

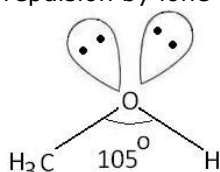
ALCOHOLS AND ETHERS

ALCOHOLS

Alcohols are the hydroxyl derivatives of aliphatic hydrocarbon in which the -OH group is attached to alkyl group.

ORBITAL STRUCTURE

- In alcohols, both carbon and oxygen atoms are sp^3 hybridised. Two of the four sp^3 hybridised orbitals of oxygen get involved in formation of σ -bond with hydrogen and carbon respectively where as rest of two sp^3 hybridised orbitals contain lone pair of electrons. C - O - H bond angle is found to be as 105° (rather than normal tetrahedral angle 109.5°) Deviation from normal angle can be explained on the basis of greater repulsion by lone pairs than bond pairs.



CLASSIFICATION OF ALCOHOLS

Alcohols can be classified as

- On the basis of number of hydroxyl groups

(1) Monohydric alcohol

Compounds in which hydrogen atom is replaced by one hydroxyl group.

CH_3OH : methyl alcohol

$(CH_3)_3C-OH$: Tert butyl alcohol

(2) Dihydric alcohol

$CH_2 - OH$ Compounds in which two hydrogen atoms are replaced by two hydroxyl groups.

$CH_2 - OH$

glycol

(3) Trihydric alcohol

$CH_2 - OH$ Compounds in which three hydrogen atoms are replaced by three hydroxyl groups.

$CH_2 - OH$

$CH_2 - OH$

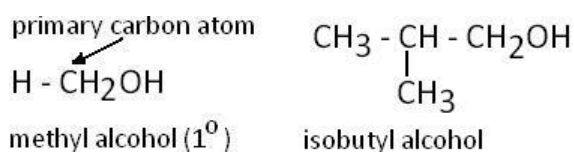
glycerol

CLASSIFICATION OF MONOHYDRIC ALCOHOLS

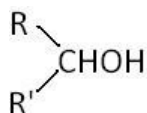
1) Compound containing sp^3 C - OH bond.

In these alcohols, the -OH group is attached to sp^3 -hybridised carbon atom of an alkyl group.

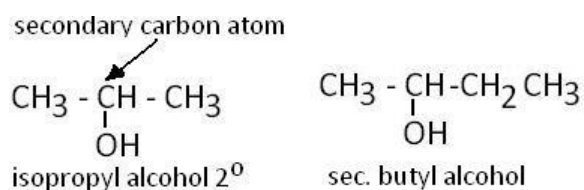
- (1) Primary alcohol(1°): In these alcohols, the hydroxyl group is attached with primary (1°) carbon atom. The general formula is $R-CH_2-OH$. R may be H or alkyl group



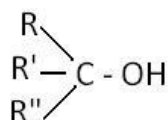
- (2) Secondary alcohol (2°): In these alcohols, the hydroxyl group is attached with secondary (2°) carbon atom. The general formula is



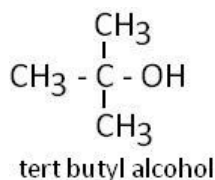
R and R' may be same or different



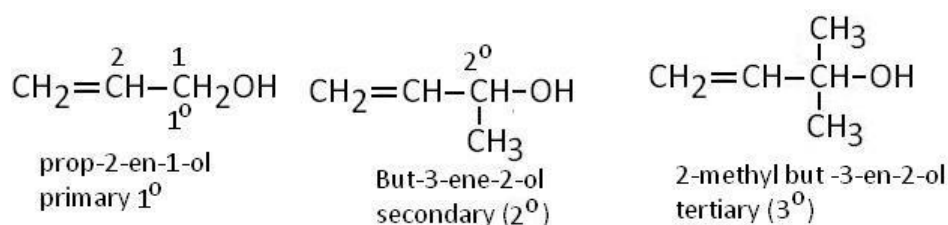
- (3) Tertiary alcohol (3°): In these alcohols, the hydroxyl group is attached with, tertiary (3°) carbon atom. General formula is



R, R', R'' may be same or different



- (4) Allylic alcohol : In these alcohol, the -OH group is attached to an sp^3 hybridized carbon next to the carbon-carbon double bond. i.e. to an allylic carbon



- (5) Benzylic alcohols:

In these alcohols, the -OH group is attached to an sp^3 - hybridized carbon atom next to an aromatic ring.

- (2) Compound containing sp^2 C-OH bond

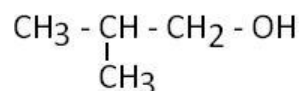
In these alcohols, the -OH group is attached to a carbon atom of double bond i.e. vinylic carbon

$\text{CH}_2 = \text{CH} - \text{OH}$ (vinyl alcohol, unstable)

ISOMERISM IN ALCOHOLS

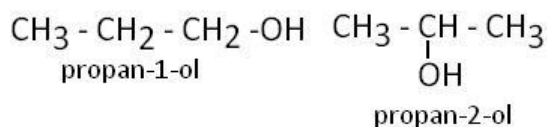
- (1) Chain isomerism : Alcohols containing four or more carbon atoms exhibit chain isomerism in which the isomers differ in the chain of carbon atoms attached to the hydroxyl group

$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$ (Butan - 1 -ol)



2-methylpropan-1-ol

- (2) Position isomerism : Alcohols containing three or more carbon atoms show position isomerism in which the isomers differ in the position of hydroxyl group when carbon chain is the same

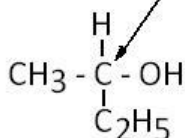


- (3) Functional group isomerism: Saturated monohydric alcohols containing two or more carbon atom show functional isomerism with ethers e.g.

