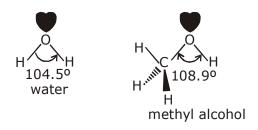
## **ALCOHOL**

#### Introduction



### **Physical Properties**

## (1) Boiling point:

- (a) Alcohols show increase in boiling point with increase in molecular weight amongst homologues.
- (b) Alcohols have higher boiling point than hydrocarbons of the same molecular weight. The reason for higher boiling point is the intermolecular H-bonding present in alcohols.

Intermolecular H bonds in alcohol

## (2) Solubility in water:

As molecular weight increases solubility in water decreases. The lower alcohols are miscible with water. This is due to intermolecular hydrogen bonding between alcohol and water molecules.

Intermolecular H bond between water & alcohol molecules

### **Preparation of alcohols**

#### (1) From alkenes

(a) By acid catalyzed hydration of alkenes: Formation of carbocation intermediate (Markovnikov addition, rearrangement possible)

General reacion 
$$R-CH=CH_2$$
 Alkene  $R-CH-CH_3$   $R-CH-CH_3$   $R-CH-CH_3$   $R-CH-CH_4$   $R-CH-CH_3$   $R-CH-CH_4$   $R-CH-CH_5$   $R-CH-CH_6$   $R-CH-CH_6$   $R-CH-CH_6$   $R-CH-CH_6$   $R-CH-CH_7$   $R-CH-CH_8$   $R-CH-$ 

- (b) By Oxymercuration demercuration process :
- (1) Oxymercuration involves an electrophilic attack on the double bond by the positively charged mercury species. The product is a mercurinium ion, an organometallic cation containing a three-membered ring.
- (2) In the second step, water from the solvent attacks the mercurinium ion to give (after deprotonation) an organomercurial alcohol.
- (3) The third step is demercuration to remove the Hg. Sodium borohydride (NaBH<sub>4</sub>, a reducing agent) re-places the mercuric acetate fragment with hydrogen.



#### **General reaction**

$$\begin{array}{c} H \\ R \\ \end{array} C = C \\ \begin{array}{c} H \\ H \end{array} + H_2O + Hg \\ \\ \begin{array}{c} 0 \\ O - C - CH_3 \\ \end{array} \\ \begin{array}{c} THF \\ R - C - C - H \\ \end{array} + CH_3COOH \\ \\ OH Hg - (O - C - CH_3) \end{array}$$

e.g. 
$$CH_3-CH=CH_2 \xrightarrow{Hg(OAc)_2 \atop THF/H_2O} CH_3-CH-CH_2 \xrightarrow{+OH^0 \atop NaBH_4} CH_3-CH-CH_3$$
  
Prop-1-ene OH Hg(OAc) OH Propan-2-ol

(c) By Hydroboration - oxidation process : (Forms anti-markovnikov alcohol, no rearrangement)

$$\label{eq:General reaction} \text{General reaction} \qquad \text{R-Ch=CH}_2 \xrightarrow{\text{(i) BH}_3, \text{THF}} \text{R-CH}_2 - \text{CH}_2 - \text{OH}$$

**Ex.** Give the major product of the following reaction

$$(a) dil H2SO4$$

$$CH3-CH-CH=CH2 (b) (i) Hg(OCOCH3)2/ H2O
$$(ii) NaBH4 / OH©$$

$$(c) (i) BH3.THF$$

$$(ii)H2O2 / OH©$$$$

**Ans.** Major product is

$$CH_3$$
 (c)  $CH_3$ - $CH$ - $CH_2$ - $CH_2$ - $OH$ 

(2) From alkyl halides: By nucleophilic substitution reactions

(a) By SN<sup>2</sup> mechanism (second-order substitution) : It is given by primary (and some secondary) halides

**General reaction :** 
$$R-CH_2-Br \xrightarrow{KOH} R-CH_2-OH$$

**e.g.** 
$$(CH_3)_2CHCH_2CH_2-Br \xrightarrow{KOH} (CH_3)_2CHCH_2CH_2-OH$$

e.g. 
$$CH_3$$
  $CH_2CH_3$   $CH_2CH_3$   $CH_2CH_3$   $CH_2CH_3$   $CH_2CH_3$   $CH_2CH_3$   $CH_3$   $CH_3$ 

## (b) By SN¹ mechanism: It is given by tertiary and some secondary halides

General reaction : 
$$\begin{array}{c} R' \\ R-C-R'' \xrightarrow{Acetone \ / \ water} \\ CI \end{array} \xrightarrow{R'} \begin{array}{c} R' \\ R-C-R'' \\ OH \end{array}$$
 CH<sub>3</sub>

