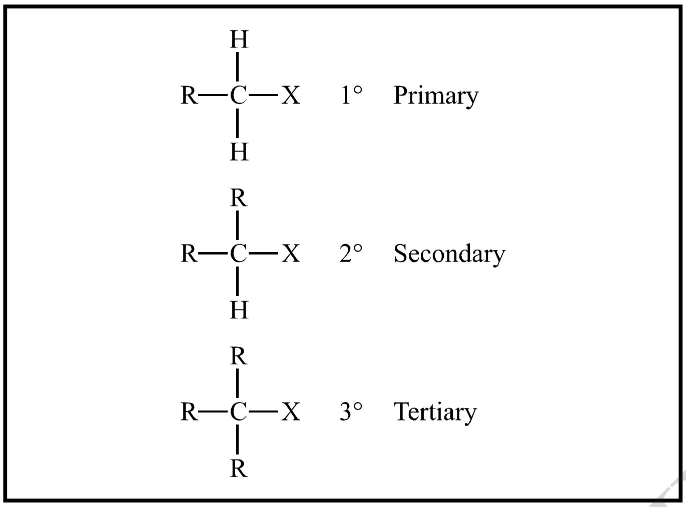
ALKYL HALIDE

1. INTRODUCTION

The **alkyl halides** or **haloalkanes** are a group of chemical compounds, derived from alkanes containing one or more halogens. They are used commonly as flame retardants, fire extinguishers, refrigerants, propellants, solvents and pharmaceuticals. The alkyl halides are classified broadly into three categories based on type of carbon atom to which the halogen atom is attached.



$R-\overset{H}{\underset{H}{C}}-X$ 1° Primary

$R-\overset{R}{\underset{H}{C}}-X$ 2° Secondary

$R-\overset{R}{\underset{R}{C}}-X$ 3° Tertiary

X may be F, Cl, Br or I.

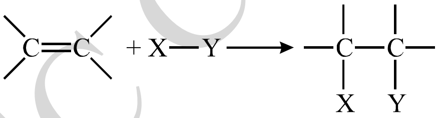
2. REACTIONS IN ORGANIC CHEMISTRY

There are various types of reactions possible in organic compounds depending on reaction conditions and attacking reagent. Reactions in organic chemistry are classified into three categories :

2.1 Addition Reaction

This reaction involves addition of groups to a π bond.

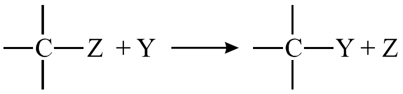
Example - 1



2.2 Substitution Reaction

This reaction involves the replacement of an atom or a group of atoms by another atom or group of atoms.

Example - 2

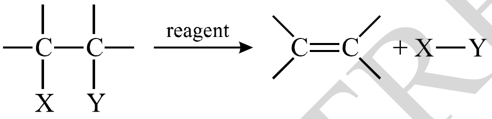


$$-\overset{|}{\underset{|}{C}}-Z + Y \longrightarrow -\overset{|}{\underset{|}{C}}-Y + Z$$

2.3 Elimination Reaction

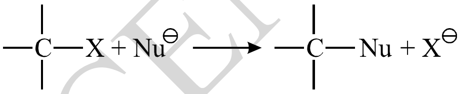
This reaction involves the loss of atoms or groups of atoms to form an unsaturated compound.

Example - 3



3. NUCLEOPHILIC SUBSTITUTIONS REACTIONS

Example - 4

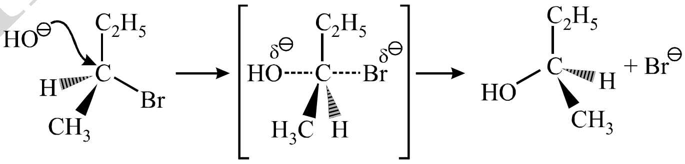


$$-\overset{|}{\underset{|}{C}}-X + Nu^{\ominus} \longrightarrow -\overset{|}{\underset{|}{C}}-Nu + X^{\ominus}$$

The replacement of halogen atom (leaving group) by the attacking nucleophile is called nucleophilic substitution reaction at sp^3 carbon. This reaction was studied in great detail and two extreme mechanisms have been outlined to explain the course of the reaction.

