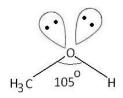
ALCOHOLS

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 sp³ hybridised. Two of the four sp³ hybridised orbitals of oxygen get involved in formation of σ-bond with hydrogen and carbon respectively where as rest of two sp³ 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.

CH₃OH : methyl alcohol

(CH₃)₃C-OH : Tert butyl alcohol

(2) Dihydric alcohol

 $\ensuremath{\mathsf{CH}_2}$ - OH Compounds in which two hydrogen atoms are replaced by two hydroxyl groups. I CH_2 - OH

glycol

(3) Trihydric alcohol

 $CH_2 - OH$ Compounds in which three hydrogen atoms are replaced by three hydroxyl I CH₂ - OH groups.

ĊH2 - ОН

glycerol

CLASSIFICATION OF MONOHYDRIC ALCOHOLS

1) Compound containing sp³ C – OH bond.

In these alcohols, the -OH group is attached to sp³ -hybridised carbon atom of an alkyl group.

 Primary alcohol(1°): In these alcohols, the hydroxyl group is attached with primary (1°) carbon atom. The general formula is R-CH₂-OH. R may be H or alkyl group primary carbon atom C H - CH₂OH methyl alcohol (1⁰) isok

(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

secondary carbon atom CH₃ - CH - CH₃ OH isopropyl alcohol 2^o sec. butyl alcohol

(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 sp³ hybridized carbon next to the carbon-carbon double bond. i.e. to an allylic carbon

C11

(5) Benzylic alcohols:

In these alcohols, the -OH group is attached to an sp³- hybridized carbon atom next to an aromatic ring.

(2) Compound containing sp² C-OH bond

In these alcohols, the –OH group is atta

 $CH_2 = CH_2 - OH$ (vinyl alcohol, unstable)

ISOMERISM IN ALCOCHOLS

(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 $CH_3 = CH_2 - CH_2 - CH_2 - OH$ (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.

 $CH_3 - CH_2 - OH$ (ethanol) and $CH_3 - O - CH_3$ (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

$$R - X + KOH(aq) \rightarrow R - OH + KX$$

$$R - X + Ag_2O(moist)(aq) \rightarrow R - OH + AgX$$

- 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 gives good yield of alcohols, while tertiary butyl halides mainly give alkenes due to dehydrohalogenation

$$CH_3 - CH_3 + NaOH \longrightarrow CH_3 - C = CH_2 + NaBr + H_2OBr$$

tert.butylbromide

• Secondary(2°) alkyl halides gives a mixture of alcohol and alkene

CH₃ - CH - CH₃ + KOH $\xrightarrow{\bigtriangleup}$ CH₃ - CH - CH₃ + CHCH=CH₂ isopropylbromide propan-2-ol propene

• Hydrolysis of 1° halides proceeds by $S_N 2$ mechanism while those of 3° halides by $S_N 1$ mechanism. The hydrolysis 2° alkyl halides may proceed by $S_N 1$ or $S_N 2$ mechanism

2. Hydration of alkene

(1) Direct hydration

 $CH_2 = CH_2 + H_2SO_4 \rightarrow CH_3 - CH_2 - H_2SO_4 + H_2O \rightarrow CH_3CH_2OH$ Mechanism:

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

Step I : Electrophilic attack by hydronium ion (H_3O^+) on alkene gives an intermediate carbocation

 $H_2SO_4 \rightarrow H^+ + HSO_4^-$

$$H - \overset{H}{\odot} - H + H^{+} \rightarrow H - \overset{H}{\odot} - H (H_{3}O^{+})$$

$$H = CH_{2} + H - \overset{H}{O} - H \xrightarrow{\text{slow}} CH_{3} - \overset{H}{C} H - CH_{3} + H_{2} \overset{H}{\odot}$$

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

$$CH_3 - CH - CH_3 + H_2O \rightarrow CH_3 - CH_3 - CH_3 - CH_3 - CH_3 + H_2O \rightarrow CH_3 + H_2O + H_3 + H_3O + H_3$$