e.g. 
$$CH_3$$
  $CH_3$   $CH$ 

## (3) From Grignard reagents

## (a) From air

A Grignard reagent may be used to synthesize an alcohol by treating it with dry oxygen and decomposing the product with acid :

$$\begin{array}{lll} \text{General reaction} & \text{RMgX} & \xrightarrow{O_2} & \text{RO}_2 \text{MgX} & \xrightarrow{\text{RMgX}} & 2 \text{ROMgX} & \xrightarrow{H_3 O^+} & 2 \text{ROH} \\ \\ \text{e.g.} & \text{C}_2 \text{H}_5 \text{MgBr} & \xrightarrow{O_2} & \text{C}_2 \text{H}_5 \text{O}_2 \text{MgX} & \xrightarrow{C_2 \text{H}_5 \text{MgX}} & 2 \text{C}_2 \text{H}_5 \text{OMgX} & \xrightarrow{H_3 O^+} & 2 \text{C}_2 \text{H}_5 \text{OH} + \text{MgBr}(\text{OH}) \\ \end{array}$$

#### (b) From ethylene oxide

Addition of Grignard reagent to ethylene oxide gives a primary alcohol (with two carbon atoms added)

General reaction 
$$CH_2 \longrightarrow RCH_2CH_2OMgX \xrightarrow{H_3O^+} RCH_2CH_2OH + MgX(OH)$$

e.g. 
$$\begin{array}{c} \text{CH}_2\\ \text{CH}_2\\ \text{O} + \text{C}_2\text{H}_5\text{MgBr} \longrightarrow \text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{OMgX} \xrightarrow{\text{H}_3\text{O}^+} \\ \text{CH}_2\\ \text{CH}_2\\ \text{CH}_2\\ \text{O} + \text{C}_2\text{H}_5\text{MgBr} \longrightarrow \text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{OH} + \text{MgBr}(\text{OH}) \\ \text{Butyl alchohol} \\ \text{IIT-JEE|AIEE}\\ \text{CBSE|SAT|NTSE}\\ \text{OLYMPIADS}\\ \text{OLYMPIADS}\\ \text{CYclohexylmagnesium bromide} \xrightarrow{\text{(1) CH}_2\text{-CH-CH}_3} \text{CH}_3 \\ \end{array}$$

(c) From carbonyl compounds: Nucleophilic addition to the carbonyl groups by Grignard reagent

## (i) Addition of formaldehyde gives a primary alcohol

**General reaction** 
$$H \subset C = O + RMgX \xrightarrow{Ether} H \subset R \xrightarrow{OMgX} \xrightarrow{H_3O^{\oplus}} RCH_2 - OH$$

## (ii) Addition to an aldehyde (other than formaldehyde) gives a secondary alcohol

## (iii) Addition to a ketone gives a tertiary alcohol

General reaction 
$$R' = C + R''MgX \xrightarrow{(1) \text{ ether} \atop (2)H_3O^{\oplus}} R - C - OH + MgX(OH)$$

ketone  $R'' = C + R''MgX \xrightarrow{(2)H_3O^{\oplus}} R - C - OH + MgX(OH)$ 

ketone  $R'' = C + R''MgX \xrightarrow{(2)H_3O^{\oplus}} R - C - OH + MgX(OH)$ 

Cyclohexanone  $R'' = C + R''MgX \xrightarrow{(2)H_3O^{\oplus}} R - C - OH + MgX(OH)$ 

Respectively.  $R'' = C + R''MgX \xrightarrow{(2)H_3O^{\oplus}} R - C - OH + MgX(OH)$ 

Respectively.  $R'' = C + R''MgX \xrightarrow{(2)H_3O^{\oplus}} R - C - OH + MgX(OH)$ 

Respectively.  $R'' = C + R''MgX \xrightarrow{(2)H_3O^{\oplus}} R - C - OH + MgX(OH)$ 

Cyclohexanone  $R'' = C + R''MgX \xrightarrow{(2)H_3O^{\oplus}} R - C - OH + MgX(OH)$ 

Cyclohexanone  $R'' = C + R''MgX \xrightarrow{(2)H_3O^{\oplus}} R - C - OH + MgX(OH)$ 

## (iv) Addition to an acid halide or an ester gives a tertiary alcohol

Esters on treatment with Grignard ragent first form ketones which then react with second molecule of Grignard reagent and form tertiary alcohol.