$\text{CH}_3 - \text{CH}_2 - \text{OH}$ (ethanol) and $\text{CH}_3 - \text{O} - \text{CH}_3$ (methoxymethane)

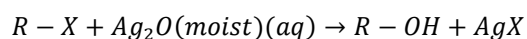
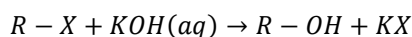
Besides the structural isomerism, alcohols having asymmetric carbon atom exhibit optical isomerism e.g.

asymmetric carbon atom

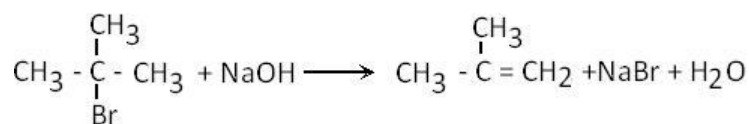


GENERAL METHOD OF PREPARATION OF ALCOHOL

1. Hydrolysis of alkyl halide

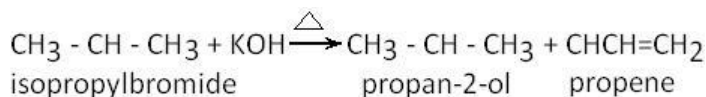


- This method is not satisfactory for preparing alcohol because haloalkanes are themselves obtained from alcohols and in higher halides, the alkenes are formed as side products.
- However, satisfactory results are obtained by using moist silver oxides (AgOH)
- Primary alkyl halides give good yield of alcohols, while tertiary butyl halides mainly give alkenes due to dehydrohalogenation



tert.butylbromide

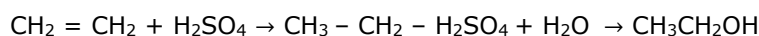
- Secondary(2°) alkyl halides give a mixture of alcohol and alkene



- Hydrolysis of 1° halides proceeds by S_N2 mechanism while those of 3° halides by S_N1 mechanism. The hydrolysis of 2° alkyl halides may proceed by S_N1 or S_N2 mechanism

2. Hydration of alkene

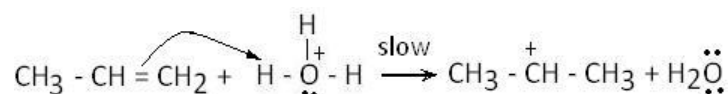
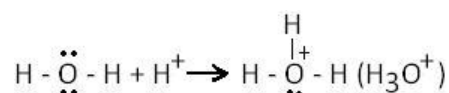
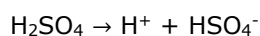
(1) Direct hydration



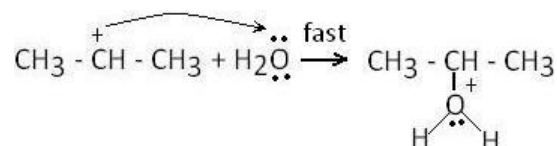
Mechanism:

The mechanism of acid catalysed addition of water (hydration) to alkenes involves the following steps:

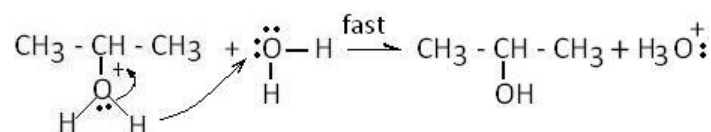
Step I: Electrophilic attack by hydronium ion (H₃O⁺) on alkene gives an intermediate carbocation



Step II: Nucleophilic attack by water on carbocation to yield protonated alcohol



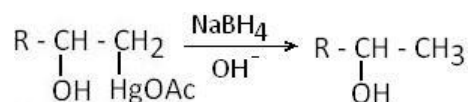
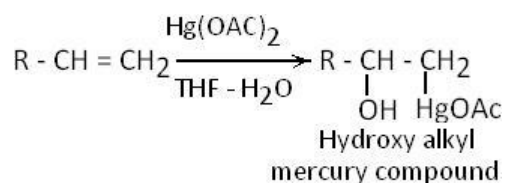
Step III: Deprotonation (loss of proton) to form an alcohol



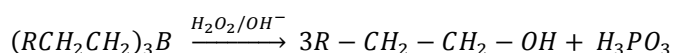
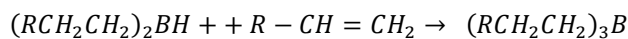
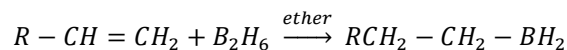
Addition of H₂SO₄ follows Markownikoff's rule

(2) Indirect hydration

(a) Oxymercuration-demercuration

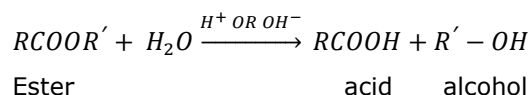


(b) Hydroboration – oxidation

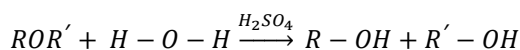


Reaction ultimately results in anti Markownikoff's addition of water.

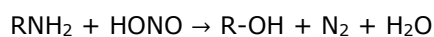
3. Hydrolysis of esters



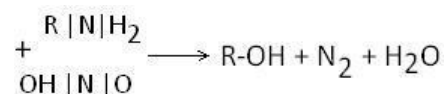
4. Hydrolysis of ethers



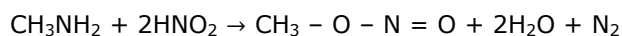
5. Action of nitrous acid (HONO) on primary amines



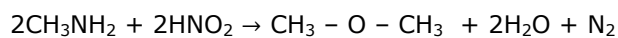
Or



- Methylamine does not yield methyl alcohol only, but in excess of nitrous acid the other products may be formed as, methyl nitrite or dimethyl ether

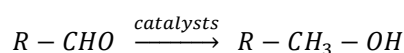
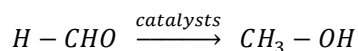


