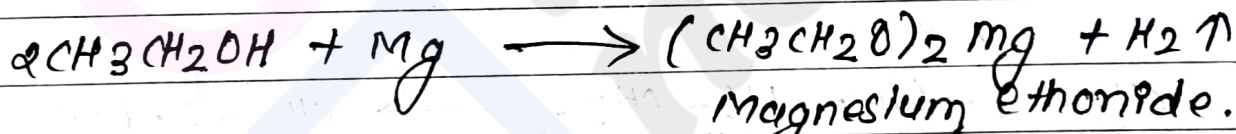
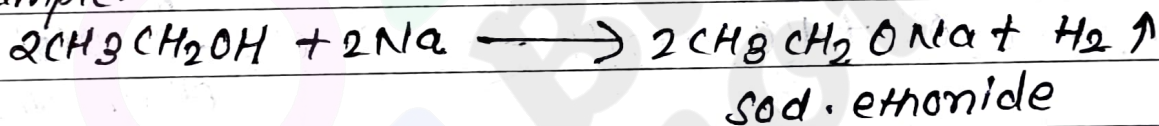
② Reaction with reactive metals like Na, K, Li \rightarrow

Alcohols react with highly reactive metals like Na, K, Li , Mg, Al etc to evolve H_2 gas and form metal alkoxide.

G.R :-

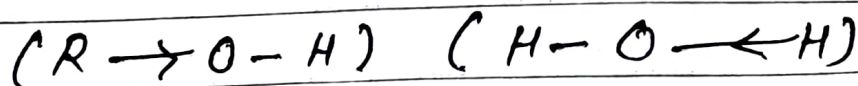


Example:-

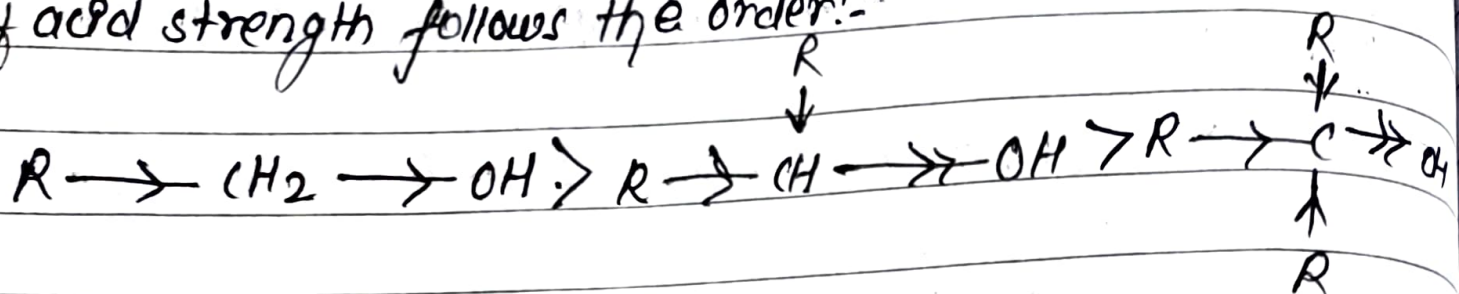


Potassium methoxide.

\rightarrow In this reaction alcohol act as weak acid. It's because of high electronegativity of O-atom. But the alcohols are weaker acid than water it is due to presence of ~~weak~~ electron releasing alkyl group in the alcohols.

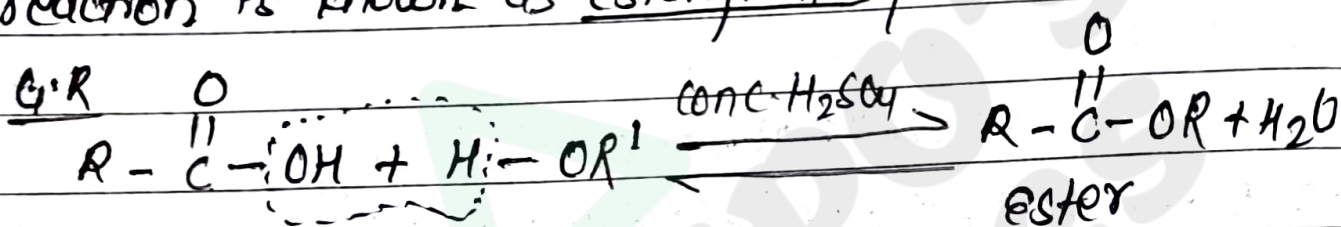


The acid strength of alcohol decreases with increase in the number of alkyl groups. Hence the order of acid strength follows the order:-