## **General reaction**

$$\begin{array}{c} O \\ R-C-OR' + R''MgX \longrightarrow R-C-R'' + Mg \\ R'' & R-C-OR' \longrightarrow R-C-R'' + Mg \\ R'' & R'' & R-C-R'' + Mg \\ R'' & R'' & R'' & R'' & R'' & R'' \\ \hline \\ R'' & R'' & R'' & R'' & R'' & R'' & R'' \\ \hline \\ R'' & R'' & R'' & R'' & R'' & R'' & R'' \\ \hline \\ R'' & R'' \\ \hline \\ R'' & R'' \\ \hline \\ R'' & R'' \\ \hline \\ R'' & R'' &$$

## (4) By reduction of carbonyl compounds

## (a) Catalytic hydrogenation of aldehydes and ketones

#### **General reaction**

R-CHO 
$$\xrightarrow{H_2/Ni}$$
 R-CH<sub>2</sub>OH  
Aldehyde 1°Alcohol  
R<sub>2</sub>C=O  $\xrightarrow{H_2/Ni}$  R<sub>2</sub>CH-OH  
Ketone 2°Alcohol

e.g. 
$$CH_3CHO + 2H \xrightarrow{H_2/Ni} CH_3CH_2OH$$

$$CH_2=CHCHO + 4H \xrightarrow{Ni} CH_3CH_2CH_2OH$$
 (Acrolein)

## (b) Lithium aluminium hydride reduction of aldehydes and ketones

#### **General reaction**

(i) 
$$R-CHO \xrightarrow{LiAlH_4} R-CH_2OH$$
  
Aldehyde  $1^{\circ}Alcohol$ 

(ii) 
$$R_2C=0$$
  $\xrightarrow{LiAIH_4}$   $R_2CH-OH$   $2^\circAlcohol$ 

(iii) RCOOH + 4H 
$$\xrightarrow{\text{LiAlH}_4}$$
 RCH<sub>2</sub>OH + H<sub>2</sub>O

(iv) 
$$R-C-CI + 4H \xrightarrow{LiAIH_4} RCH_2OH + HCI$$
 $II$ 
 $O$ 

(v) 
$$R-C-O-R' \xrightarrow{LiAlH_4} R-CH_2OH + R'OH$$

e.g. 
$$CH_{3}-C-O-H \xrightarrow{LiAlH_{4}} CH_{3}CH_{2}OH$$

$$O$$

$$\parallel$$

$$C_{2}H_{5}-C-CI + 4H \longrightarrow C_{2}H_{5}CH_{2}OH + HCI$$

(c) By NaBH<sub>4</sub> (sodium borohydride): It is insoluble in ether and is used in aqueous ethanolic solution to reduce carbonyl compounds. It does not reduce esters and acids.

$$CH_3CH=CHCHO+4H \xrightarrow{NaBH_4} CH_3CH=CHCH_2OH$$

(ii) Reduction of a ketone gives a secondary alcohol

$$\begin{array}{c} O \\ \hline \\ Cyclohexanone \end{array} \begin{array}{c} NaBH_4 \\ \hline \\ Cyclohexanol \end{array}$$



**(d) Bouveault-Blanc reduction :** The reduction of aldehydes, ketones or esters by means of excess of sodium and ethanol or n-butanol as the reducing agent.

#### **General reaction**

(i) Aldehyde RCHO 
$$\xrightarrow{\text{Na}}$$
 RCH<sub>2</sub>OH

(ii) Esters 
$$R'CO_2R'' \xrightarrow{Na} R'CH_2OH + R''OH$$

(iii) Ketones 
$$R_2CO \xrightarrow{Na} R_2CHOH$$

The Bouveault-Blanc reduction is believed to occur in steps involving transfer of one electron at a time.