3.1 Substitution Nucleophilic Bimolecular – S_N2

Example - 5



Transition State

Note.. **Key Features of S_N2 Mechanism**

1. Single step reaction.
2. Rate = k [RX] [Nu]
3. No intermediate is formed. Reaction goes through a transition state.
4. Rearrangement is not observed.
5. Inversion of configuration is observed.
6. Order of reactivity of alkyl halides :

$$CH_3X > 1° > 2° > 3°$$

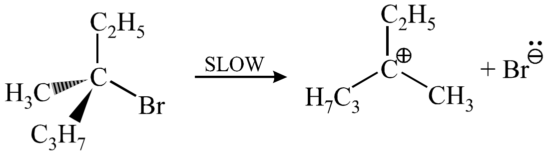
This can be attributed to the steric hinderance to back side attack of nucleophile.

7. Favoured by aprotic solvents.

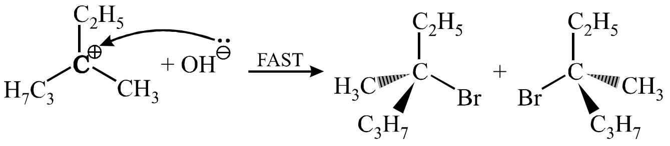
3.2 Substitution Nucleophilic Unimolecular – S_N1

Example - 6

Step 1 :



Step 2 :



Note..

Key Features of S_N1 Mechanism

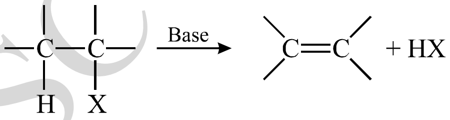
1. Two step reaction. First step is the formation (and rearrangement) of carbocation while second step is the attack of nucleophile on the carbocation.
2. Rate = k [RX]
3. Carbocation is formed.
4. Rearrangement is commonly observed.
5. Racemic mixture is obtained.
6. Order of reactivity of alkyl halides :

   $$3° > 2° > 1° > CH_3X$$

   This can be attributed to the stability of the carbocation that is formed.
7. Favoured by protic solvents.

4. ELIMINATION REACTIONS

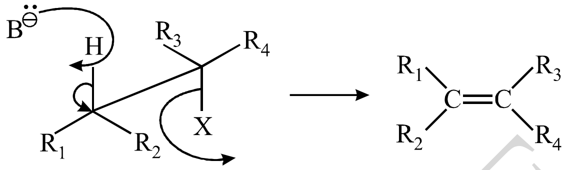
Example - 7



The removal of halogen from the carbon to which it is attached along with the removal of hydrogen from adjacent carbon is called α, β-elimination or simply elimination. Three mechanisms have been outlined for elimination reactions.

4.1 Elimination Bimolecular – E2

Example - 8



Note..

Key Features of E2 Mechanism

1. Single step reaction.
2. Rate = k [RX] [Base]
3. No intermediate is formed. Reaction goes through a transition state.
4. Rearrangement is not observed.
5. Observed in presence of strong bases.
6. Order of reactivity of alkyl halides :

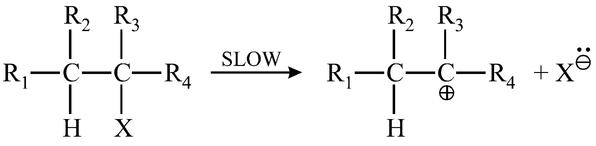
   $$3° > 2° > 1°$$

   This can be attributed to the stability of alkene formed.
7. Favoured by aprotic solvents.

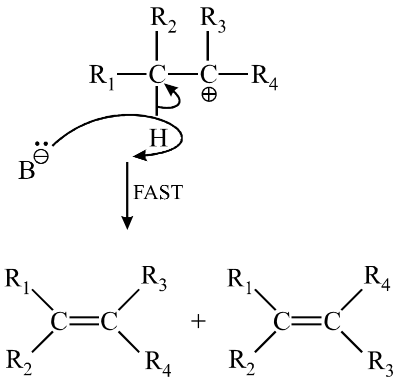
4.2 Elimination Unimolecular – E1

Example - 9

Step 1 :



Step 2 :



Note.. **Key Features of E1 Mechanism**

1. Two step reaction. First step is the formation of carbocation while second step is the loss of proton by a base.
2. Rate = k [RX]
3. Carbocation is formed.
4. Rearrangement is commonly observed.
5. Observed in presence of weak bases.
6. Order of reactivity of alkyl halides :

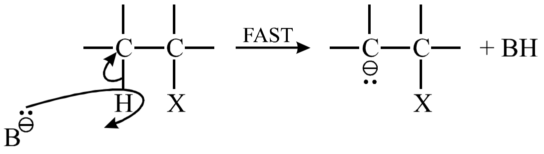
   $$3° > 2° > 1°$$

   This can be attributed to the stability of carbocation as well as the stability of alkene formed.
7. Favoured by protic solvents.