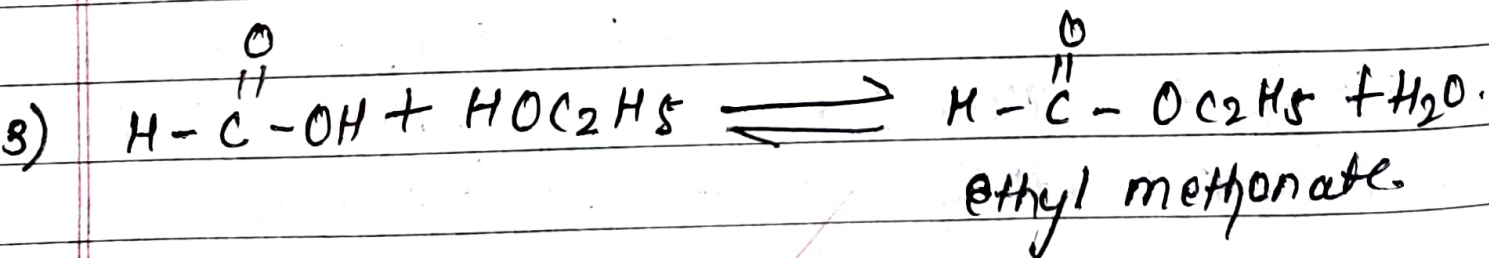
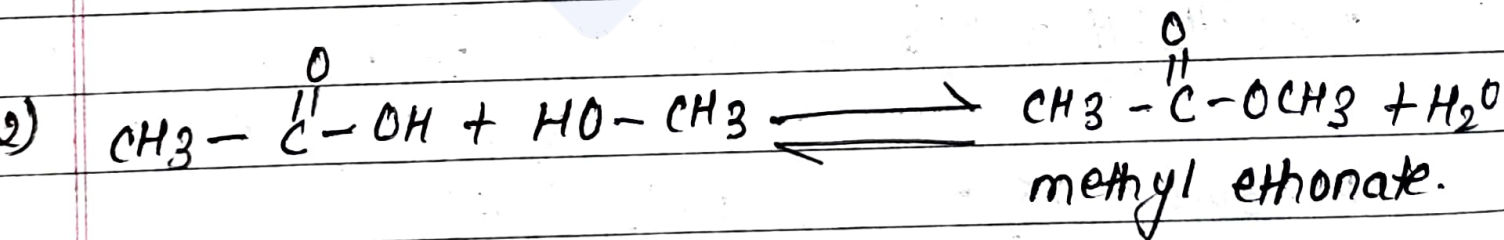
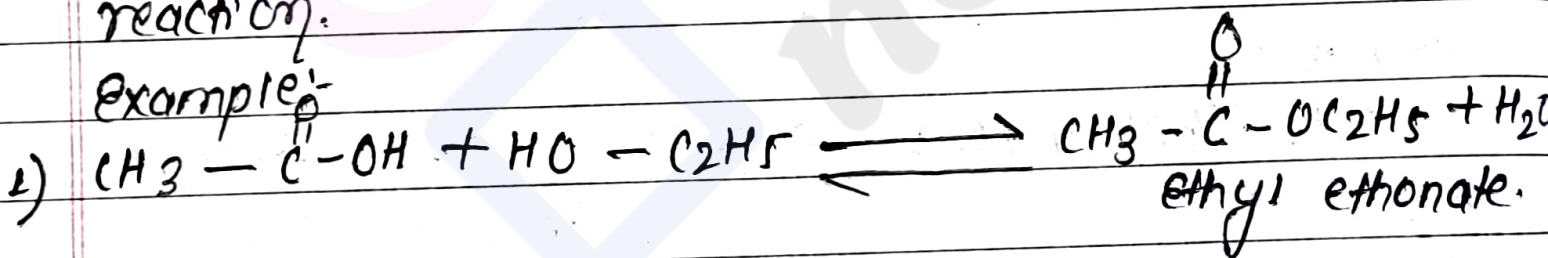
Esterification process:-

Alcohols when heated with carbonyl compound in the presence of conc. H_2SO_4 gives esters. This reaction is known as esterification.



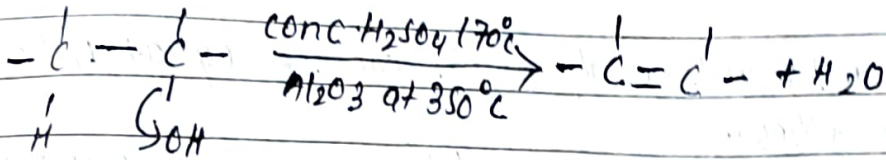
H_2SO_4 act as dehydrating agent and it's reversible reaction.