#### **Mechanism**

$$R-C-OEt \xrightarrow{Na} R\overset{\bullet}{C}-OEt \xrightarrow{EtOH} RCH-OEt \xrightarrow{Na} R-CH\overset{\bullet}{OEt} \xrightarrow{IG}$$

$$RCH_{2}OHO\overset{EtOH}{\longleftarrow} RCH_{2}-O\overset{\bullet}{\longleftarrow} \overset{Na}{\longleftarrow} RCH_{2}-O\overset{\bullet}{\longleftarrow} \overset{EtOH}{\longleftarrow} R\overset{\bullet}{C}-\overset{\bullet}{O}\overset{\bullet}{\longleftarrow} \overset{Na}{\longleftarrow} RCH=O+OEt^{\bullet}$$

e.g. 
$$CH_3CHO + 2H \xrightarrow{Na} CH_3CH_2OH$$

$$CH_3COOC_2H_5 + 4H \xrightarrow{Na} 2CH_3CH_2OH$$

$$CH_3-C-CH_3+2H \xrightarrow{Na} CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

**Ex.** Identify (X) in the following reaction

$$\begin{array}{c}
O \\
\parallel \\
CH_3-CH-CH_2-CH \xrightarrow{LiAlH_4} X \\
\downarrow \\
OH
\end{array}$$

**Ex.** What are the product A, B, C, D and E in the following reactions? PIADS

Nurturing potential through education NaBH<sub>4</sub> B 
$$CH_4OH$$
  $CH_3OH$   $CH_3OH$ 

B:

Ester part is not affected by NaBH<sub>4</sub>

C:

Ester part and keto parts are affected by LiAlH<sub>4</sub>

D:

#### By reaction of nitrous acid on aliphatic primary amines (5)

**General reaction** Mech.

$$\text{R-NH}_2\text{+HONO} \xrightarrow{\quad \text{NaNO}_2\,/\text{HCI} \quad} \text{R-OH} + \text{N}_2 + \text{H}_2\text{O}$$

e.g.

$$R-NH_{2} \xrightarrow{HNO_{2}} (RN_{2}^{\oplus}) \xrightarrow{H_{2}O} ROH + N_{2} + H^{\oplus}$$

$$C_{2}H_{5}NH_{2} + HNO_{2} \xrightarrow{} C_{2}H_{5}OH + N_{2} + H_{2}O$$

(ii) 
$$CH_3-CH_2-C-CH_3+HONO \xrightarrow{NaNO_2/HCI} CH_3-CH_2-C-CH_3+N_2+H_2O$$

$$NH_2 OH$$

Mech.

#### Hydroxylation: Forms vicinal diols (glycols) (6)

Converting an alkene to a glycol requires adding a hydroxy group to each end of the double bond. This addition is called hydroxylation of the double bond.

OLYMPIADS

## (a) Syn hydroxylation, using KMnO<sub>4</sub>/NaOH or using OsO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> **General reaction:**

e.g.

cis-3-hexene

$$\begin{array}{c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & \\ & & \\ &$$

cis-Cyclopentane-1, 2-diol

## (b) Anti hydroxylation, using per acids

$$\begin{array}{c} & & & \\ &$$

trans-Cyclopentane-1, 2-diol

#### **Chemical reactions of alcohols**

#### Reaction with hydrogen halides

#### **General reaction:**

$$\begin{array}{lll} R-OH+HX & \longrightarrow R-X+H_2O & (R \ may \ rearrange) \\ Reactivity \ of \ HX: & HI>HBr>HCI \\ Reactivity \ of \ ROH: & allyI, \ benzyI>3^\circ>2^\circ>1^\circ \end{array}$$

**Mechanism** 
$$R - OH \xrightarrow{H^{\oplus}} R - \overset{\oplus}{OH}_2 \longrightarrow \overset{\oplus}{R} \xrightarrow{X^{\ominus}} R - X$$

e.g. 
$$CH_3$$
 $CH_3$ 
 $CH_$ 

#### 2. Reaction with Phosphorus trihalides

- (1) Several phosphorus halides are useful for converting alcohols to alkyl halides. PBr<sub>3</sub>, PCl<sub>3</sub>, & PCl<sub>5</sub> work well and are commercially available.
- (2) Phosphorus halides produce good yields of most primary and secondary alkyl halides, but none works well with ter. alcohols. The two phosphorus halides used most often are  $PBr_3$  and the  $P_4/I_2$  combination.

