# Part-I (Alkyl Halides/Aryl Halides)

# Introduction :

# (A) Alkyl halides :

There are three major classes of organohalogen compounds ; the alkyl halides, the vinyl halides, and the aryl halides.

An alkyl halide simply has a halogen atoms bonded to one of the sp<sup>3</sup> hybrid carbon atoms of an alkyl group. (A vinyl halide or Aryl halide has a halogen atom bonded to one of the sp<sup>2</sup> hybrid carbon atoms of an aromatic ring. They are different from alkyl halides because their bonding and hybridization are different.)

# **Classification of halides :**

## (a) Alkyl halides or haloalkanes (R—X) Compounds Containing sp<sup>3</sup> C–X Bond :

They are classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached.



#### (b) Allylic halides :

These are the compounds in which the halogen atom is bonded to an sp<sup>3</sup>-hybridised carbon atom next to carbon-carbon double bond (C=C) i.e. to an allylic carbon.



#### (c) Benzylic halides :

These are the compounds in which the halogen atom is bonded to an sp<sup>3</sup>-hybridised carbon atom next to an aromatic ring.



(d) Compounds Containing sp<sup>2</sup> C–X Bond : Vinylic halides  $\longrightarrow_{X}$  Aryl halides [

Structure of alkyl halide :



The carbon-halogen bond in an alkyl halide is **polar** because halogen atoms are more electronegative than carbon atoms. Most reactions of alkyl halides result from breaking this polarized bond. The carbon atom has a partial positive charge, making it some what electrophilic.

# 1. Types of Reagents :

Reagents are of two types : (i) Electrophiles (ii) Nucleophiles

# 1.1 Electrophiles :

Electrophiles are electron deficient species.

**Ex.**  $\overrightarrow{CI}$ ,  $\overrightarrow{Br}$ ,  $\overrightarrow{NO}_2$  (positively charged species),

PCl<sub>5</sub>, SO<sub>2</sub>, SO<sub>3</sub> (species with vacant orbital at central atom).

# 1.2 Nucleophiles and their nucleophilicity :

Nucleophile is a species having negative charge or lone pair of electrons. They are electron rich species.

**Ex.**  $H_2^{\dot{O}}$ : (I.p on O-atom),  $CI^{\Theta}$  (negatively charged species)

## Note : :CCl<sub>2</sub> is not a nucleophile because it is electron deficient species and act as electrophile.

Negative ions have more nucleophilic than their neutral species

$$OH^{\Theta} > H_2O$$
,  $NH_2^{\Theta} > NH_3$ ,  $OR > ROH$ 

• Down the group nucleophilicity increases because the more polarizable donar atom is better nucleophyle

Polarizability size of donar atom

 $F^{\Theta} < CI^{\Theta} < Br^{\Theta} < I^{\Theta}, OH^{\Theta} < SH^{\Theta}$ 

- Across the period nucleophilicity decreases  $CH_3^{\Theta} > NH_2^{\Theta} > OH^{\Theta} > F^{\Theta}$
- Bulky base has less nucleophilic character.

$$CH_3$$
  
 $H_3 - C - O^{\Theta} < CH_3 - CH_2 - O^{\Theta}$   
 $CH_3$ 

• Effect of solvent : In case of polar aprotic solvents nucleophilicity order of halides is just reversed.  $F^{\Theta} > CI^{\Theta} > Br^{\Theta} > I^{\Theta}$ 

# **1.3** Bases and their basicity :

Bases are the species which accept the proton or which donates l.p. of electron to proton.

- Basicity decreases down the group while nucleophilicity increases  $F^- > CI^- > Br^- > I^-$
- Nucleophilicity and basicity order will be same across the period.
- For the same donor atom nucleophilicity and basicity order will be same

# 1.4 Leaving group ability :

- Weaker base is better leaving group.
- More resonance stabilised ion will be better leaving group.
- Weaker the carbon-leaving group bond (C–X) better will be the leaving group.
- If activation energy of a reaction is low then reaction will be fast and leaving group will be better.

Ex.





Note : More stable anions are weak bases & hence better leaving group.