Example:-

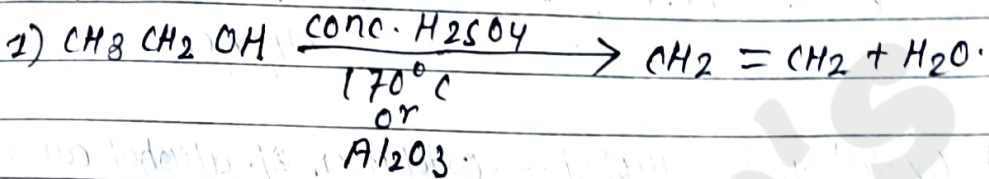


4) Dehydration of alcohol \rightarrow Alcohol when heated with conc. H_2SO_4 or their vapours are passed over heated alumina undergo dehydration to form alkene.

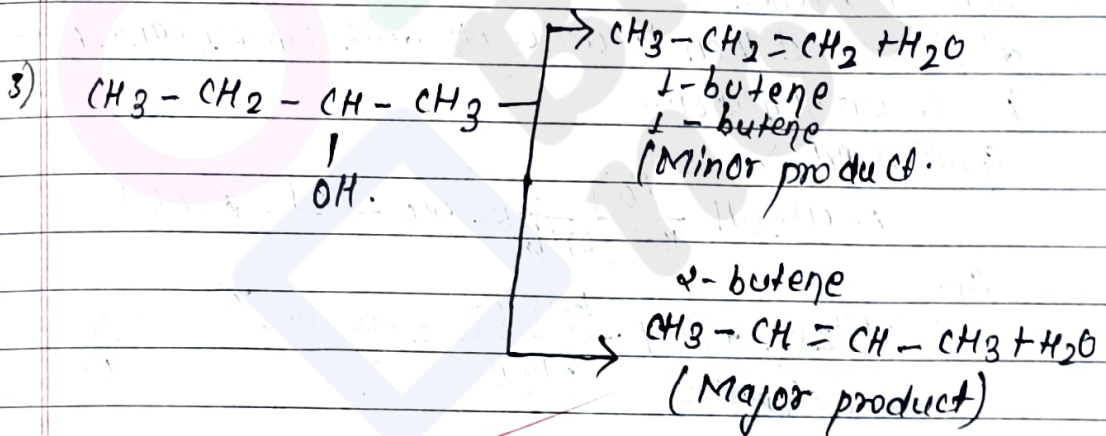
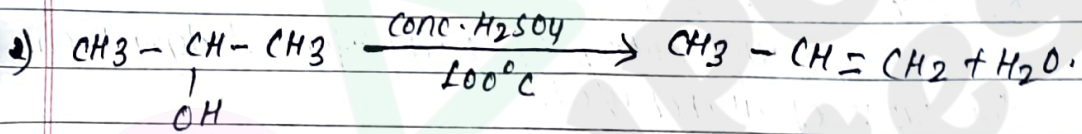
Q.R:-



Example:-



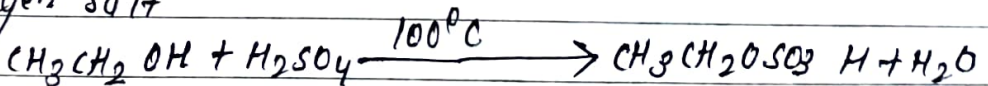
[Removal of OH and H takes at near by C-atom].



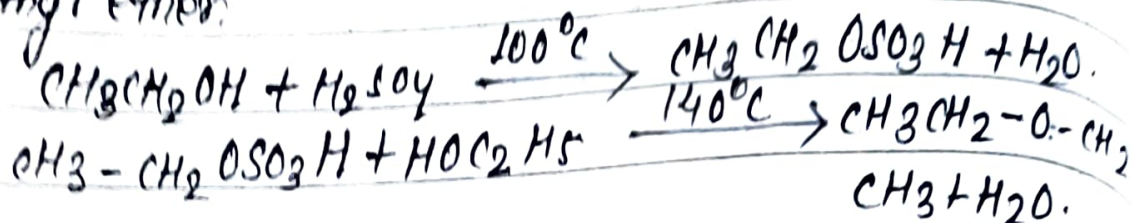
* Note:-

A) The reaction of ethanol with conc. H_2SO_4 gives different products under different conditions.