#### **General reaction:**

$$3R - OH + PX_3 \xrightarrow{(PX_3 = PCI_3, PBr_3, PI_3)} 3R - X + H_3PO_3$$

#### Mechanism

The mechanism for the reaction involves attach of the alcohol group on the phosphorus atom, displacing a bromide ion and forming a protonated alkyl dibromophosphite (see following reaction).

alkyl dibromophosphite

In second step a bromide ion acts as nucleophile to displace HOPBr<sub>2</sub>, a good leaving group due to the electronegative atoms bonded to the phosphorus.

$$X = RCH_2 + RCH_2 + HOPX_2$$

$$H$$

A good leaving group

$$\begin{array}{c|cccc} CH_3 & CH_3 \\ & & & | \\ \hline \textbf{e.g.} & CH_3CH_2CHCH_2OH & \xrightarrow{PBr_3} & CH_3CH_2CHCH_2Br \\ 2-Methyl-1-butanol & 2-Methyl-1-bromobutane \\ \hline & CH_3CH_2OH & \xrightarrow{P+I_2} & CH_3CH_2I \\ & Ethyl \ alcohol & Ethyl \ iodide \\ \end{array}$$

#### 3. Reaction with thionyl chloride

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{R-OH+CI-S-CI} & \xrightarrow{\text{Heat}} & \text{R-CI+SO}_2\text{+HCI} \end{array}$$

#### 4. **Dehydration of alcohols**

(Rearrangement may occur)

#### Mechanism

Step 1: 
$$CH_{3} - C - O - H + H - O = CH_{3} - C - O - C - O - H + H - O = CH_{3} - C - O - C - O - H + H - O = CH_{3} - C - O - C - O - H + H - O = CH_{3} - C$$

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CH<sub>3</sub> H

CH<sub>3</sub> - C - O - H

CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> Step 2:

Step 3: 
$$\begin{array}{c} H \\ H - C - H \leftarrow H \\ C \oplus H \end{array}$$
 
$$\begin{array}{c} CH_2 \\ C \oplus C \end{array}$$
 
$$\begin{array}{c} H \\ C \oplus C \end{array}$$
 
$$\begin{array}{c} CH_3 \\ CH_3 \end{array}$$

Reactivity of ROH:  $3^{\circ} > 2^{\circ} > 1^{\circ}$ 

#### 5. Reaction with metals

$$RO-H+M \longrightarrow RO^{\ominus}M^{\oplus} + \frac{1}{2}H_{2}$$
 M=Na, K, Mg, Al, etc  
Reactivity order of ROH:  $CH_{3}OH > 1^{\circ} > 2^{\circ} > 3^{\circ}$ 

e.g. 
$$CH_3CH_2OH \xrightarrow{Na} CH_3CH_2O^{\Theta}M^{\oplus} + \frac{1}{2}H_2$$
  
Ethyl alcohol Sodium ethoxide

$$\begin{array}{cccc}
CH_3 & CH_3 \\
CH_3-C-OH & CH_3-C-O^{\odot}K^{\oplus} \\
CH_3 & CH_3 \\
CH_3 & CH_3
\end{array}$$
tert-Butyl alcohol Potassium tert-butovide

### 6. Ester formation

#### **General reaction**

$$R - C \underset{Acid}{ \bigcirc O } O + \underset{Alcohol}{R'OH} + \underset{Alcohol}{R'OH} R'OH \underset{Ester}{ \bigcirc OR'} + H_2O$$

e.g. 
$$CH_3CH_2O - H + CH_3C \stackrel{O}{\underset{OH}{=}} O \xrightarrow{H^{\oplus}} CH_3C \stackrel{O}{\underset{OC_2H_5}{=}} + H_2O$$
Acetic acid Ethyl acetate

#### 7. Oxidation reactions

## (a) oxidation of primary alcohols

Oxidation of a primary alcohol initially forms an aldehyde obtaining the aldehyde is often difficult, since most oxidizing agents are strong enough to oxidize the adehydes formed.  $CrO_3$  acid generally oxidizes a primary alcohol all the way upto the carboxylic acid

### (b) oxidation of secondary aldohols

Sec. alcohols are easily oxidized to give excellent yields of ketones. The chromic acid reagent is often best for laboratory oxidations of secondary alcohols. The active species in the mixture is probably chromic acid,

 $\rm H_2CrO_4$ , or the acid chromate ion,  $\rm HCrO_4^{\odot}$ 

## (c) Resistance of tertiary alcohols to oxidation

Oxidation of ter-alcohol is not an important reaction is organic chemistry. Ter-alcohols have hydrogen atoms on the carbinol carbon atom, so oxidation must take place by breaking C–C bonds. These oxidations require severe conditions and result in mixtures of products.