Methyl nitrite



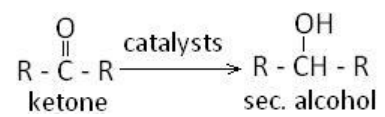
6. Reduction of aldehydes and ketones

Catalysts : H_2/Ni or Na/C_2H_5OH or $LiAlH_4$ or $NaBH_4$



Aldehyde

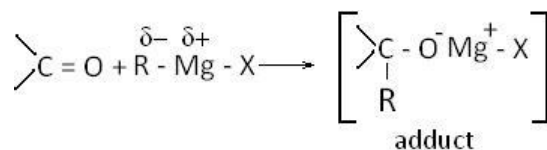
primary alcohol



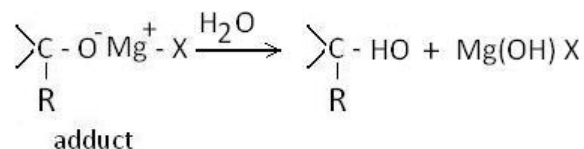
7. Action of Grignard reagents

It occurs in two steps

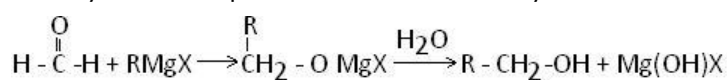
Step I : Nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct



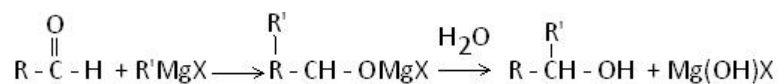
Step II : hydrolysis of adduct to yield alcohol



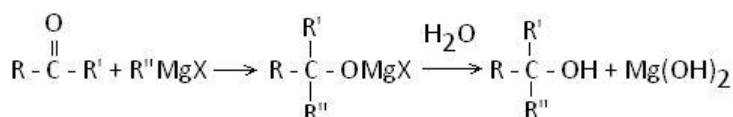
(i) Primary alcohol is produced with formaldehyde



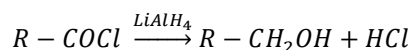
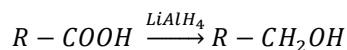
(ii) Secondary alcohol is obtained with other aldehydes



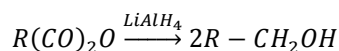
(iii) Tertiary alcohol is produced with ketones



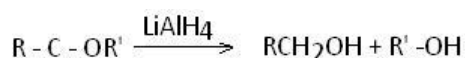
8. Reduction of carbonyl group including carboxylic acid and esters



Acid chloride



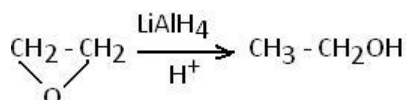
Acid anhydride



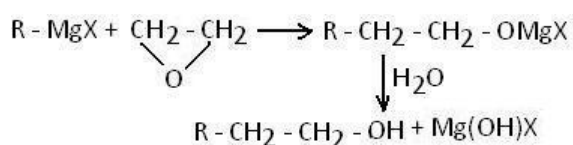
Reduction of carboxyl compounds and esters to alcohol by using alcoholic sodium is called Bouveault - Blanc reduction.

9. From epoxides

(i) Reduction

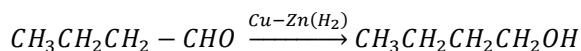
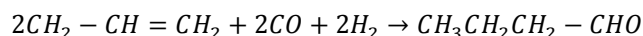


(ii) Action of Grignard reagent



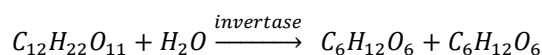
10. Oxo process

This reaction is also known as carbonylation or hydroformylation reaction

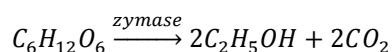


11. Fermentation of carbohydrates

(i) Molasses is the mother liquor after crystallization of sugar from sugar solution

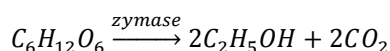
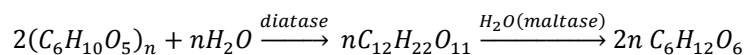


Glucose fructose



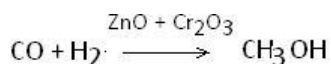
Ethyl alcohol

(ii) From starch



12. Reduction of water gas

It is an industrial method for preparation of methanol



PHYSICAL PROPERTIES OF ALCOHOLS

(i) Physical state

The lower members upto C_{11} are colourless liquids. Higher members are wax like solids
The lower members have a characteristic smell and a burning taste while solid members are almost colourless and tasteless

(ii) Density

Alcohol are lighter than water

(iii) Boiling point

- Boiling points of alcohols increases gradually with increase of carbon chain
- Among isomeric alcohol, the boiling points are in the following order
Primary > Secondary > tertiary
- The boiling point decreases with branching
- The boiling points of alcohols are much higher as compared to the corresponding alkanes, ether and haloalkanes

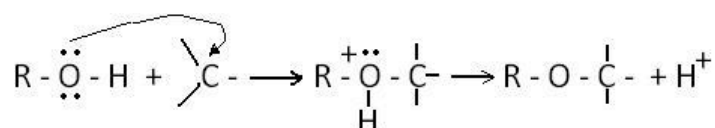
The high boiling points of alcohol are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ether and hydrocarbons

(iv) Solubility

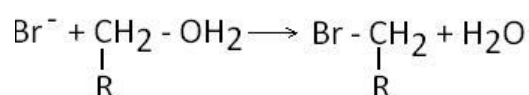
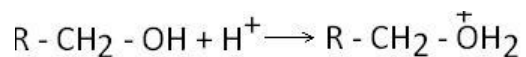
- Lower alcohols are soluble in water due to hydrogen bonding but solubility decreases with increase of molecular mass since hydrocarbon part increases which interrupts the hydrogen bond formation
- Solubility increases with branching since surface area of hydrocarbon part decreases with increase of branching
- Alcohols can form hydrogen bonds with water and break H-bond between water molecule

CHEMICAL PROPERTIES OF ALCOHOLS

- Alcohols are versatile compounds. They react both as nucleophile and electrophile
- Alcohol as nucleophile