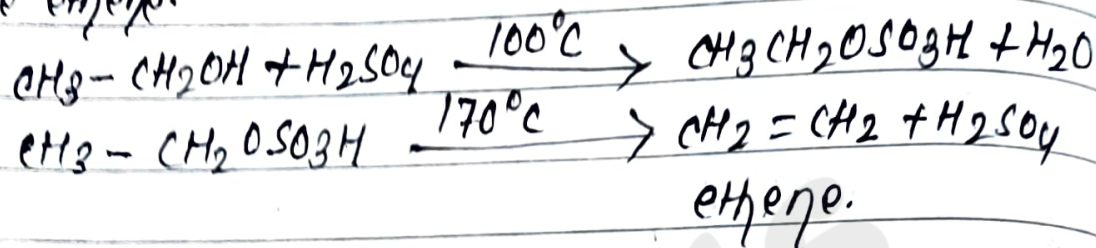
(I) Ethanol reacts with conc. H_2SO_4 at 100°C to give ethyl hydrogen sulfate



II) Excess ethanol reacts with conc. H_2SO_4 at $140^\circ C$ to give diethyl ether.



III) Ethanol reacts with excess conc. H_2SO_4 at $170^\circ C$ to give ethene.



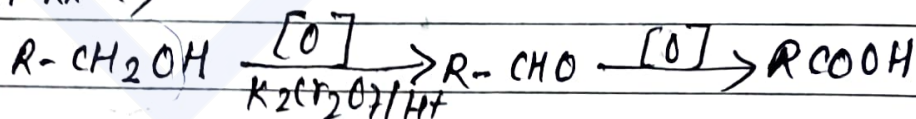
VIMP
4)

Oxidation of alcohol \rightarrow Oxidation of alcohol can be carried out with acidic or alkaline $KMnO_4$ or acidified $K_2Cr_2O_7$ or $Na_2Cr_2O_7$.

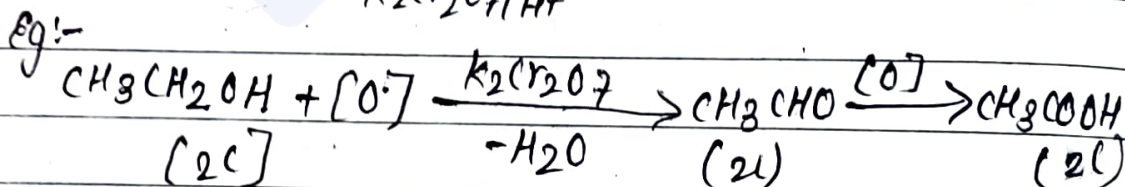
The nature of product formed depends on the types of alcohol used.

(I) primary alcohols (1°) are easily oxidised to aldehyde at first and then to carboxylic acids having same number of carbon atom.