Primary 
$$R-CH_2OH$$
  $\xrightarrow{C_2H_5NH^{\oplus}CrO_3Cl^{\ominus}}$   $R-C=O$  An aldehyde  $KMnO_4$   $\xrightarrow{R-COOH}$  A carboxylic acid

Secondary 
$$\begin{array}{c} R \\ I \\ R-CHOH \xrightarrow{\quad K_2Cr_2O_7 \text{ or } CrO_3/H^\oplus} \\ & A \text{ ketone} \end{array}$$

Tertiary 
$$R-C-OH \xrightarrow{KMnO_4} no reaction$$
  $R$ 

e.g. 
$$CH_3CH_2CH_2OH \xrightarrow{C_5H_5NH^\oplus CrO_3Cl^\Theta} CH_3CH_2C=O$$
  
n-Propyl alcohol Propionaldehyde (1°)

Nurturing potential through education

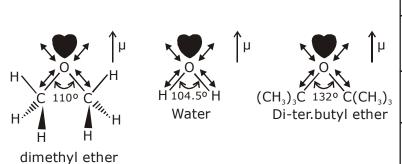
Ex. 
$$\begin{array}{c}
OH \\
& CrO_3 \\
& H_2SO_4 \\
& acetone
\end{array}$$

Identify A

Ans. 
$$\begin{array}{c}
OH & O \\
\hline
CrO_3 \\
H_2SO_4 \\
acetone
\end{array}$$

# **ETHER**

#### Structure of ether



Compound	Hybridization	Bond angle
H Ö H water	sp³	104.50
R H Alcohol	sp³	108.50
R Ö R Ether	sp³	111.70

## **Classification of Acyclic ethers**

S.No.	Туре	Example	Name
1	Simple ether	CH <sub>3</sub> -O-CH <sub>3</sub>	Methoxy methane
		CH <sub>3</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>3</sub>	Ethoxy ethane
2	Mixed ether	CH <sub>3</sub> -O-CH <sub>2</sub> -CH <sub>3</sub>	Methoxy ethane

## **IUPAC Nomenclature of ether "Alkoxy Alkane"**

S.N.	Compound	IUPAC Name
1.	CH₃-CH-O-CH₃	2-Methoxy propane
	CH₃	
2.	CI-CH <sub>2</sub> -O-CH <sub>3</sub>	Chloromethoxy methane
3.	OCH <sub>3</sub>	Methoxy benzene (Anisole)
4.	CH <sub>3</sub> CH <sub>3</sub> Nuc Hring pot OCH <sub>2</sub> -CH <sub>3</sub>	3-Ethoxy-1, 1-dimethyl cyclohexane
5.	CI """H .,,,,\(\) OCH <sub>3</sub>	trans-1-Chloro-2-methoxy cyclobutane
6.	CH <sub>2</sub> -OH   CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>3</sub>	2-Ethoxy ethan-1-ol

## **Method of Preparation of Ether**

# (1) Williamson synthesis

# General reaction

$$RX + R'O^{\circ}Na^{\circ} \longrightarrow R - OR'$$

e.g. (i) n-PrOH 
$$\xrightarrow{n-PrBr}$$
 CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
Di-n-propyl ether

(ii) MeOH 
$$\xrightarrow{\text{Na}}$$
 MeO $^{\Theta}$   $\xrightarrow{\text{PhCH}_2\text{Br}}$   $\longleftrightarrow$  CH $_2$ -O-CH $_3$ 

(iii) t-BuOH  $\xrightarrow{Na}$  t-BuO $^{\Theta}$   $\xrightarrow{EtBr}$  t-Butyl ethyl ether (This reaction produces a poor yield of ether because of the bulkiness of t-BuO $^{-}$ )

## 2. Williamson's Continuous Etherification process or by Dehydration of Alcohols

(i) 
$$ROH + \overset{\oplus}{H} \longrightarrow RO\overset{\oplus}{H_2}$$
  
 $ROH + \overset{\oplus}{R} - OH_2 \xrightarrow{S_N^2} R_2OH + H_2O \longrightarrow ROR + H_3O^{\oplus}$ 

(ii) 
$$ROH + H \longrightarrow ROH_2 \longrightarrow R$$
 ....  $S_N^1$   
 $ROH + R \longrightarrow ROR \longrightarrow ROR$   
 $H$ 

e.g. 
$$CH_3CH_2OH$$

$$H_2SO_4 \longrightarrow CH_2=CH_2$$
Ethene
$$H_2SO_4 \longrightarrow CH_3CH_2OCH_2CH_3$$

$$140^{\circ}C \longrightarrow CH_3CH_2OCH_2CH_3$$
Diethyl ethene

#### Mechanism

Step-1: 
$$CH_3CH_2 - 0 - H + H - OSO_3H - CH_3CH_2 - 0 - H + OSO_3H$$

This is an acid-base reaction in which the alcohol accepts a proton from the sulfuric acid

Another molecule of the alcohol acts as a nucleophile and attacks the protonated alcohol in an  $S_N^2$  reaction.