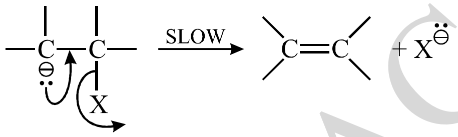
4.3 Elimination Unimolecular via Conjugate Base – E1cB

Example - 10

Step 1 :



Step 2 :

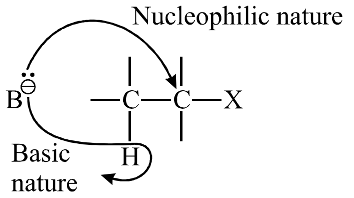


Note.. **Key Features of E1cB Mechanism**

1. Two step reaction. First step is the formation of carbanion and second step is the loss of leaving group.
2. Rate = k [RX] [Base]
3. Carbanion is formed.
4. Occurs when poor leaving group is present.

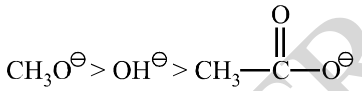
5. SUBSTITUTION AND ELIMINATION

Any species that acts as a base can also act as a nucleophile. To understand how elimination and substitution compete with each other, we compare the nucleophilic behaviour with the basic behaviour.



5.1 Nucleophilicity vs Basicity

(a) Nucleophilicity & basicity will be parallel if the comparing nucleophile have same attacking atom e.g.



$$CH_3O^{\ominus} > OH^{\ominus} > CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus}$$

(b) Negatively charged nucleophiles are stronger than neutral nucleophiles. e.g.

$$OH^{\ominus} > H_2O \quad \text{or} \quad NH_2^{\ominus} > NH_3$$

(c) Electrons on larger atoms are less tightly bound by the nucleus and are more polarisable and more readily available to carbon & will be better nucleophile. But they will be weaker base as their bond with smaller H-atom will be weaker & their conjugate acids will be more reactive. If the attacking atoms are of same size, the stronger bases are better nucleophile. (In a period basicity of anions decreases) e.g.

Acidic Strength :

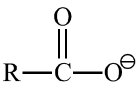
$$CH_4 < NH_3 < H_2O < HF$$

Basic Strength and Nucleophilicity :

$$^{\ominus}CH_3 > {}^{\ominus}NH_2 > {}^{\ominus}OH > F^{\ominus}$$

(d) If the attacking atoms are different in size, the nucleophilicity depends on the solvents. However, in gaseous phase nucleophilicity parallels basicity.

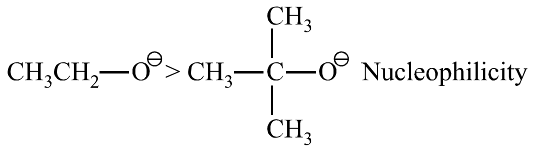
(e) Nucleophilicity is inversely proportional to stability of anion.



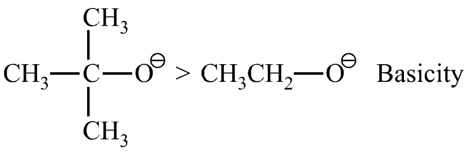
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus}$$

is a weaker nucleophile as it is resonance stabilized.

(f) Steric factor limits nucleophilicity



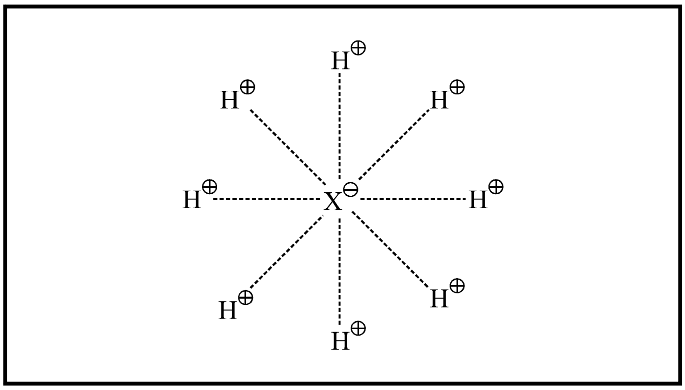
$$CH_3CH_2-O^{\ominus} > CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-O^{\ominus} \quad \text{Nucleophilicity}$$



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-O^{\ominus} > CH_3CH_2-O^{\ominus} \quad \text{Basicity}$$

(g) A strong base can be made a good leaving agent e.g. Oxygen containing group like $OH^{\ominus}$ can be made a weak base in acidic medium by protonation & become a better leaving agent $-\overset{\oplus}{O}H_2$.