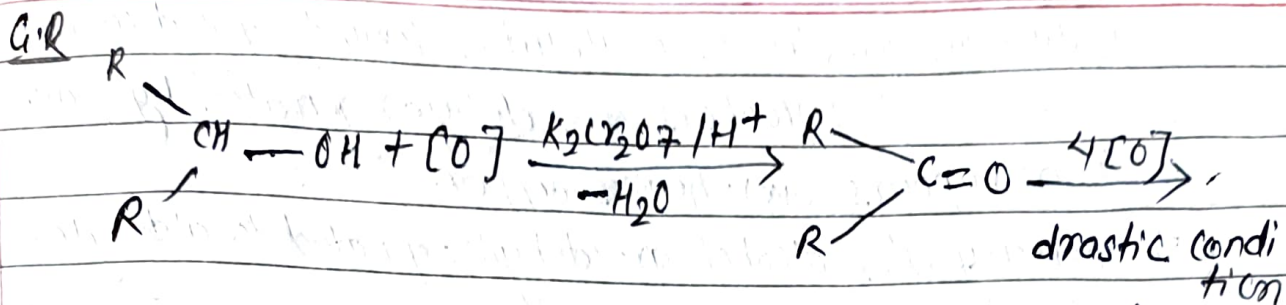
General Rxn \rightarrow



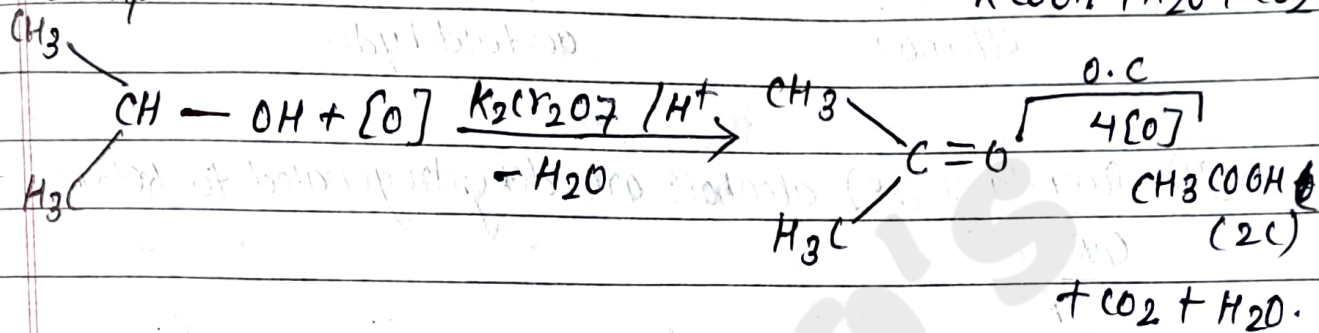
Eg:-



(II) 2° alcohol are easily oxidised to ketones having same no of carbon atoms. The ketones is further oxidised only under drastic condition to give carboxylic acid having less number of carbon atom.



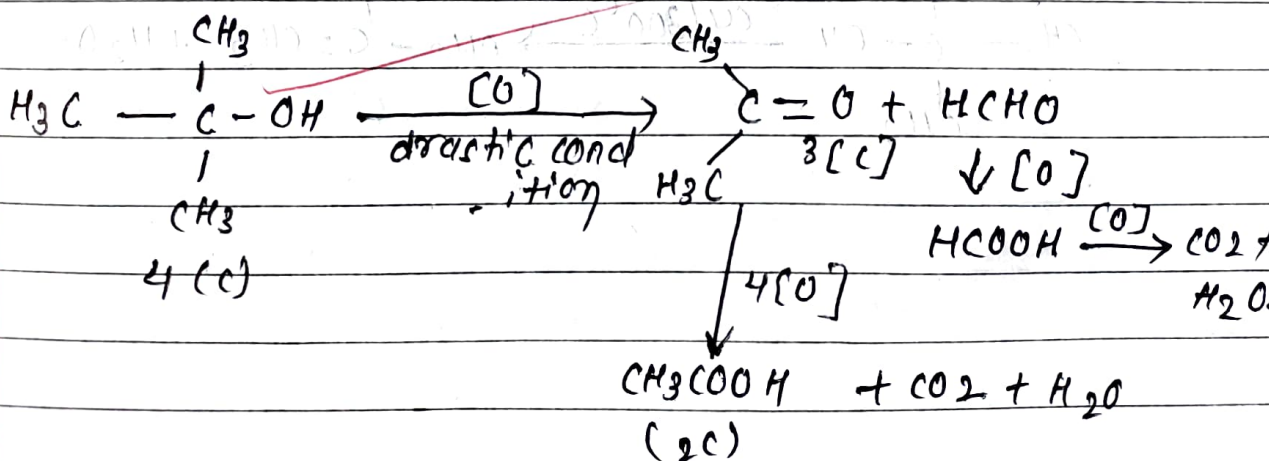
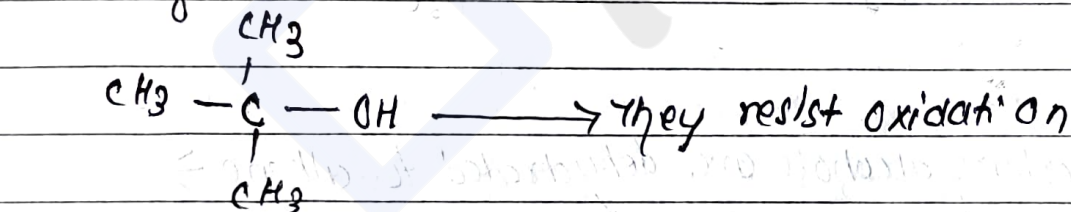
Example:-



III

III. Tertiary (3°) alcohol do not contain hydrogen in carbon carrying -OH (hydroxyl group) therefore they resist oxidation.

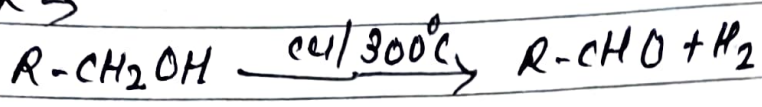
Under drastic condition they are oxidized to ketones having less number of carbon atom and then to carbonylic acids having less number of carbon atom.