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

$$CH_3 - CH - CH_3 + \ddot{O} - H \xrightarrow{\text{tast}} CH_3 - CH_3 - CH_3 + H_3O^+$$

Addition of H_2SO_4 follows Markownikoff's rule

(2) Indirect hydration

(a) Oxymercuration-demercuration

$$R - CH = CH_{2} \xrightarrow{\text{THF} - H_{2}O} R - CH - CH_{2}$$

$$R - CH - CH_{2} \xrightarrow{\text{THF} - H_{2}O} H = H_{2}OAC$$

$$Hydroxy alkyl$$

$$Mercury compound$$

$$R - CH - CH_{2} \xrightarrow{\text{NaBH}_{4}} R - CH - CH_{3}$$

(b) Hydroboration – oxidat

$$R - CH = CH_2 + B_2H_6 \xrightarrow{etner} RCH_2 - CH_2 - BH_2$$

$$RCH_2 - CH_2 - BH_2 + R - CH = CH_2 \rightarrow (RCH_2CH_2)_2BH$$

$$(RCH_2CH_2)_2BH + R - CH = CH_2 \rightarrow (RCH_2CH_2)_3B$$

$$(RCH_2CH_2)_3B \xrightarrow{H_2O_2/OH^-} 3R - CH_2 - CH_2 - OH + H_3PO_3$$

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

3. Hydrolysis of esters

$$\begin{array}{ccc} RCOOR' + H_2O \xrightarrow{H^+ \circ R \circ H^-} RCOOH + R' - OH \\ \text{Ester} & \text{acid} & \text{alcohol} \end{array}$$

4. Hydrolysis of ethers

$$ROR' + H - O - H \xrightarrow{n_2 \cdot o_4} R - OH + R' - OH$$

5. Action of nitrous acid (HONO) on primary amines RNH₂ + HONO \rightarrow R-OH + N₂ + H₂O Or

 $+ \frac{R |N|H_2}{OH |N|O} \longrightarrow R-OH + N_2 + H_2O$

• 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

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

Methyl nitrite

 $2CH_3NH_2 + 2HNO_2 \rightarrow CH_3 - O - CH_3 + 2H_2O + N_2$

6. Reduction of aldehydes and ketones

Catalysts : H₂/Ni or Na/C₂H₅OH or LiAlH₄ or NaBH₄

$$H - CHO \xrightarrow{catalysts} CH_3 - OH$$

$$R - CHO \xrightarrow{catalysts} R - CH_3 - OH$$

Aldehyde

primary alcohol

$${}^{\mathrm{Page}}\mathbf{5}$$

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

$$\begin{array}{c} \searrow_{I} c - o^{T}Mg^{+} - X \xrightarrow{H_{2}O} \\ R \\ R \\ \end{array} \xrightarrow{} C - HO + Mg(OH) X \\ R \\ R \\ R \\ \end{array}$$

adduct

(i) Primary alcohol is produced with formaldehyde

$$H = C - H + RMgX \longrightarrow CH_2 = O MgX \xrightarrow{H_2O} R - CH_2 - OH + Mg(OH)X$$

$$\begin{array}{ccc} O & R' & H_2O & R' \\ \parallel & \parallel & R - C - H + R'MgX \longrightarrow R - CH - OMgX \longrightarrow R - CH - OH + Mg(OH)X \end{array}$$

$$\begin{array}{c} O \\ \parallel \\ R - C - R' + R'' MgX \longrightarrow R - C - OMgX \xrightarrow{R'} R - C - OHgX \xrightarrow{R'} R - C - OH + Mg(OH)_2 \end{array}$$

8. Reduction of carbonyl group including carboxylic acid and esters

$$R - COOH \xrightarrow{LiAlH_4} R - CH_2OH$$

$$R - COCl \xrightarrow{LiAlH_4} R - CH_2OH + HCl$$

Acid chloride

$$R(CO)_2 O \xrightarrow{LiAlH_4} 2R - CH_2 OH$$

Acid anhydride

$$R - C - OR' \xrightarrow{LIAIH4} RCH_2OH + R' - OH$$

.....