(h) **Protic solvent :** These solvents have a hydrogen atom attached to an atom of a strongly electronegative element (e.g. oxygen). Molecules of protic solvent can, therefore form hydrogen bonds to nucleophiles as :

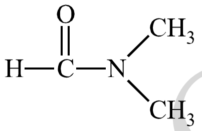


A small nucleophile which is having high charge density than the larger nucleophile is strongly solvated and this solvation hinders the direct approach to the nucleophilic centre. Hence the smaller nucleophile doesn't act as a good nucleophile as the larger one. Hence in protic solvent nucleophilicity is reverse of basicity.

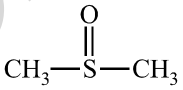
$$\underset{\text{increasing basicity}}{\xleftarrow{F^{\ominus}\quad Cl^{\ominus}\quad Br^{\ominus}\quad I^{\ominus}}}$$

$$\underset{\text{increasing nucleophilicity}}{\xrightarrow{\hspace{4cm}}}$$

(i) **Aprotic solvents :** These are the polar solvents that don't have H atom, capable of forming H-bonds e.g.

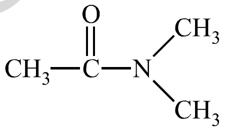


N, N-Dimethyl formamide
(DMF)



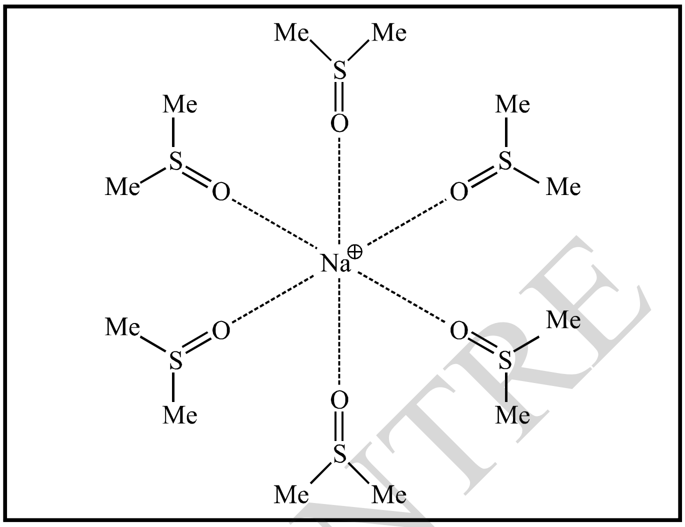
$CH_3-\overset{O}{\overset{\|}{S}}-CH_3$

Dimethyl sulphoxide
(DMSO)



Dimethyl acetamide
(DMA)

These solvents dissolve ionic compounds and solvate the cations.



Now the naked anions are highly reactive as nucleophile and now nucleophilicity follows the basicity e.g.

$$\underset{\text{increasing basicity}}{\xleftarrow{F^{\ominus}\quad Cl^{\ominus}\quad Br^{\ominus}\quad I^{\ominus}}}$$

$$\underset{\text{increasing nucleophilicity in aprotic solvents}}{\xleftarrow{\hspace{6cm}}}$$

5.2 Saytzeff vs. Hofmann Rule

When alkene is formed by elimination of alkyl halides, the orientation of the double bond formed is governed by two rules.

5.2.1 Saytzeff's Rule/Zaitsev Rule

This rule suggests the formation of more stable alkene and therefore more substituted double bond. Reactions following this rule are said to be **thermodynamically controlled.**

5.2.2 Hofmann Rule

This rule suggests the formation of less stable alkene and therefore less substituted double bond. In such cases, the more acidic β-hydrogen is abstracted to produce alkene. Such reactions are said to be **kinetically controlled.**

5.3 Effect of Temperature

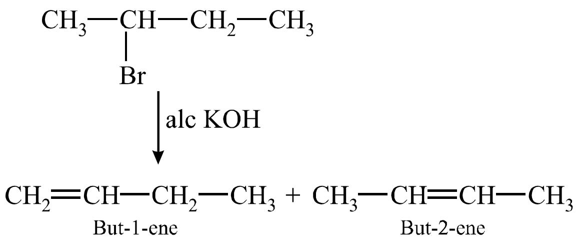
High temperature favours elimination while low temperature favours substitution reaction.