# 2. Types of solvents :

S.N.	Solvent	Polar	Nonpolar	Protic	Aprotic
1.	CH₃ COOH	$\checkmark$	×	$\checkmark$	×
2.		$\checkmark$	×	×	$\checkmark$
3.	H <sub>2</sub> O	$\checkmark$	×	$\checkmark$	×
4.	ROH	$\checkmark$	×	$\checkmark$	×
5.	CH <sub>3</sub> — CH <sub>3</sub>	$\checkmark$	×	×	$\checkmark$
6.	CH <sub>3</sub> CH <sub>3</sub> S = O	$\checkmark$	×	×	$\checkmark$
7.	R-0-R	$\checkmark$	×	×	$\checkmark$
8.	$\bigcirc$	×	$\checkmark$	×	$\checkmark$
9.	DMF	$\checkmark$	×	×	$\checkmark$
10.	DMA	$\checkmark$	×	×	$\checkmark$

Note : If H atom is attached to oxgyen, nitrogen or sulphur then it is said to be protic solvent.

# 3. Nucleophilic substitution reactions of alkyl halides :

Alkyl halide undergoes nucleophilic substitution reaction.

 $\mathsf{R}\text{--}\mathsf{X} + \mathsf{N}\mathsf{u}^{\scriptscriptstyle \Theta} \longrightarrow \mathsf{R} - \mathsf{N}\mathsf{u} + \mathsf{X}^{\scriptscriptstyle \Theta}$ 

Nucleophilic substitution reactions are of two types :

# 3.1 Unimolecular nucleophilic substitution reaction $(S_N 1)$ :

- It is a two step process.

 $\begin{array}{ccc} \mathsf{R}-\mathsf{X} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$ 

In the second step nucleophile attacks from either side of carbocation to generate product (racemic mixture).

$$R^{\oplus} + Nu^{-} \longrightarrow \begin{bmatrix} \delta + & \delta - \\ R^{+} & Nu \end{bmatrix} \longrightarrow R - Nu \quad (II^{nd} \text{ is fast step})$$

$$T.S_{2}$$
Mechanism :
$$R^{+} \quad Ionisation \text{ of} \quad Ionisation$$

• Carbocation intermediate  $(d + \ell mix)$ • Carbocation intermediate is formed so rearrangement is possible in S<sub>N</sub>1 reaction.

#### Kinetics :

- Rate ∝ [Alkyl halide]
- It is unimolecular and first order reaction.
- Rate of  $S_N 1$  reaction is independent of the concentration and reactivity of nucleophile.

### Stereochemistry :



- Catalyst used is Ag<sup>+</sup>.
- More polar protic solvent is more favourable for  $S_N 1$ .

 $H_2O > ROH > NH_3$  (order of polar protic solvent).

- In S<sub>N</sub>1 reaction carbocation is formed along with anion and to solvate these ions, polar protic solvent is used.
- Decreasing order of reactivity of alkyl halides. ; R-I > R-Br > R-CI > R-F

(a)  $CH_2-Br H_2O/CH_3C-CH_3 \longrightarrow OH$ 



# **3.2** Bimolecular nucleophilic substitution reaction (S<sub>N</sub>2) :

It is a single step reaction as the rate of reaction depends upon concentration of substrate as well as nucleophile.

#### Mechanism :

In this reaction nucleophile attack from back side on the carbon atom bearing leaving group. it is a
concerted reaction where bond breaking and bond formation takes place simultaneously to
achieve a transition state (trigonal bipyramidal shape) where half bond has been formed and half
bond has been broken.



#### Kinetics :

- rate  $\infty$  [alkyl halide] [nucleophile]
- It is a bimolecular, one step **concerted** process.
- It is a second order reaction because in the r.d.s. both species are involved.

#### Steriochemistry :

Only one product is formed where inversion of configuration takes place.



- Polar aprotic solvent is favourable not polar protic solvent. Becuase in case of polar protic solvent nucleophilicity of anion is decreased due to solvation and such solvation is not possible in case of polar aprotic solvent.
- Electron withdrawing group increases the rate of  $s_{N}^{2}$  reaction.

 $O=CH-CH_2-Br > CH_3-O-CH_2-Br > H-CH_2-Br > CH_3-CH_2-Br$ 

Que. Which one in the given reaction is favourable



- Ans. (a) In case of (i) rate is slower than (ii) because nucleophilicity increases down the group.
  - (b) In case of (i) rate of reaction is faster than (ii) becuase (i) ion is more basic than (ii) it is known that for the same donar atom nucleophilicity and basicity have same order. Acetic acid is stronger acid than ethyl alcohol hence ethoxide ion is stronger base and better nucleophile than acetate ion.