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

9. From epoxides

(i) Reduction

$$CH_2 - CH_2 \xrightarrow{\text{LIAIH}_4} CH_3 - CH_2OH$$

10. Oxo process

This reaction is also known as carbonylation or hydroformylation reaction

$$2CH_2 - CH = CH_2 + 2CO + 2H_2 \rightarrow CH_3CH_2CH_2 - CHO$$

$$CH_3CH_2CH_2 - CHO \xrightarrow{Cu-Zn(H_2)} CH_3CH_2CH_2CH_2OH$$

- 11. Fermentation of carbohydrates
 - (i) Molasses is the mother liquor after crystallization of sugar from sugar solution

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$

Glucose fructose

$$C_6H_{12}O_6 \xrightarrow{zymase} 2C_2H_5OH + 2CO_2$$

Ethyl alcohol

(ii) From starch

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{diatase}} nC_{12}H_{22}O_{11} \xrightarrow{H_2O(\text{maltase})} 2n C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow{zymase} 2C_2H_5OH + 2CO_2$$

12. Reduction of water gas

It is an industrial method for preparation of methanol

 $CO + H_2 \xrightarrow{ZnO + Cr_2O_3} CH_3OH$

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

$$R - \overleftrightarrow{Q} - H + \bigwedge^{P} - \longrightarrow R + \dddot{Q} - \swarrow - \swarrow - R - O - \swarrow - H^{+}$$

• Alcohol as electrophile

$$R - CH_2 - OH + H^+ \longrightarrow R - CH_2 - OH_2$$

Br⁻ + CH₂ - OH₂ \longrightarrow Br - CH₂ + H₂O
I
R R R

- 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):

 $2R - O - H + 2Na \rightarrow \qquad 2R - O - Na \qquad + \qquad H_2$

Sodium alkoxide

$$\begin{array}{c} \mathsf{CH}_{3} \\ \mathsf{CH}_{3} \\ \mathsf{CH}_{3} \\ \mathsf{CH}_{3} \end{array} \cdot \mathsf{C} - \mathsf{OH} + 2\mathsf{AI} \longrightarrow 2 \begin{pmatrix} \mathsf{CH}_{3} \\ \mathsf{CH}_{3} - \mathsf{C} - \mathsf{O} \\ \mathsf{CH}_{3} \\ \mathsf{CH}_{3} \end{pmatrix} \mathsf{AI} + 3\mathsf{H}_{2} \\ \begin{array}{c} \mathsf{CH}_{3} \\ \mathsf{CH}_{3} \\ \mathsf{CH}_{3} \\ \end{array} \right)$$

Alcohols are stronger acid than acetylenes and acidic nature is in the order H-OH > ROH> CH=CH > NH_3RH

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

 $RCH_2OH > R_2CHOH > R_3COH$

Order of +I effect in various isomeric alcohols is

CH₃OH < Primary < secondary < tertiary

2. Esterification

 $H_2SO_4 \xrightarrow[]{0}{H_2SO_4} R' - C - OR' + H_2O$

- 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 CH₃OH > RCH₂OH > R₂CHOH > R₃COH

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

 H_2O

3. Reaction with inorganic acid

 $\begin{array}{cccc} C_2H_5OH &+ &HOSO_2OH &\rightarrow &C_2H_5OS_2OH &+ \\ & & Sulphuric acid & ethyl hydrogen sulphate \\ C_2H_5OH &+ HO-NO_2 &\rightarrow &C_2H_5-O-NO_2 &+ H_2O \\ & & Nitric acid & ethyl nitrate \end{array}$

- 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 CH₃CO- (acetyl) group, the process is termed acetylation.