Step-3: 
$$CH_3CH_2 = 0$$
  $CH_2CH_3 + 10$   $CH_3CH_2 = 0$   $CH_3CH_3 + 10$   $CH_3CH_3 = 0$   $CH_3CH_3 + 10$   $CH_3CH_3 = 0$   $CH_3CH_3$ 

Another acid-base reaction converts the protonated ether to an ether by transferring a proton to a molecule of water (or to another molecule of the alcohol).

Only one combination of alkythalide and alkoxide is appropriate for the preparation of each of the following ethers by Willianson ether synthesis. What is the correct combination in each case ?



#### 3. Form alkenes

## (a) By addition of alcohols in alkenes

When alcohol is added to alkenes in presence of acid, we get ethers.

#### **General reaction**

(I) 
$$C = C \leftarrow \xrightarrow{H_2SO_4}$$
 carbocation

**e.g.** (I) 
$$Me_2C = CH_2 + H^{\oplus}(H_2SO_4) \longrightarrow Me_3C^{\oplus}$$

(II) 
$$Me_3C^{\oplus} + EtOH \longrightarrow Me_3C-\overset{\oplus}{O}-Et \xrightarrow{-H^{\oplus}} Me_3COEt$$

## (b) Alkoxymercuration - demercuration

$$C = C \left( \begin{array}{c} \frac{\text{Hg(OAc)}_2}{\text{ROH}} \\ \end{array} \right) - \begin{array}{c} \frac{1}{\text{C}} - \begin{array}{c} \frac{1}{\text{C}} - \\ \frac{1}{\text{C}} - \\ \end{array} \\ AcOHg \begin{array}{c} \text{O} - H \\ \end{array} \right) - \begin{array}{c} \frac{1}{\text{C}} - \begin{array}{c} \frac{1}{\text{C}} - \\ \frac{1}{\text{C}} - \\ \end{array} \\ H \begin{array}{c} \text{OR} \\ \end{array}$$

e.g.

(i) 
$$RCH=CH_2+R'OH \xrightarrow{\text{(i) Hg(OCOCF}_3)_2} RCH(OR')CH_3$$

(ii) 
$$\begin{array}{ccc} & CH_3 & CH_3 \\ I & I \\ CH_2 = CHCH_3 + CH_3CH(OH)CH_3 & \xrightarrow{(i) \ Hg(OCOCF_3)_2} & CH_3 - CH - O - CH - CH_3 \end{array}$$

#### Reactions of ethers

#### 1. With HX

#### **General reaction**

$$R-\ddot{\bigcirc}-R'+\overset{\oplus}{H}\overset{\ominus}{X} \longleftrightarrow \overset{X\overset{\ominus}{\longleftarrow}}{R}\overset{H}-\overset{H}{\overset{\bigcirc}{\bigcirc}}-R' \longrightarrow \overset{X-R}{\underset{alkyl \ halide}{X-R}}+\overset{H}{\overset{\downarrow}{\overset{\downarrow}{\bigcirc}}}-R' \xrightarrow{HX} X-R+X-R'$$

e.g. (i) 
$$CH_3CH_2CH_2CH_3 \xrightarrow{HBr} 2CH_3-CH_2Br$$

## 2. Reaction with sulphuric acid

Ethers dissolve in concentrated solutions of strong inorganic acids to from oxonium salts, i.e. ether behave as bronsted Lowry bases.

$$R_{2}O + H_{2}SO_{4} \xrightarrow{conc.H_{2}SO_{4}} (R - \overset{\oplus}{O}^{-}R)HSO_{4}^{\Theta} \xrightarrow{\Delta} R-OH + R-O-SO_{2}OH$$
alkyl hydrogen sulphate

When heated with dilute H<sub>2</sub>SO<sub>4</sub>

$$R_2O + H_2SO_4 \xrightarrow{\Delta} 2ROH$$

$$\textbf{e.g.} \quad C_2 H_5 O C_2 H_5 + H_2 S O_4 \xrightarrow{\quad \Delta \quad} C_2 H_5 O H + C_2 H_5 O H S O_4 \xrightarrow{\quad H_2 O \quad} C_2 H_5 O H + H_2 S O_4 O H_5 O H_5$$

#### 3. Autoxidation of ethers:

When ethers are stored in the presence of atmospheric oxygen, they slowly oxidize to produce hydroperoxides and dialkyl peroxides, both of which are explosive. Such a spontaneous oxidation by atmospheric oxygen is called an autoxidation.