- Alcohol as electrophile



- Chemical reactions of alcohols can be classified into following categories

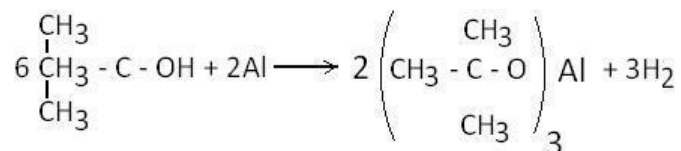
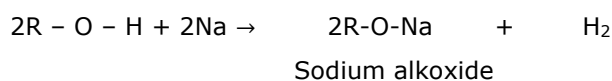
- (A) Reactions due to O-H bond, breaking
 (B) Reactions due to C-OH bond breaking
 (C) Reaction of alcohol molecule as a whole

(A) Reactions due to O-H bond, breaking

Order of ease of cleavage of O-H bond and thus order of reactivity is

CH₃OH > primary > secondary > tertiary

1. Reaction with metals (acidic nature):

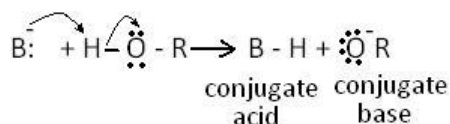


Alcohols are stronger acid than acetylenes and acidic nature is in the order

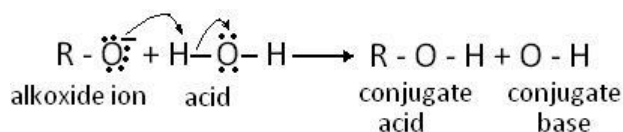
H-OH > ROH > CH≡CH > NH₃RH

Acidic character of alcohol and water

- Alcohols act as Bronsted acids which lose a proton to strong base
- Electron releasing inductive effect (+I) of the alkyl group makes the alcohol weaker acids than water.

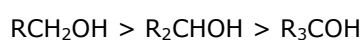


- On treating alkoxide ion with water, the starting alcohol is obtained.

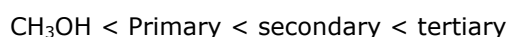


Comparison of acidic character of primary, secondary and tertiary alcohols

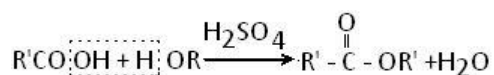
The acidic character of alcohols is due to the polar nature of O – H bond. An electron releasing group increases electron density on oxygen tending to decrease the polarity of O – H bond. This decreases the acidic strength and so the acid strength of alcohol decreases in the following order



Order of +I effect in various isomeric alcohols is



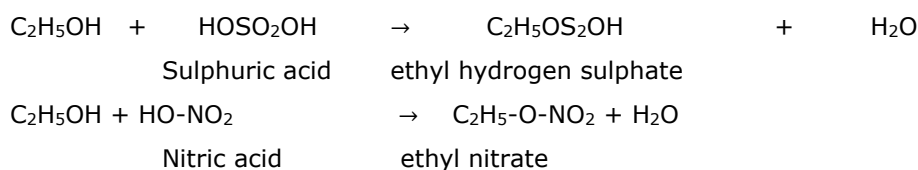
2. Esterification



- If the above reaction is carried out with dry HCl gas as catalyst, the reaction is known as Fischer-Speier esterification.
- Order of reactivity of different alcohols towards esterification is $\text{CH}_3\text{OH} > \text{RCH}_2\text{OH} > \text{R}_2\text{CHOH} > \text{R}_3\text{COH}$

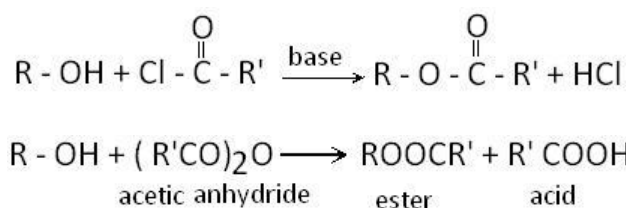
AS the size of hydrocarbon part (R) around –OH increases, rate of reaction decreases due to steric hinderance

3. Reaction with inorganic acid



4. Acylation or reaction with acid chloride and acid anhydrides

- When alcohols reacts with acid chloride or acid anhydrides, the hydrogen of the hydroxyl group is replaced by an acyl group (RCO-) resulting in the formation of esters. The process is known as acylation
- When the hydrogen of –OH group is replaced by $\text{CH}_3\text{CO-}$ (acetyl) group, the process is termed acetylation.



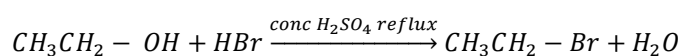
- The acetylation of alcohol is usually carried out in the presence of base such as pyrimidine
- (B) Reaction due to C – OH bond breaking

Order of ease of cleavage of C – OH bond and thus reactivity of different alcohols is

Tertiary > Secondary > Primary > CH₃OH

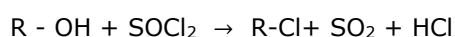
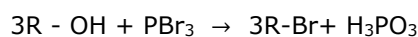
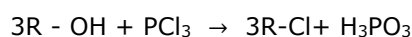
(1) Reaction with halogen acids

- Order of reactivity of HX is
HI > HBr > HCl
- For a given hydrogen halide order of reactivity of different alcohol is
Allyl > benzyl > 3° > 2° > 1°
R – OH + H – X → R-X + H₂O
- Alcohols require some catalyst like ZnCl₂ or acidic conditions to undergo nucleophilic substitution, since – OH is a poor leaving group

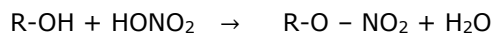


Mechanism above reaction is hydride shift.