# Comparision between $S_N 1 / S_N 2$ reaction :

Characteristics		S <sub>N</sub> 2	S <sub>N</sub> 1
1.	Kinetics	$r \propto [RX] [Nu:]$ $r \propto [F$	RX]
2.	Stereochemistry	inversion	racemisation
3.	Rearrangement	not possible	possible
4.	Nature of R – X	$CH_3 - X > R CH_2 X > R_2 CH X > R_3 CX$	$R_3CX > R_2CHX > RCH_2X > CH_3X$
5.	Nucleophile	strong anionic $R^- > NH_2^- > OR^- > OH^- H_2O >$	weak neutral MeOH>EtOH>NH <sub>3</sub>
6.	Leaving group	I⁻ > Br⁻ > Cl⁻ > F⁻	(same)
7.	Solvent	polar aprotic	polar protic

# Examples of $S_N 2$ reaction of alkyl halides :



## (i) Williamson's synthesis of ethers :

• It is used for the preparation of symmetrical as well as unsymmetrical ether.

 $R \rightarrow Br + NaOEt \rightarrow R \rightarrow OEt + NaBr$ 

- Williamson's synthesis involve attack of an alkoxide on alkyl halide to give ethers. In place of alkoxide, phenoxide can also be used.
- This is an  $S_N^2$  reaction because alkoxide is a strong nucleophile.
- On using 2° & 3° alkylhalide we get alkene not ether as a product.

Ex.



(Elimination reaction)



Note : Vinyl or Aryl halide should not be used because they don't give S<sub>N</sub>2 reaction.

**Ex.** 
$$H_3 \rightarrow No$$
 reaction

Que. Which of the following ethers cannot prepared by Williamson's synthesis reaction : ~ 1

(1) CH <sub>3</sub> —CH <sub>2</sub> —O—CH <sub>3</sub>	(2) $CH_3 \xrightarrow{C} O \xrightarrow{C} O \xrightarrow{C} CH_3$
(3) Ph–O–Ph	$CH_3 CH_3$ (4) Ph–O–CH <sub>3</sub>

#### Ans. 2&3

#### (ii) Reaction with AgCN and NaCN :

$$R-X \xrightarrow{\text{NaCN}} R-CN + NaX$$

NaCN is a more ionic hence ionized to give free  $\stackrel{\Theta}{CN}$  (an ambident nucleophile) where carbon side is more active than nitrogen side. That is why with NaCN, RCN is formed.

On the other hand AgCN is more covalent so it is not ionized therefore only nitrogen side is free to act as a nucleophile and give isocyanide (R-NC)

## (iii) Reaction with NH<sub>3</sub>:



$$(exess)$$

$$(exess)$$

$$H_{2}^{+} CH_{3} - Br \longrightarrow O(CH_{3})_{3}Br$$

## (iv) Finkelstein reaction :

 $R - OH + HI - R - I \xrightarrow{HI} R - H + I_2 \text{ (reduced) [Final product is Alkane (R-H) not R-I]}$ 

This is a problems that is why iodides are best prepared through halogen exchange reaction. It is also known as Finkelstein reaction. In this reaction R—CI and R—Br is treated with sodium iodide in acetone.

$$Ph-CH_{2}-Br \xrightarrow{NaI} Ph-CH_{2}-I + NaBr \downarrow$$
(Soluble)
$$R-Br \xrightarrow{NaI} R-I + NaBr \downarrow$$

- NaI is soluble in acetone. In this reaction acetone is used because sodium iodide is soluble in acetone but NaBr and NaCl are insoluble so precipitated out. This eliminates any possibility of reverse reaction.
- It is an  $S_N 2$  reaction therefore only 1°RX and 2°RX is used.



# 4. Aryl Halides :

## 4.1 **Preparation of Aryl Halides**

1. By Halogenation :

$$\bigcirc + X_2 \xrightarrow{\text{Lewis acid}} \bigcirc + HX$$

 $X_2 = CI_2$ ,  $Br_2$ ; Lewis acid = FeCI<sub>3</sub>, AlCI<sub>3</sub>, ZnCI<sub>2</sub>, etc.