#### **General reaction**

$$R-O-CH_2-R' \xrightarrow{excess O_2 \\ ether} (Slow) \xrightarrow{(Slow)} R-O-CH-R' + R-O-O-CH_2-R' \\ Hydroperoxide dialkl peroxide$$

Ex. (i) 
$$\begin{array}{c} H_3C \\ H_3C \end{array} C = C \\ \begin{array}{c} CH_3 \\ CH_3 \end{array} \xrightarrow{\text{excess O}_2 \\ \text{(weeks or months)}} \\ \begin{array}{c} H_3C \\ CH - O - C - CH_3 \\ CH_3 \end{array} + \\ \begin{array}{c} H_3C \\ CH - O - O - CH \\ CH_3 \end{array} \xrightarrow{\text{Diisopropyl peroxide}} \\ \end{array}$$

(ii) 
$$CH_3CH_2-O-CH_2CH_3 \xrightarrow{h_0} CH_3-CH-O-CH_2CH_3$$
Diethyl ether 1-Ethoxyethyl hydroperoxide

## 4. Reaction with acid chlorides and anhydrides

**Reagent:** ZnCl<sub>2</sub>, AlCl<sub>3</sub> etc.

**General reaction** (i) 
$$R-O-R+R-CO-CI \xrightarrow{AICI_3} R-CI+RCOOR$$

Mech.

$$\begin{aligned} & \text{RCOCI} + \text{AICI}_3 & \longrightarrow \text{RCO}^+ + \text{AICI}_4^- \\ & \text{R'-O} + \text{RCO}^+ & \longrightarrow \text{R'-O}^+ & \text{COR} & \longrightarrow \text{RCOOR'} + \overset{\scriptscriptstyle\oplus}{\text{R}"} & \xrightarrow{\text{AICI}_4^{\scriptscriptstyle\ominus}} & \text{R"CI} + \text{AICI}_3 \end{aligned}$$

$$\textbf{e.g.} \quad C_2 H_5 O C_2 H_5 + C H_3 C O C I \xrightarrow{\quad \text{Anhydous} \\ \quad \text{ZnCl}_2 \quad \quad } C_2 H_5 C I + C H_3 C O O C_2 H_5$$

(ii) 
$$R_2O + (CH_3CO)_2O \xrightarrow{ZnCl_2} 2CH_3COOR$$
 acid anhydride

e.g. 
$$C_2H_5OC_2H_5 + (CH_3CO)_2O \xrightarrow{\text{anhydrous} \\ AlCl_3} \rightarrow 2CH_3COOC_2H_5$$

## 5. Reaction with carbon monoxide:

Ether react with CO at 125-180 $^{\circ}$ C and at a pressure of 500 atm, in the presence of BF $_{_3}$  plus a little water.

$$R_2O + CO \xrightarrow{BF_3 \atop 500 \text{atm}} RCOOR$$

$$| IIT-JEE | AIEEE \atop CBSE | SAT | NTSE \atop OLYMPIADS$$

# 6. Reaction with halogens uring potential through education

When treated with chlorine or Br, ether undergo substitution, the extent of which depends on the conditions.

$$\begin{split} & \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 \xrightarrow{\text{Cl}_2} \text{CH}_3\text{CHClOCH}_2\text{CH}_3 \xrightarrow{\text{Cl}_2} \text{CH}_3\text{CHClOCHClCH}_3 \\ & \text{in presence of light} \\ & (\text{C}_2\text{H}_5)_2\text{O} \xrightarrow{\text{Cl}_2} \text{hv} \xrightarrow{\text{Cl}_2} \text{(C}_2\text{Cl}_5)_2\text{O} \\ & \text{Perchloro} \\ & \text{Highlands of the state of the$$

#### Mech.

The reaction proceeds by a free-radical mechanism, and  $\alpha$ -substitution occurs readily because of resonance stabilization of the intermediate radical