- It has been discussed in detail in alkyl halides
- (2) Reaction with phosphorus halides and thionyl chloride

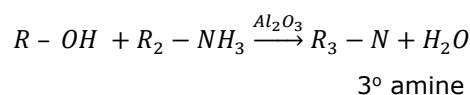
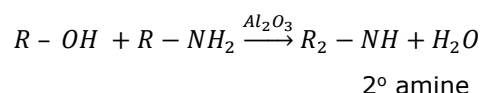
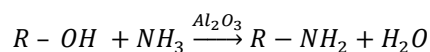


(3) Reaction of Nitric acid



Alkyl nitrate

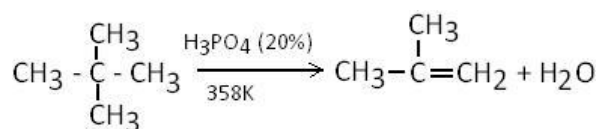
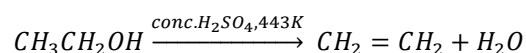
(4) Reaction with ammonia



(R₄N⁺) OH⁻ : Quaternary alkyl ammonium hydroxide

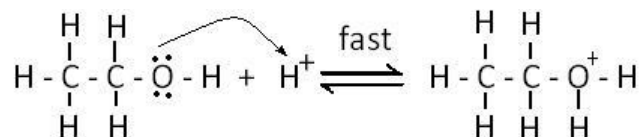
(C) Reaction involving alcohol molecule as a whole

1. Dehydration

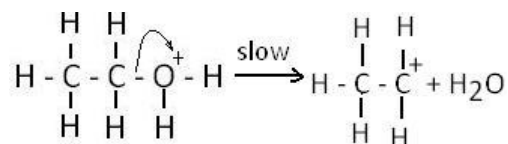


Mechanism of dehydration

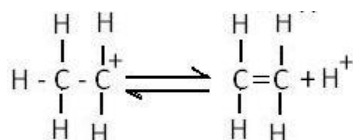
Step I: Formation of protonated alcohol



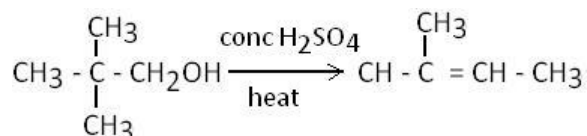
Step II : Formation of carbocation. It is the slowest step and hence the rate determining step of the reaction



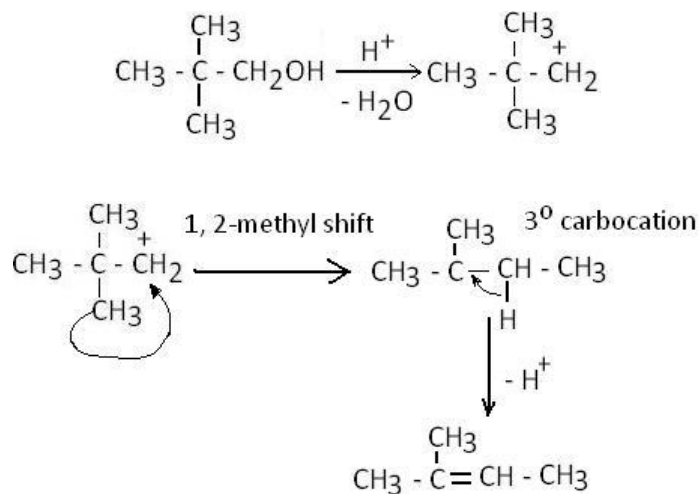
Step III : Formation of ethene by elimination of proton



- Formation of 2-methyl but-2-ene



Mechanism

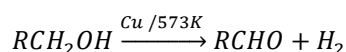


In case of secondary and tertiary alcohols, Saytzeff's rule is followed and the ease of dehydration of alcohol is in the order

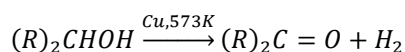
Tertiary > Secondary > Primary

2. Dehydration

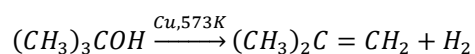
(a) A primary alcohol loses hydrogen and forms aldehyde



(b) A secondary alcohol loses hydrogen and form a ketone

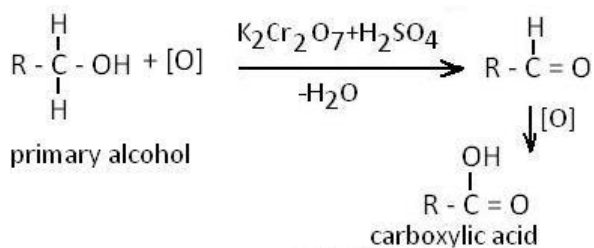


(c) A tertiary alcohol undergoes dehydration of alkene



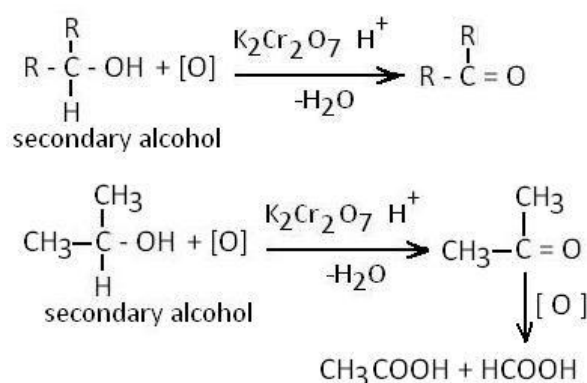
3. Oxidation

- (i) Primary alcohols on oxidation gives aldehydes which further get oxidized to carboxylic acid