2. By Decarboxylation :



# 4.2 Chemical reaction of Aryl halide (Bimolecular nucleophilic substitution $S_N 2$ Ar)

• An electron withdrawing group at ortho or para positions with respect to a good leaving groups are necessary conditions for  $S_N 2$  Ar.





Intermediate ion is stabilized by resonance and are stable salts called Meisenheimer salts.



• A group that withdraws electrons tends to neutralize the negative charge of the ring and this dispersal of the charge stabilizes the carbanion.



G withdraws electrons : stabilizes carbanion, activates the  $Ar-S_N 2$  reaction.

$$(-N(CH_3)_3, -NO_2, -CN, -SO_3H, -COOH, -CHO, -COR, -X)$$

• A group that releases electrons tends to intensify the negative charge, destabilizes the carbanion, and thus slows down reaction.



G ( $-NH_2$ , -OH, -OR, -R) releases electrons : destabilizes carbanion, deactivates the Ar-S<sub>N</sub>2 reaction. **Element effect** :- The fact that fluoro is the best leaving group among the halogens in most ArS<sub>N</sub>2 but in S<sub>N</sub>1 & S<sub>N</sub>2 mechanism where fluoro is the poorest leaving group among halogens.

# 5. Elimination reactions of alkyl halides :

In an elimination reaction two atoms or groups (YZ) are removed from the substrate and generally resulting into formation of  $\pi$  bond.

$$\begin{array}{c|c} & | & | \\ -C - C - & \underline{\mathsf{Elimination}} \\ | & | & - YZ \\ Y & Z \end{array} \right) > C = C \le C$$

# 5.1 Unimolecular elimination reaction (E1) :

Proton and leaving group depart in two different step.

Mechanism :

Step 1 : Formation of the carbocation (r.d.s.)

$$- \overset{|}{\overset{C}{\overset{}}} - \overset{|}{\overset{C}{\overset{}}} - \overset{|}{\overset{\leftarrow}{\overset{\leftarrow}{\overset{}}}} - \overset{|}{\overset{C}{\overset{}}} - \overset{|}{\overset{C}{\overset{}}} - \overset{|}{\overset{\leftarrow}{\overset{}}} + \overset{\otimes}{\overset{\times}{\overset{\times}}}$$

Step 2 : Base ( ) abstracts a proton (fast step)

$$-C = C = C + B - H$$

$$H$$

$$Alkene$$

Reaction intermediate is carbocation, so rearrangment is possible

Kinetics :

O B

- Rate ∝ [Alkylhalide]
- It is a unimolecular and first order reaction.
- Reactivity order is similar to S<sub>N</sub>1 becuase Carbocation Intermediate is formed in the rds step.

 $S_{N}1 \text{ v/s E1}$  :

• In case of alkyl halides  $S_{N}$ 1 product is generally more than E1 product

Ex. (a) 
$$CH_3 - CH_2 - C - CH_3 \xrightarrow{CH_3OH} CH_3 - CH_2 \xrightarrow{C} - CH_3 \xrightarrow{CH_3OH} CH_3 - CH_3 \xrightarrow{C} - CH_3 \xrightarrow{CH_3OH} CH_3 \xrightarrow{C} - - CH_3 \xrightarrow{C} - - CH_3 \xrightarrow{C} - - CH_3 \xrightarrow{$$

# 5.2 Bimolecular elimination reaction (E2) :

• It is a second order reaction because rate of reaction depends upon conc. of substrate as well as base.

#### Mechanism :

• Orientation of eliminated proton and leaving group are antiparallel or antiperiplanar to each other because in anti conformation the transition state is more stable due to minimum electronic repulsion.



Transition state (antiperiplaner)

- E2 reaction is stereospecific.
- E2 reaction also depends upon size of base which decides major or minor product.

#### Kinetics :

- Rate  $\propto$  [R X] [Base]
- This is a single step, bimolecular reaction
- No carbocation intermediate is formed hence there is no rearrangement but a transition state is achieved because it is a single step reaction.
- More favourable substrate is tertiary alkyl halide because it will give more stable alkene according to saytzeff rule.



#### Some important terms :

(a) **Regioselective reaction :** Those reaction in which more than one structural isomeric products are possible, said to be regioselective reaction.

$$CH_{3} - CH_{2} - CH_{3} - C$$

(b) Regiospecific reaction : Those reaction in which only one structural isomer product is formed out of the possible products, said to be regiospecific reaction.