$$\begin{array}{c} O & O \\ R - OH + CI - C - R' \xrightarrow{\text{base}} R - O - C - R' + HCI \end{array}$$

 $\begin{array}{c} \text{R} - \text{OH} + (\text{ R'CO})_2 \text{O} \longrightarrow \text{ROOCR'} + \text{R' COOH} \\ \text{acetic anhydride} & \text{ester} & \text{acid} \end{array}$

- The acetylation of alcohol is us
- (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 > CH_3OH

- (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

 $\mathsf{Allyl} > \mathsf{benzyl} > 3^\circ > 2^\circ > 1^\circ$

 $R - \underline{OH + H} - X \rightarrow R-X + H_2O$

 Alcohols require some catalyst like ZnCl₂ or acidic conditions to undergo nucleophilic substitution, since – OH is a poor leaving group

$$CH_3CH_2 - OH + HBr \xrightarrow{conc H_2SO_4 reflux} CH_3CH_2 - Br + H_2O$$

Mechanism above reaction is hydride shift.

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

$$R - OH + PCI_5 \rightarrow R-CI+ POCI_3 + HC$$

 $3R - OH + PCI_3 \rightarrow 3R - CI + H_3PO_3$

 $3R \text{ - OH } + \text{ PBr}_3 \ \rightarrow \ 3R \text{ - Br} + \text{ H}_3\text{PO}_3$

- $R OH + SOCI_2 \rightarrow R-CI+SO_2 + HCI$
- (3) Reaction of Nitric acid

 $R-OH + HONO_2 \rightarrow R-O - NO_2 + H_2O$ Alkyl nitrate

(4) Reaction with ammonia

$$R - OH + NH_3 \xrightarrow{Al_2O_3} R - NH_2 + H_2O$$

$$R - OH + R - NH_2 \xrightarrow{Al_2O_3} R_2 - NH + H_2O$$

$$2^{\circ} \text{ amine}$$

$$R - OH + R_2 - NH_3 \xrightarrow{Al_2O_3} R_3 - N + H_2O$$

$$3^{\circ} \text{ amine}$$

$$R - OH + R_3 - NH \xrightarrow{R_2O_3} (R_4N^+)OH^-$$

 $(R_4N^{\scriptscriptstyle +})$ $OH^{\scriptscriptstyle -}~$: Quaternary alkyl ammonium hydroxide

- (C) Reaction involving alcohol molecule as a whole
 - 1. Dehydration

$$CH_{3}CH_{2}OH \xrightarrow{conc.H_{2}SO_{4},443K} CH_{2} = CH_{2} + H_{2}O$$

$$CH_{3} \xrightarrow{CH_{3}} \stackrel{CH_{3}}{\xrightarrow{I_{3}PO_{4}(20\%)}} CH_{3} \xrightarrow{CH_{3}} CH_{3} - C = CH_{2} + H_{2}O$$

$$CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{I_{3}S8K} CH_{3} - C = CH_{2} + H_{2}O$$

Mechanism of dehydration

Step I: Formation of protor

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

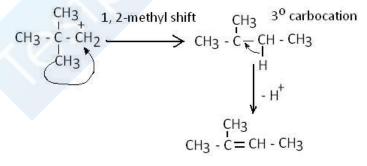
$$\begin{array}{ccc} H & H & H & H \\ I & I_{+} & & I & I \\ H - C - C & \longrightarrow & C = C + H^{1} \\ I & I & & I & I \\ H & H & H & H \end{array}$$

• Formation of 2-methyl but-2-ene

$$\begin{array}{ccc} & \begin{array}{c} CH_3 & conc H_2 SO_4 & \begin{array}{c} CH_3 \\ H_3 & CH_3 & CH_2 OH & \end{array} \\ & \begin{array}{c} CH_3 & CH_2 OH & \end{array} \\ & \begin{array}{c} H_1 & \\ CH_3 & \end{array} \end{array} \xrightarrow{\begin{array}{c} CH_2 OH & CH_2 OH \end{array}} CH_2 CH_2 CH_3 \end{array}$$