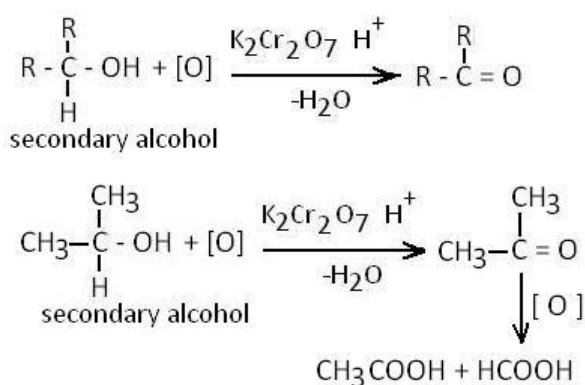
Oxidation can be stopped at aldehyde stage by using collin's reagent ($\text{CrO}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$, chloroform trioxide-pyridine complex) or pyridinium chlorochromate, PCC ($\text{CrO}_3 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$)

- (ii) Secondary alcohols on oxidation give mixture of carboxylic acids

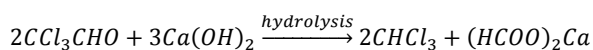
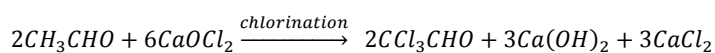
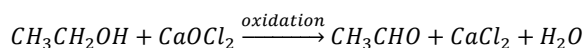


This oxidation can be stopped at ketone stage by using chromium anhydride (CrO_3)

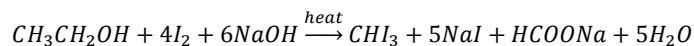
- (iii) A tertiary alcohol having no oxidisable hydrogen linked to carbon atom bearing hydroxyl group, is stable to oxidation in neutral or alkaline KMnO_4 solution



4. Reaction with bleaching powder

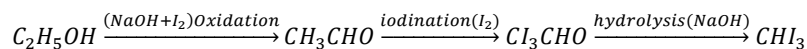


5. Haloform reaction



Sodium formate

This reaction like the preparation of chloroform also occurs in three steps

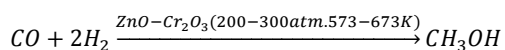


In place of iodine, bromine or chlorine can be taken when the corresponding compounds bromoform or chloroform are to be formed. This reaction in general is known as haloform reaction

SOME COMMERCIALY IMPORTANT ALCOHOLS

1. Methanol

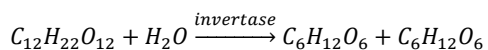
- Methanol is produced by catalytic hydrogenation of carbon monoxide at high temperature and pressure and in presence of ZnO-Cr₂O₃ catalyst



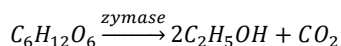
- Methanol is a colourless liquid and boiling point is 337K
- It is poisonous in nature.
- Ingestion of small quantities of methanol can cause blindness.
- It is used as solvent in paints, varnishes and chiefly for making formaldehyde

2. Ethanol

Ethanol is produced by fermentation of molasses into glucose and fermentation gives ethanol and carbon dioxide



Glucose fructose



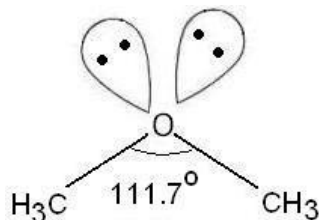
- In wine making, grapes are the source of sugar. As grapes ripen the quantity of sugar increases and yeast grows on outer skin. When grapes are crushed, sugar and the enzyme comes in contact and fermentation starts. Fermentation takes place in anaerobic conditions. i.e in absence of air
- The action of zymase is inhibited once the percentage of alcohol formed exceeds 14%
- Ethanol is a colourless liquid with boiling point 351K. It is used as a solvent in paint industry
- The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

ETHERS

- Ethers have a general formula $R - O - R'$, where R and R' may be same or different
- Ethers are isomeric with mono-hydric alcohol
Eg. C_2H_6O
 CH_3CH_2OH (ethyl alcohol); $CH_3 - O - CH_3$ (dimethyl ether)
- Ethers can be classified as follows:
 - Aliphatic ethers
If both R and R' groups are alkyl groups, then ether is aliphatic ether
 $CH_3 - O - CH_2CH_3$ (ethyl methyl ether)
 $CH_3CH_2 - O - CH_2CH_3$ (diethyl ether)
 - Aromatic ether
If both R and R' or any of them is aryl group then ether is aromatic ether
 $CH_3 - O - C_6H_5$ (methyl phenyl ether)
 $C_6H_5 - O - C_6H_5$ (Diphenyl ether)
 - Simple or symmetrical ether
If two group R and R' present in ether are same, then it is known as simple or symmetric ether
 $CH_3 - O - CH_3$ (Dimethyl ether)
 $C_2H_5 - O - C_2H_5$ (Diethyl ether)
 $C_6H_5 - O - C_6H_5$ (Diphenyl ether)
 - Mixed or unsymmetrical ether
If R and R' present in ether are different, then ether is known as mixed or unsymmetrical ether
 $CH_3 - O - C_2H_5$ (ethyl methyl ether)
 $CH_3 - O - C_6H_5$ (methyl phenyl ether)
 $C_6H_5 - O - CH_2C_6H_5$ (Benzyl phenyl ether)

STRUCTURE

Ether may be considered as dialkyl derivative of water

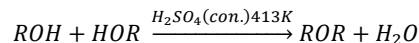


- Oxygen atom in ether is sp^3 hybridised and forms two sigma bonds with sp^3 hybridised alkyl group
- Oxygen atom has two lone pairs of electron in remaining two sp^3 hybridised orbital C - O - C bond angle in ether is slightly greater, than tetrahedral bond angle due to repulsion between two bulky alkyl group. In dimethyl ether C - O - C bond angle is 111.7°

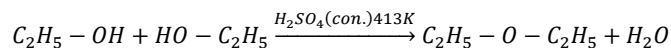
- As the size of R (alkyl group) in ethers increases, van der Waals repulsion increases and hence bond angle also increases