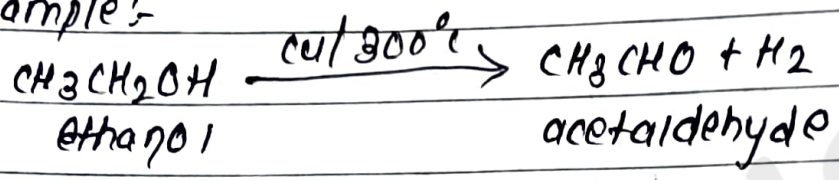
6. Reduction of alcohol (catalytic dehydrogenation).
Alcohols are dehydrogenated by passing their vapours over heated copper.

(I) primary (1°) alcohol are dehydrogenated to aldehyde.

G.R →

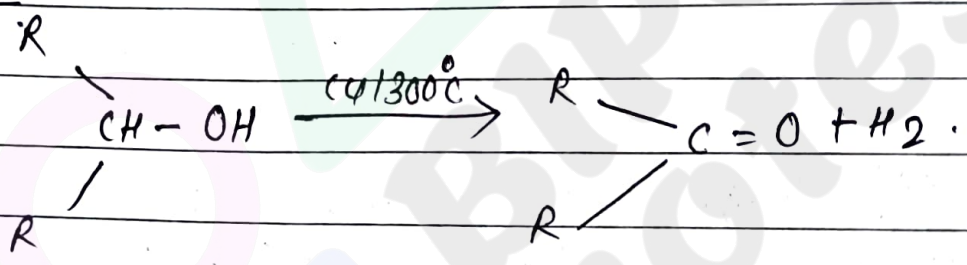


Example:-

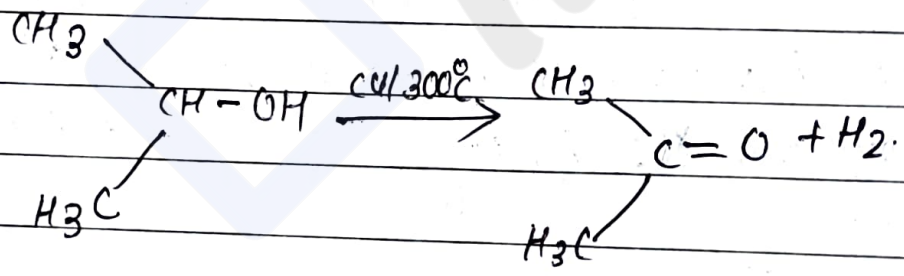


(II) Secondary (2°) alcohols are dehydrogenated to ketones

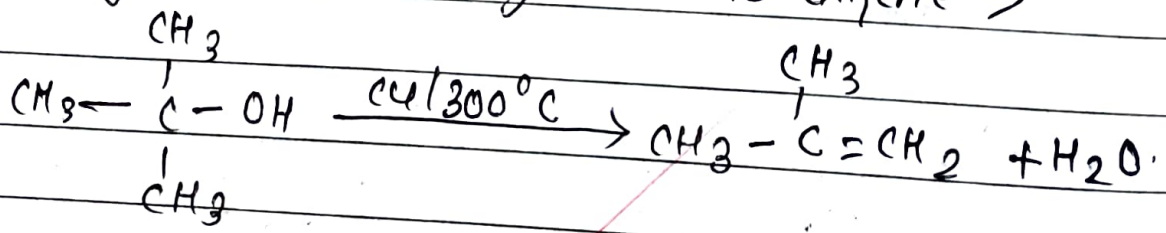
G.R



Example:-

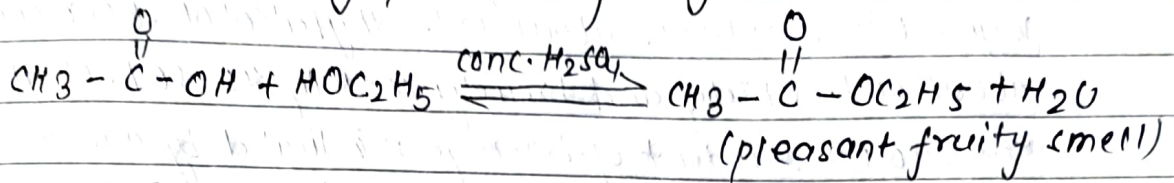


(III) tertiary alcohols are dehydrated to alkene →



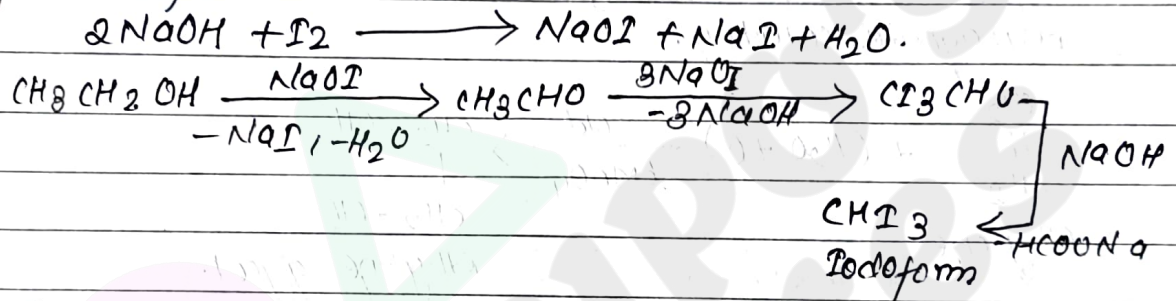
Laboratory Test of ethanol \rightarrow

① Esterification test:- Ethyl alcohol reacts with acetic acid and when heated in the presence of conc H_2SO_4 forms ester, ethyl acetate having pleasant fruity smell.



\rightarrow This test is given by ethanol & methanol.

② Iodoform test: \rightarrow In this test ethyl alcohol is warmed with iodine in the presence of alkali - pale yellow crystals of iodoform are formed.