Mechanism

$$\begin{array}{c} CH_3 \\ CH_3 - C - CH_2OH \xrightarrow{H^+} CH_3 - CH_3 \\ I \\ CH_3 \end{array} \xrightarrow{H^+} CH_3 - CH_2 \\ CH_3 \end{array} \xrightarrow{CH_3} CH_3 + CH_2 \\ CH_3 \\ CH_3 \end{array}$$



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

$$RCH_2OH \xrightarrow{Cu/573K} RCHO + H_2$$

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

$$(R)_2 CHOH \xrightarrow{Cu,573K} (R)_2 C = O + H_2$$

(c) A tertiary alcohol undergoes dehydration of alkene

$$(CH_3)_3COH \xrightarrow{Cu, s \neq s \times} (CH_3)_2C = CH_2 + H_2$$

CHETON

- 3. Oxidation
- Primary alcohols on oxidation gives aldehydes which further get oxidized to carboxylic acid

$$\begin{array}{c} \begin{array}{c} H \\ R - \overset{H}{C} - OH + [O] \\ H \end{array} & \xrightarrow{K_2 Cr_2 O_7 + H_2 SO_4} \\ \hline & H_2 O \end{array} & \begin{array}{c} H \\ R - \overset{H}{C} = O \\ \hline & & \downarrow [O] \\ \hline & & & \\ R - \overset{I}{C} = O \\ \hline & & \\ & & \\ R - \overset{I}{C} = O \\ \hline & & \\$$

Oxidation can be stopped at aldehyde stage by using collin's reagent ($CrO_3 \cdot 2C_5H_5N$, chloroform trioxide-pyridine complex) or pyridinium chlorochromate, PCC ($CrO_3 \cdot 2C_5H_5N \cdot HCl$)

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

$$R - C - OH + [O] \xrightarrow{K_2 Cr_2 O_7 H^+} R - C = O$$

$$H$$
secondary alcohol

$$\begin{array}{c} CH_{3} \\ CH_{3}-C-OH + [O] \\ H \\ secondary alcohol \end{array} \xrightarrow{K_{2}Cr_{2}O_{7}} H^{+} \\ H \\ CH_{3}-C$$

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 KMnO₄ solution

$$R - \frac{R}{L} - OH + [O] \xrightarrow{K_2 Cr_2 O_7 H^+} R - \frac{R}{L} = O$$

secondary alcohol

$$\begin{array}{c} CH_{3} \\ CH_{3}-C - OH + [O] \\ H \\ Secondary alcohol \end{array} \xrightarrow{K_{2}Cr_{2}O_{7}} H^{+} CH_{3} \\ -H_{2}O \\ -H_{2}O \\ -H_{2}O \\ \hline \left(O \right) \end{array}$$

CH3COOH + HCOOH

4. Reaction with bleaching powder

 $CH_3CH_2OH + CaOCl_2 \xrightarrow{oxidation} CH_3CHO + CaCl_2 + H_2O$

 $2CH_3CHO + 6CaOCl_2 \xrightarrow{chlorination} 2CCl_3CHO + 3Ca(OH)_2 + 3CaCl_2$

 $2CCl_3CHO + 3Ca(OH)_2 \xrightarrow{hydrolysis} 2CHCl_3 + (HCOO)_2Ca$

5. Haloform reaction

 $CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{heat} CHI_3 + 5NaI + HCOONa + 5H_2O$

Sodium formate

This reaction like the preparation of chloroform also occurs in three steps $C_2H_5OH \xrightarrow{(NaOH+I_2)Oxidation} CH_2CHO \xrightarrow{iodination(I_2)} CI_2CHO \xrightarrow{hydrolysis(NaOH)} CHI_3$