- (c) Stereoselective : Those reactions in which mixture of two stereoisomeric products are formed with one major product. Examples : S<sub>N</sub>1, S<sub>N</sub>2 and E2
- (d) Stereospecific reaction : Those reactions in which two stereoisomeric reactants give two different stereoisomeric products, are called as stereospecific reactions. Examples : S<sub>N</sub>2 and E2

Note : All stereospecific reactions are stereo selective.

#### Comparison between E1 and E2 reactions :

	E1	E2		
Base	Weak base	Strong base required		
Substrate	3° > 2° > 1°	3° > 2° > 1°		
Leaving group	Better one required	Better one required		
Kinetics	K [R – X], first order	K [R – X] [Base] second order		
Orientation	Saytzeff alkene	Saytzeff alkene		

#### 5.3 E1cB Reaction :

- It is two step reaction.
- In first step base takes proton from adjacent carbon atom of halogen bearing carbon and generate carbanion intermediate.



• In second step there is loss of leaving group by carbanion to get alkene :

$$\xrightarrow{\Theta}_{I} \xrightarrow{C}_{C} \xrightarrow{C}_{C} \xrightarrow{-Br}_{I} \xrightarrow{-Br}_{I} \xrightarrow{-C}_{I} \xrightarrow{C}_{C} \xrightarrow{I}_{C}$$

Ex.

- $C_{6}H_{5} \xrightarrow{O} C \xrightarrow{O} CH_{2} \xrightarrow{C} CH \xrightarrow{C} CH_{3} \xrightarrow{\text{base}} C_{6}H_{5} \xrightarrow{O} \xrightarrow{O} \xrightarrow{O} CH \xrightarrow{C} CH \xrightarrow{C} CH_{3} \xrightarrow{O} C_{6}H_{5} \xrightarrow{O} CH \xrightarrow{O} CH \xrightarrow{C} C$ 
  - β-hydrogen atom should be more acidic which is possible only if carbon atom having β-hydrogen atom should be link to with electron withdrawing group (-m, -l group).
  - Leaving group should be more electronegative because it also increases acidity of  $\beta$ -hydrogen atom.
  - Experimentally it is found that 1st step i.e. formation of carbanion intermediate is fast step and second step i.e. removal of leaving group is slow step thus r.d.s. in E1cB is second step.

# 6. Reactions of chloroform :



- Purity of chloroform (presence of phosgene) can be tested before use as anaesthetic by treating with aqueous solution of AgNO<sub>3</sub> because the presence of COCl<sub>2</sub> may cause cardiac failure.
- Chloroform is stored in dark colour bottle containing small amount of ethyl alcohol. (It converts phosgene into diethylcarbonate).



- CCl<sub>4</sub> is stable to heat and its vapours do not catch fire thus it is used as fire extinguisher.
- CCl<sub>4</sub> used as medicine for elimination of hook worms.

# Freons (Polychlorofluoro alkane)

7.

- $\xrightarrow{\text{SbCl}_4\text{F}}$ (i) CCl<sub>4</sub> + HF CCI<sub>3</sub>F + HCI (Freon-11) (ii)  $CCl_3F$  +  $HF \longrightarrow CCl_2F_2$  + HCl(Freon-12) (iii)  $C_2Cl_6$  + 2HF  $\longrightarrow$   $C_2Cl_4F_2$  + 2HCI (Freon-112) Nomenclature of Freons : Freon is expressed as Freon - cba Where a - [Number of F-atoms] b - [1 + Number of H-atoms] c - [Number of C-atoms -1] Example : C<sub>2</sub>Cl<sub>4</sub>F<sub>2</sub> is expressed as Freon-112
  - a = 2; b = 1 + 0; c = 2 1cba = 112
- Freon is odourless, non-corrosive, non-toxic gas. It can easily be liquefied hence widely used as refrigerant.

# Part-II (Alcohol & Ether)

# Alcohols :

Alcohols have sp<sup>3</sup> hybridized oxygen atoms, but the C – O – H bond angle in methanol (108.9°) is considerably larger than the H – O – H bond angle in water (104.5°) because the methyl group is much larger than a hydrogen atom.

The bulky methyl group counteracts the bond angle compression caused by oxygen's nonbonding pairs of electrons. The O – H bond lengths are about the same in water and methanol (0.96 Å), but the C – O bond is considerably longer (1.4 Å), reflecting the larger covalent radius of carbon compared to hydrogen.