\rightarrow This iodoform test is given by alcohols having $-CH_2OH$ - all methyl ketones and acetaldehyde but not by methanol.

* Absolute alcohol \rightarrow Absolute alcohol is 100% pure ethyl alcohol. It is obtained from rectified spirit by distillation.

* Denaturated or methylated spirit \rightarrow Ethyl alcohol is made unfit for drinking purpose by adding poisonous substances like methyl alcohol or acetone or pyridine, such alcohol is called denaturated alcohol.

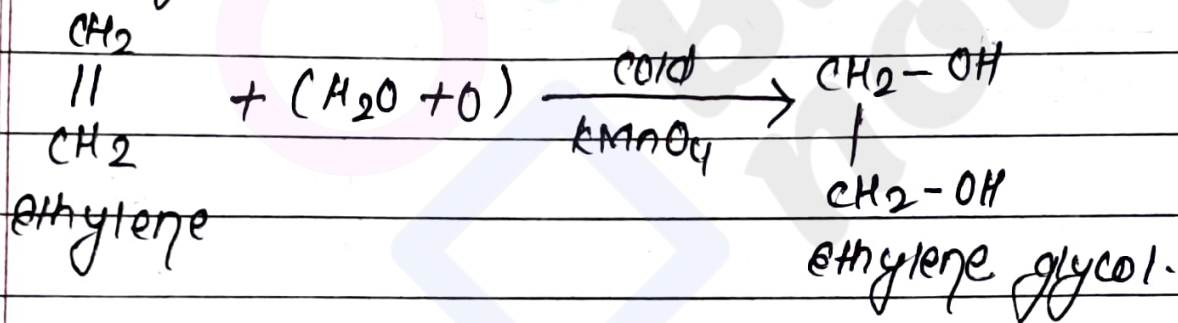
Wood spirit \rightarrow Methyl alcohol is called wood spirit. It is poisonous in nature. It causes blindness and death.

Rectified spirit \rightarrow ethyl alcohol containing 5% water and ethyl alcohol 95% is called rectified spirit.

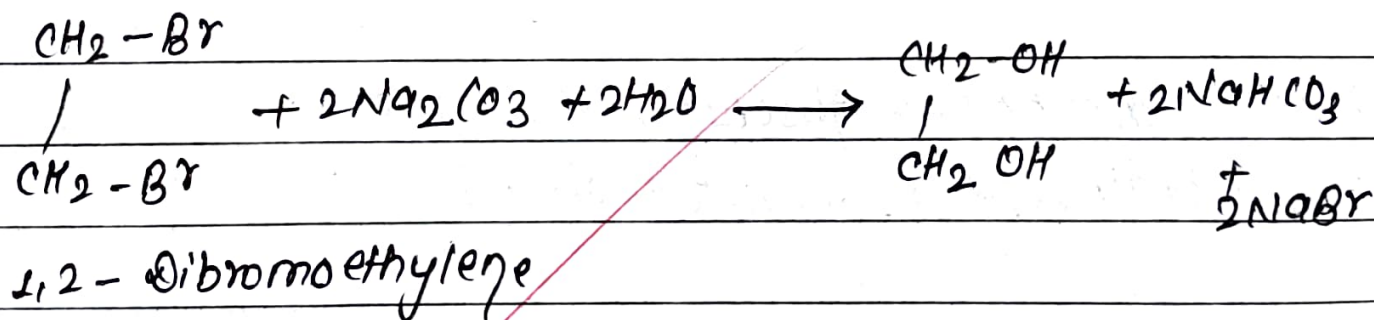
Alcoholic Beverage \rightarrow The largest use of ethyl alcohol is in beverages. Wines contain about 12% ethyl alcohol, Beer contains about 4%. Whisky and brandy contain 40-50% ethyl alcohol. The alcoholic content of beverage is indicated by a measure known as proof spirit.