In place of iodine, bromide 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 COMMERCIALLY 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 $CO + 2H_2 \xrightarrow{ZnO-Cr_2O_3(200-300atm.573-673K)} CH_3OH$
- 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

$$C_{12}H_{22}O_{12} + H_2O \xrightarrow{invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$

Glucose fructose

 $C_6H_{12}O_6 \xrightarrow{zymase} 2C_2H_5OH + CO_2$

- 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

CH₃CH₂OH (ethyl alcohol); CH₃ – O –CH₃ (dimethyl ether)

- Ethers can be classified as follows:
 - (i) 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)
 - (ii) 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) (iii) Cingula around the set
 - (iii) 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)

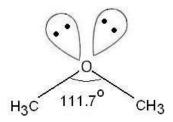
 $C_2H_5 - O - C_2H_5$ (Diethyl ether)

 $C_6H_5 - O - C_6H_5$ (Diphenyl ether)

(iv) 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) $C_6 H_5 - O - CH_2C_6H_5$ (Benzyl phenyl ether)

STRUCTURE

Ether may be considered as dialkyl derivative of water



- Oxygen atom in ether is sp³ hybridised and forms two sigma bonds with sp³ hybridised alkyl group
- Oxygen atom has two lone pairs of electron in remaining two sp³ 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^o

• As the size of R (alkyl group) ir hence bond angle also increases

GENERAL METHOD OF PREPARATION OF ETHERS

1. Acidic dehydration of alcohols

 $ROH + HOR \xrightarrow{H_2SO_4(con.)413K} ROR + H_2O$

This method is used to prepare simple or symmetrical ether

$$C_2H_5 - OH + HO - C_2H_5 \xrightarrow{H_2SO_4(con.)413K} C_2H_5 - O - C_2H_5 + H_2O$$

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.

$$C_2H_5 - OH \xrightarrow{H_2SO_4(con.)413K} CH_2 = CH_2 + H_2O$$

Mechanism

 $S_N 1$ mechanism

$$R \stackrel{+ \circ}{-} H \stackrel{- H_2 \circ}{\longrightarrow} R^+ + R \stackrel{- \circ}{-} R$$

S_N2 mechanism

$$R - \ddot{o} + R - \dot{0} - R \longrightarrow R - \ddot{o} - R - \dot{0} - H$$

$$\downarrow -H_2 O$$

$$\downarrow R - O - R \longleftarrow R - \ddot{O} - R$$

$$\downarrow H$$

$$\downarrow -H_2 O$$

$$\downarrow H$$

- Primary alcohols reacts by generally $S_{\rm N}2$ mechanism where as secondary and tertiary alcohols undergo the reaction by $S_{\rm N}1$ mechanism
- Order of ease of dehydration of alcohol to form ethers 1^o alcohol > 2^o alcohol > 3^o alcohol
- Catalytic dehydration

2. Williamson synthesis

 $R' - ONa + X - R \rightarrow R' - O - R + NaX$

• Both symmetric and unsymmetrical ethers can be prepared by this method Mechanism

 $C_2H_5ONa \Rightarrow C_2H_5O^- + Na^+$

$$C_{2}H_{5}O^{-} + CH_{3}CH_{2}I \xrightarrow{\text{slow}} C_{2}H_{5}O^{-} - C_{---}O^{+} O^{-} O^{+} O^{-} O^{+} O^{-} O^$$