## **Classification of alcohols:**

(a) Alcohols may be classified as mono-, di-, tri- or polyhydric alcohols depending on whether they contain one, two, three,......hydroxy group.

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Monohydric : Contains one –OH group (C_2H_5OH ; CH_3-CH_2-CH_2-OH)
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Dihydric : Contains two –OH group

CH₂OH (Glycol) I CH₂OH



#### Ethers :

Like water, ethers have a bent structure, with an sp<sup>3</sup> hybrid oxygen atom giving a nearly tetrahedral bond angle.



dimethyl ether

Bonding in ethers is readily understood by comparing ethers with water and alcohol. Van der Waals strain involving alkyl groups causes the bond angle at oxygen to the larger in ethers than in alcohol, and larger in alcohols than in water. An extreme example is di-tert-butyl ether, where steric hindrance between the tert-butyl groups is responsible for a dramatic increase in the C - O - C bond angle.

#### Classificiation of ethers :

(a) Simple or symmetrical : If the alkyl or aryl groups attached to the oxygen atom are the same.

 $CH_3OCH_3, C_2H_5OC_2H_5$ 

(b) Mixed or unsymmetrical : If the two groups attached to the oxygen atom are different.

 $C_2H_5OCH_3$ ,  $C_2H_5OC_6H_5$ .

## General Reactions of alkyl halides, alcohols & ethers :



# 1. Nucleophilic substitution $(S_N)$ reaction of alcohols :



### 1.1 In presence of HX :

 $R-OH + HX \longrightarrow RX + H_2O$ 

This is a nucleophilic substitution  $(S_N 1/S_N 2)$ 

Mechanism : 
$$R \rightarrow OH \xrightarrow{HX} R \rightarrow Q \xrightarrow{\oplus} H_2 \xrightarrow{S_N 1} R \xrightarrow{\oplus} H_2 O \xrightarrow{X^{\oplus}} R - X$$
  
 $X \xrightarrow{\oplus} S_N^2$   
 $R - X + H_2 O$ 

Note : Mainly  $\beta$  - unsubstituted 1° alcohol give S<sub>N</sub>2 reaction with HX.

Ex.

(a) 
$$CH_{3}$$
— $CH_{2}$ — $CH_{2}$ — $OH$ — $HCI \rightarrow CH_{3}$ — $CH_{2}$ — $CH_{2} + H_{2}O$ ;  $(S_{N}2)$   
(b)  $CH_{3}$ — $CH_{2}$ — $CH$ — $CH_{3}$ — $HCI \rightarrow CH_{3}$ — $CH_{2}$ — $CH$ — $CH_{3} + H_{2}O$ ;  $(S_{N}1)$   
 $OH$ 
 $CI$ 
(c)  $CH_{3}$ — $CH$ — $CH$ — $CH_{3}$ — $HCI \rightarrow CH_{3}$ — $CH_{2}$ — $CH_{3} + H_{2}O$ ;  $(S_{N}1)$   
 $CI$ 
(d)  $CH_{3}$ — $CH_{3}$  +  $H_{2}O$ ;  $(S_{N}1)$   
 $CH_{3}$ — $CH_{3}$ ;  $(S_{N}1)$   
 $CH_{3}$ — $CH_{3}$ ;  $(S_{N}1)$   
 $CH_{3}$ — $CH_{3}$ —

• Reactivity of HX is HI > HBr > HCl > HF.

#### 1.2 Finkelstein reaction :

 $R - OH + HI \longrightarrow R - I \xrightarrow{HI} R - H + I_2 \text{ (reduced) [Final product is Alkane (R-H) not R-I]}$ 

This is a problems that is why iodides are best prepared through halogen exchange reaction. It is also known as Finkelstein reaction. In this reaction R—CI and R—Br is treated with sodium iodide in acetone.

$$Ph-CH_{2}-Br \xrightarrow{\text{NaI}} Ph-CH_{2}-I + NaBr \downarrow$$

$$(Soluble)$$

$$R-Br \xrightarrow{\text{NaI}} R-I + NaBr \downarrow$$

- NaI is soluble in acetone. In this reaction acetone is used because sodium iodide is soluble in acetone but NaBr and NaCl are insoluble so precipitated out. This eliminates any possibility of reverse reaction.
- It is an  $S_N^2$  reaction therefore only 1°RX and 2°RX is used.