GENERAL METHOD OF PREPARATION OF ETHERS

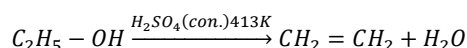
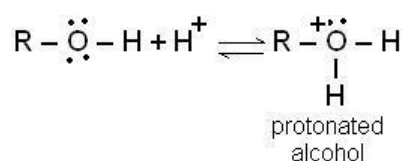
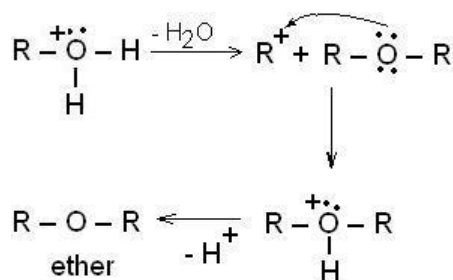
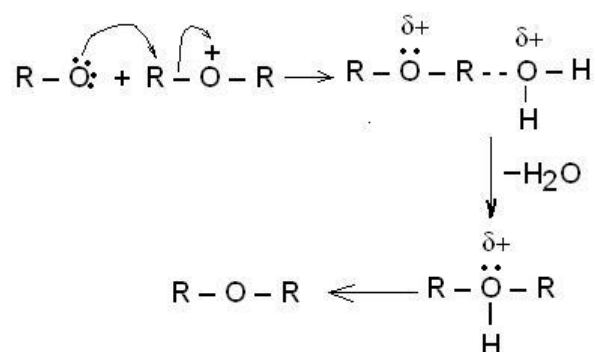
1. Acidic dehydration of alcohols



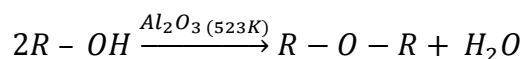
This method is used to prepare simple or symmetrical ether



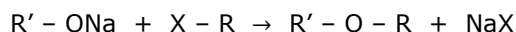
In this reaction, reaction conditions have to be carefully controlled, to get the maximum yield of ether. At a slightly higher temperature (150°C) alkene is obtained instead of ether.

**Mechanism****S_N1 mechanism****S_N2 mechanism**

- Primary alcohols reacts by generally S_N2 mechanism where as secondary and tertiary alcohols undergo the reaction by S_N1 mechanism
- Order of ease of dehydration of alcohol to form ethers
1° alcohol > 2° alcohol > 3° alcohol
- Catalytic dehydration

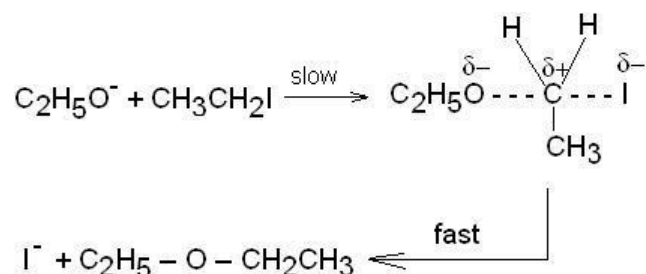
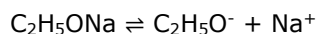


2. Williamson synthesis



- Both symmetric and unsymmetrical ethers can be prepared by this method

Mechanism

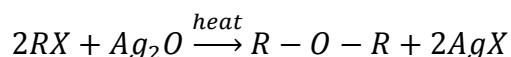


Order of reactivity of alkyl halides towards this reaction is

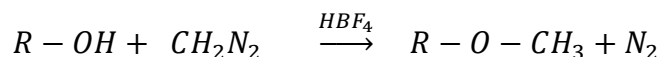
Primary > secondary > tertiary

For better yield, the alkyl halide should be primary and alkoxide should be secondary or tertiary

3. Action of silver oxide on alkyl halide

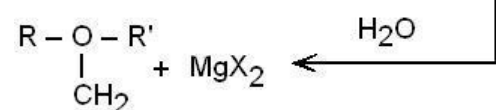
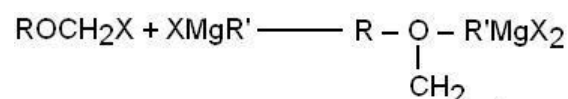


4. Action of diazomethane on alcohols

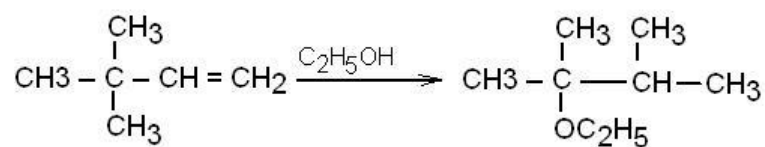
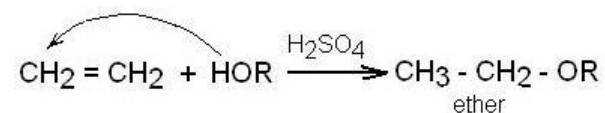


Diazomethane

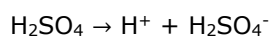
5. Reaction of lower halogenated ether with Grignard reagent

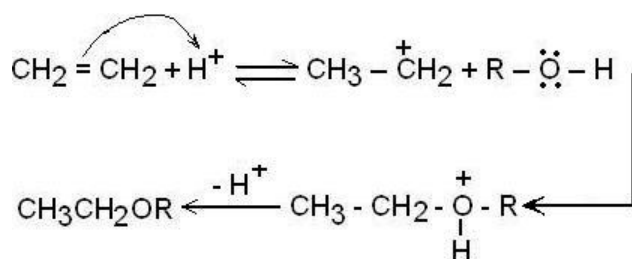


6. Addition of alcohols to alkene



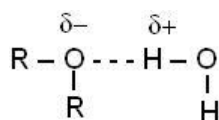
Mechanism





PHYSICAL PROPERTIES OF ETHERS

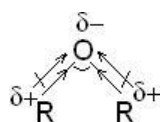
- All ethers are colourless liquids except dimethyl ether and ethyl ether are gases at room temperature
- Boiling point
 - Ethers have lower boiling points than isomeric alcohols
 - Lower ethers have slightly higher boiling point than n-alkanes of comparable molecular masses due to weak van der Waals force of attraction
 - Solubility
 - Ethers are soluble in water to a certain extent due to hydrogen bonding