Ethane-1,2-diol (Glycol) \rightarrow
preparation \rightarrow (2ab)

1. By passing ethene through cold and dilute alkaline potassium permanganate solution.

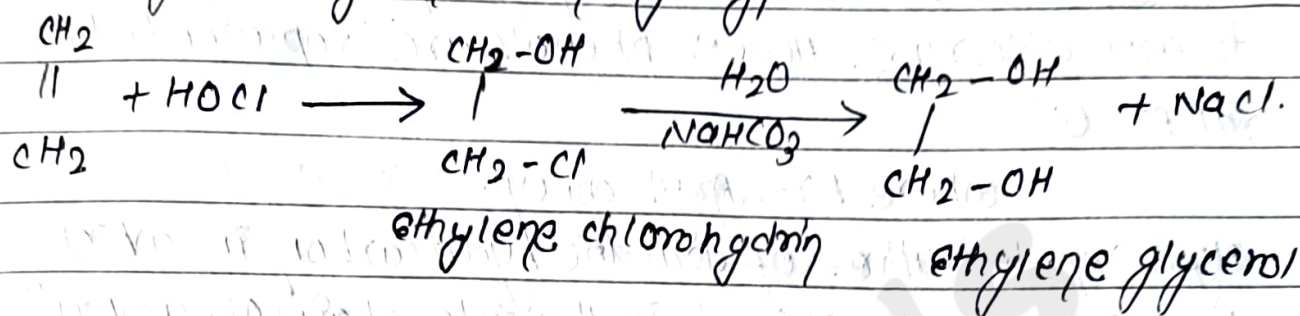


2. By hydrolysis of 1,2-dibromoethane with aqueous Na_2CO_3 solution

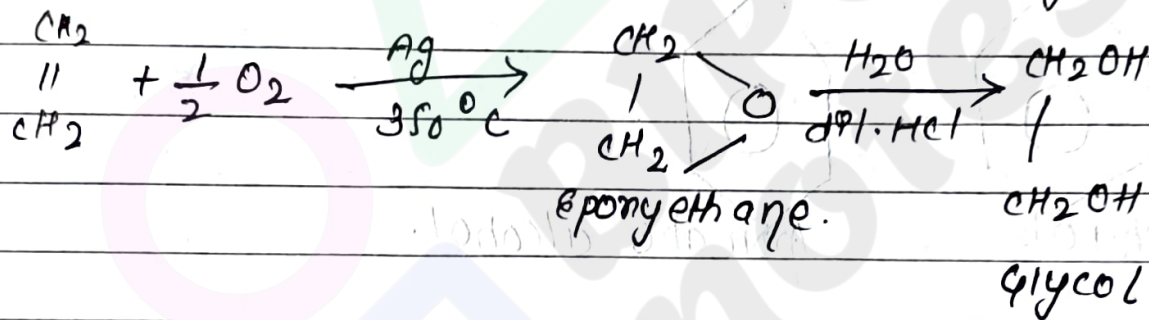


Industrial preparation:-

1. By the hydrolysis of ethylene chlorohydrin, which in turn is obtained by passing ethene through hypochlorous acid.



2. By the hydrolysis of epoxyethane which is in turn obtained by heating ethene with air in presence of silver (Ag) as catalyst.



Uses of ethylene glycol →







1. As an antifreeze for automobile radiators and a coolant for aeroplane motor.
2. In the manufacture of dacron (terylene) and other polymer.
3. As solvent for stamp pad ink.
4. In the preparation of nitroglycerol (explosive) and solvents like dioxane, cellosolve etc.
5. As lubricant and preservative.


Bipin Khatri

(Bipo)

Class 12 complete notes and paper collection.

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