## 1.3 Lucas reagent :

The 1 : 1 mixture of anhydrous  $ZnCl_2$  : HCI (conc.) is called Lucas reagent which is used to distinguish between 1<sup>o</sup>, 2<sup>o</sup> and 3<sup>o</sup> alcohols.

$$R-CH_2-OH \xrightarrow{HCI}{ZnCl_2} R-CH_2-CI$$

Mechanism :

$$R - \overset{\oplus}{O} H + ZnCl_2 \longrightarrow R - \overset{\oplus}{O} ZnCl_2 \longrightarrow \overset{\oplus}{R} + [HOZnCl_2]^- \xrightarrow{HCl} R - Cl + H_2O + ZnCl_2$$

- ZnCl<sub>2</sub> increases the rate of reaction by making –OH group into a much better leaving group just through complexation.
- Reactivity of alcohols is 3°ROH > 2°ROH > 1°ROH

Ex.

(a) 
$$CH_{3} \xrightarrow{CH_{3}}_{I} \xrightarrow{HCl_{2}ZnCl_{2}}_{(r.t.)} CH_{3} \xrightarrow{C}_{I} \xrightarrow{C}_{I} CH_{3}$$
  
(Turbidity appears quickly)  
(b)  $CH_{3} \xrightarrow{-CH_{-}CH_{-}CH_{3}}_{I} \xrightarrow{HCl_{2}ZnCl_{2}}_{(r.t.)} CH_{3} \xrightarrow{-CH_{-}CH_{3}}_{C} CH_{3}$   
(Turbidity appears within 5 to 10 min.)  
(c)  $CH_{3} \xrightarrow{-CH_{2}}_{I} \xrightarrow{-CH_{2}}_{I} \xrightarrow{HCl_{2}ZnCl_{2}}_{(r.t.)} CH_{3} \xrightarrow{-CH_{2}-CH_{2}-Cl_{2}}_{C} CH_{3}$ 

# 1.4 In presence of $PX_3$ :

 $R-OH \xrightarrow{PBr_3} R-Br$ Mechanism :



 $2R - OH + HOPBr_2 - 2R - Br +$ 

1.5 In presence of  $PX_5$ :

- Both the  $PX_3 \& PX_5$  proceeds via  $S_N 2$  pathways, No.rearrangement occurs.
- Only 1°R—OH and 2°R—OH undergo this types of reaction. 3° R—OH undergoes elimination reaction.



1.6 In presence of SOCI<sub>2</sub> (Thionyl chloride) :

 $R - OH \xrightarrow{SOCI_{2}} R - CI + SO_{2} (S_{N}2) ; \qquad R - OH \xrightarrow{SOCI_{2}} R - CI + SO_{2} (S_{N}i)$ 

(A) Mechanism of SOCI<sub>2</sub> with pyridine :



• SOCI<sub>2</sub> with pyridine undergo  $S_N 2$  reaction so inversion of configuration is obtained in product.

#### (B) Mechanism of SOCI<sub>2</sub> without pyridine : (Darzen method)



SOCI<sub>2</sub> without pyridine or base undergo S<sub>N</sub>i reaction, so retention of configuration is obtained in product.



## **1.7** Victor Mayer test :

#### 1° Alcoholપ્

$$R-CH_{2}-OH \xrightarrow{P+I_{2}} R-CH_{2}I \xrightarrow{AgNO_{2}} R-CH_{2}-NO_{2} \xrightarrow{HNO_{2}} R-C=N-OH \xrightarrow{base} Blood Red colour$$
2° Alcoholų
$$R_{2}CH-OH \xrightarrow{P+I_{2}} R_{2}CH-I \xrightarrow{AgNO_{2}} R_{2}CH-NO_{2} \xrightarrow{HNO_{2}} R_{2}C-NO_{2} \xrightarrow{base} Blue colour$$
3° Alcohol ų
$$R_{3}C-OH \xrightarrow{P+I_{2}} R_{3}C-I \xrightarrow{AgNO_{2}} R_{3}C-NO_{2} \xrightarrow{HNO_{2}} no reaction \xrightarrow{base} no colour$$

### 1.8 Cerric Ammonium Nitrate test :

Alcohols( $1^{\circ}, 2^{\circ}, 3^{\circ}$ ) also give characteristic red colour with cerric ammonium nitrate [(NH<sub>4</sub>)Ce(NO<sub>3</sub>)<sub>6</sub>] solution.