- Ethers are fairly soluble in organic solvent
- Density

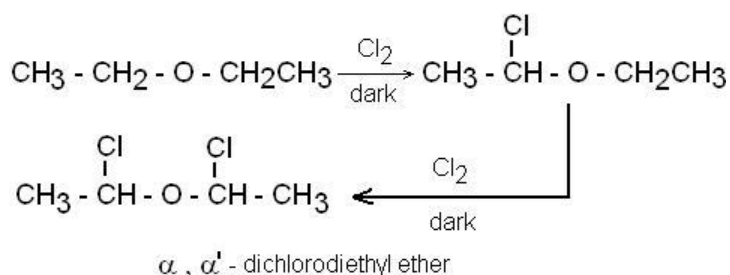
Ethers have low density. All ethers are lighter than water and are highly volatile and flammable
 - Polarity

Ethers are polar in nature and its dipole moment ranges from 1.15D to 1.30D

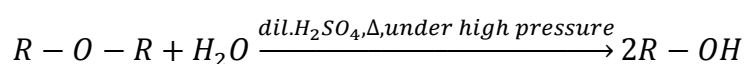


CHEMICAL PROPERTIES OF ETHERS

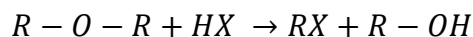
- Halogenation



- Hydrolysis



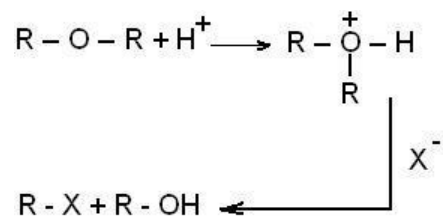
3. Reaction with halogen acid



Reactivity of halogen acid

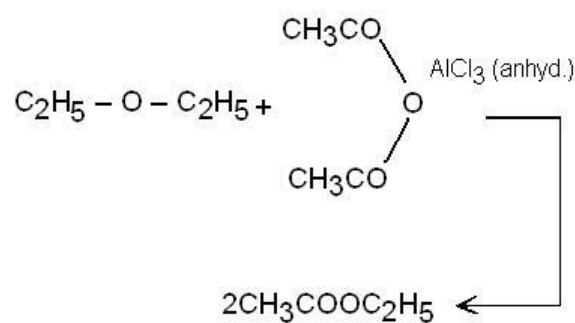
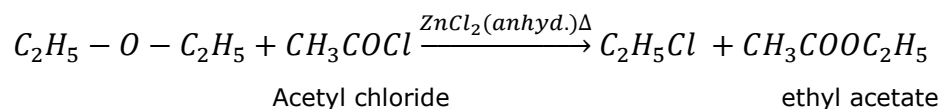


Mechanism



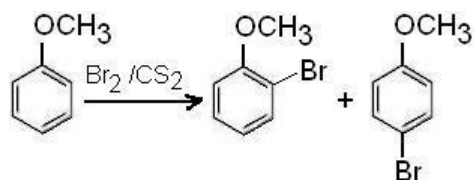
During the cleavage of unsymmetrical ethers, smaller alkyl group produces alkyl halides

4. Reaction with acid chlorides and anhydrides

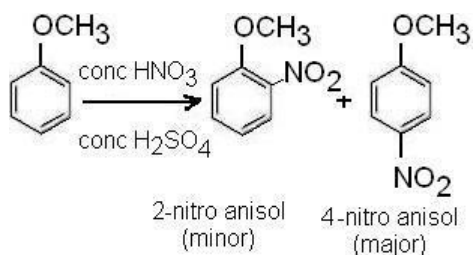


5. Electrophilic substitution reaction

(i) Halogenations

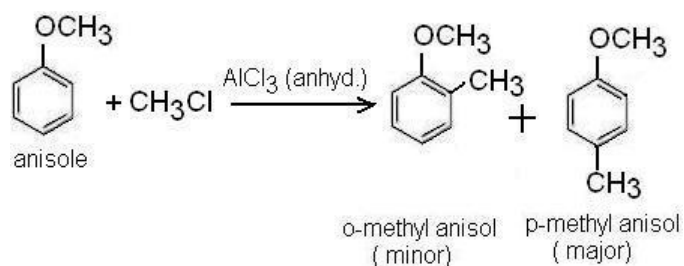


(ii) Nitration

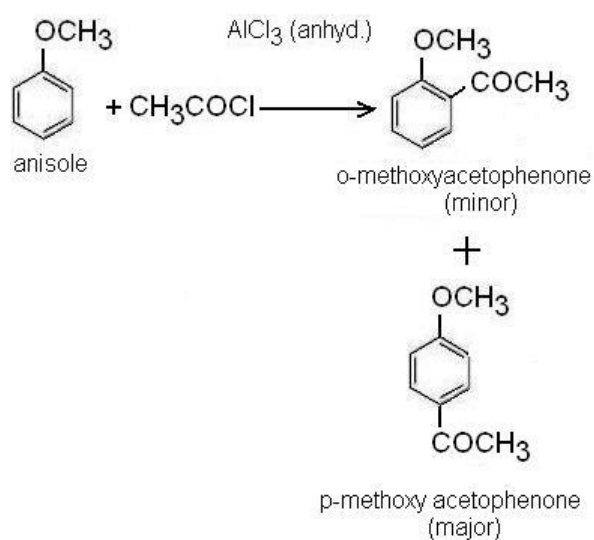


(iii) Friedel crafts reaction

• Alkylation



• Acetylation



USES OF ETHER

- It act as a solvent for oil, fat, waxes, plastics.
- It is used in perfumery.
- It is used as an inhalation.
- It is used as an inhalation anesthetic agent in surgery.
- It is used as refrigerant for cooling.