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

$$2RX + Ag_2 O \xrightarrow{heat} R - O - R + 2AgX$$

4. Action of diazomethane on alcohols

$$R - OH + CH_2N_2 \xrightarrow{HBF_4} R - O - CH_3 + N_2$$

Diazomethane

5. Reaction of lower halogenated ether with Grignard reagent

$$ROCH_{2}X + XMgR' \longrightarrow R - O - R'MgX_{2}$$

$$I$$

$$CH_{2}$$

$$R - O - R' \qquad H_{2}O$$

$$I \qquad H_{2}O$$

$$I \qquad H_{2}O$$

6. Addition of alcohols to alkene

$$CH_2 = CH_2 + HOR \xrightarrow{H_2SO_4} CH_3 - CH_2 - OR$$

ether

$$CH3 - CH3 - CH = CH2 \xrightarrow{C_2H_5OH} CH3 - C$$

Mechanism $H_2SO_4 \rightarrow H^+ + H_2SO_4^-$

$$CH_2 = CH_2 + \dot{H}^+ \Longrightarrow CH_3 - \dot{C}H_2 + R - \ddot{Q} - H$$
$$CH_3CH_2OR \xleftarrow{-H^+} CH_3 - CH_2 - \dot{O} - R \xleftarrow{-H^+} H$$

PHYSICAL PROPERTIES OF ETHERS

- All ethers are colourless liquids except dimethyl ether and ethyl ether are gases at room temperature
- 1. Boiling point
- Ether 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
- 2. Solubility
- Ethers are soluble in water to a certain extent due to hydrogen bonding

- Ethers are fairly soluble in organic solvent
- 3. Density

Ether have low density. All ethers are lighter than water and are highly volatile and flammable

4. Polarity

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



CHEMICAL PROPERTIES OF ETHERS

1. Halogenation

$$CH_3 - CH_2 - O - CH_2CH_3 \xrightarrow[dark]{Cl_2} CH_3 - CH - O - CH_2CH_3$$

$$CH_3 - CH - O - CH_2CH_3 \xrightarrow[dark]{Cl_2} CH_3 - CH - O - CH_2CH_3$$

$$CH_3 - CH - O - CH - CH_3 \xrightarrow[dark]{Cl_2} dark$$

lpha , lpha' - dichlorodiethyl ether

2. Hydrolysis

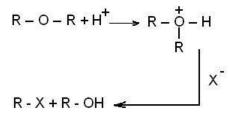
$$R - O - R + H_2 O \xrightarrow{dil.H_2SO_4,\Delta,under \ high \ pressure} 2R - OH$$

3. Reaction with halogen acid

$$R - O - R + HX \rightarrow RX + R - OH$$

Reactivity of halogen acid HI > HBr > HCl

Mechanism



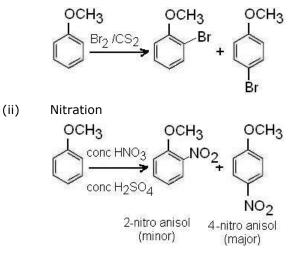
During the cleavage of unsymmetrical ethers, smaller alkyl group produces alkyl halides

4. Reaction with acid chlorides and anhydrides

$$C_{2}H_{5} - O - C_{2}H_{5} + CH_{3}COCl \xrightarrow{ZnCl_{2}(anhyd.)\Delta}{C_{2}H_{5}Cl} + CH_{3}COOC_{2}H_{5}$$

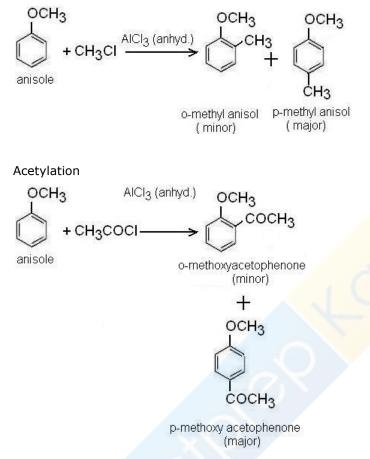
Acetyl chloride ethyl acetate
$$C_{2}H_{5} - O - C_{2}H_{5} + CH_{3}CO \xrightarrow{AlCl_{3}(anhyd.)}{C_{2}H_{5} - O - C_{2}H_{5} + CH_{3}COOC_{2}H_{5}}$$

- 5. Electrophilic substitution reaction
- (i) Halogenations



 e^{100}

- (iii) Friedel crafts reaction
- Alkylation



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.

Page.

• It is used as refrigerant for cooling.