# 2. E1 Reaction of alcohols :

For E1 mechanism reagents are  $H_3PO_4$  /  $\Delta\Box$ ,  $H_2SO_4$  / 160°

 $\begin{array}{c|c} | & | \\ -C - C - & \xrightarrow{acid} & | & | \\ | & | \\ H & OH \end{array}$  (Rearrangement may occur)

#### Mechanism :





# 3. E2 Reaction of alcohols :

Alcohols gives E2 reaction with Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, ThO<sub>2</sub>, WO<sub>3</sub>

 $\mathsf{R-CH_2-CH_2-OH} \xrightarrow{\mathsf{Al_2O_3, P_2O_5 or ThO_2}} \mathsf{R-CH}{==}\mathsf{CH_2}$ 

 With Al<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> Saytzeff alkene is major product but with ThO<sub>2</sub> and WO<sub>3</sub> Hofmann alkene is major product.

# Pinacol-Pinacolone rearrangement :



Note : For unsymmetrical diol that –OH group will be replaced first which will generate stable carbocation as below .





- (Trace)
- By intermolecular dehydration of alcohols ethers can be prepared in presence of trace amount of H₂SO₄.

#### Mechanism :

$$R-OH \xrightarrow{H_2SO_4} R_{\overrightarrow{O}} H_2 \longrightarrow R^{\oplus} + H_2O$$

$$R-OH \xrightarrow{H^{\oplus}} R \xrightarrow{\oplus} R_{\overrightarrow{O}} H_2 \longrightarrow R^{\oplus} + H_2O$$

$$R-OH \xrightarrow{H^{\oplus}} R \xrightarrow{H^{\oplus}} R \longrightarrow R-O-R + H_2O$$

## **Purification of ethers :**

On standing in contact with air they form unstable peroxide ( $R_2O \rightarrow O$ ) which is explosive in nature.

Peroxide is formed at the carbon atom next to the etherial oxygen.

$$(CH_3 - CH_2)_2O \xrightarrow{air} CH_3 - CH_0 - CH_2CH_3$$
  
OOH

The presence of peroxide in ether can be identified on shaking it with freshly prepared ferrous sulphate solution followed by addition of potassium thiocyanate. This result into red colour of ferric thiocyanate. During the reaction peroxide oxidises Fe<sup>2+</sup> to Fe<sup>3+</sup> which reacts with thiocyanate ion to give red colour of ferric thiocyanate.

$$\begin{array}{ccc} \mathsf{Fe}^{_{2^{+}}} & \stackrel{\mathsf{peroxide}}{\longrightarrow} & \mathsf{Fe}^{_{3^{+}}} & \stackrel{\mathsf{CNS}^{\Theta}}{\longrightarrow} & \mathsf{Fe}(\mathsf{CNS})_{_{3}} \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ &$$

- Ethers are purified from peroxide before use. The peroxide from ether can be removed by treating ether with KI solution where peroxide is reduced to ether and iodide ion is oxidised to I<sub>2</sub> molecule.
- Peroxide formation can be checked by adding few ammount of Cu<sub>2</sub>O in ether
- Ether is lewis base hence forms co-ordinate bond with lewis acid



## Chemical properties of ethers :

(i) Reaction with HI :  

$$R-O-R' \xrightarrow{HI} R-OH + R' I$$

$$CH_{3}-CH_{2}-O-CH_{2}-CH_{3} \xrightarrow{HI} CH_{3}-CH_{2}-OH + CH_{3}-CH_{2}-I$$

$$HI \xrightarrow{(1eq.)} CH_{3}-CH_{2}-I$$

- Those protic acids whose conjugate base is a good nucleophile leads to cleavage of ethers. HI is such a very prominent acid of this kind.
- In most cases of unsymmetrical ethers 1 eq. of HI leads to give a mixture of four products in which it is not possible to predict the major product. However if 2 eq. of HI is used then two iodides are obtained.

Ex. (a) 
$$CH_3 - CH_2 - O - CH_3 \xrightarrow{HI (1eq)} CH_3 - I + CH_3 - CH_2 - OH.$$