6. STEREOCHEMISTRY

6.1 Regioselectivity

It is the preference of one direction of chemical bond making or breaking over all other possible directions.

Example - 11

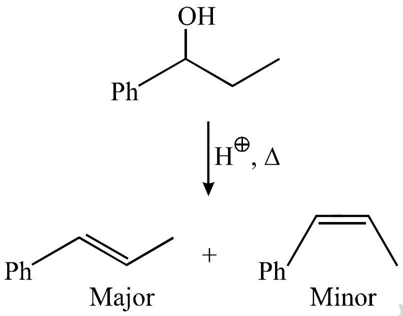


$$CH_3-\underset{Br}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow{alc\ KOH} CH_2=CH-CH_2-CH_3 + CH_3-CH=CH-CH_3$$

6.2 Stereoselectivity

Stereoselective reactions give one predominant product because the reaction pathway has a choice. Either the pathway of lower activation energy (kinetic control) is preferred or the more stable product (thermodynamic control).

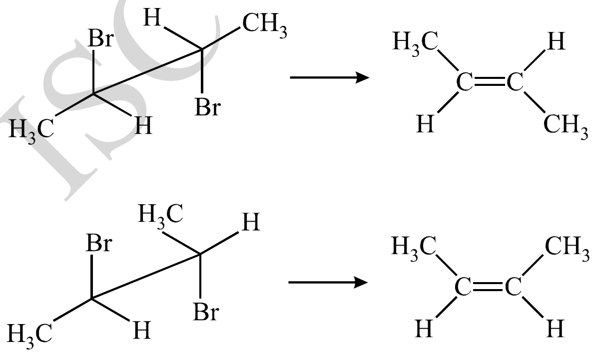
Example - 12



6.3 Stereospecificity

Stereospecific reactions lead to the production of a single isomer as a direct result of the mechanism of the reaction and the stereochemistry of the starting material. There is no choice. The reaction gives a different diastereomer of the product from each stereoisomer of the starting material.

Example - 13

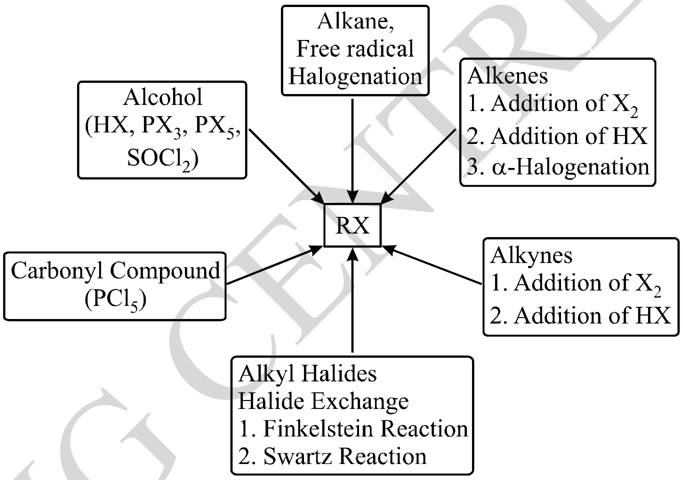


6.4 Chemoselectivity

When there are two or more functional groups in a molecule, a given reagent may react preferentially with one rather than the other. Such reactions are called chemoselective.

7. ALKYL HALIDES

7.1 Preparation of Alkyl Halides

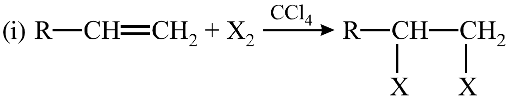


1. **Alkanes**

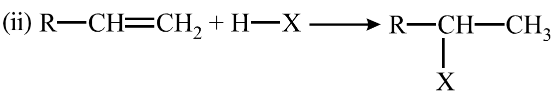
$$RH \xrightarrow{Cl_2} RCl + HCl$$

This method gives a mixture of mono, di & trihalides.

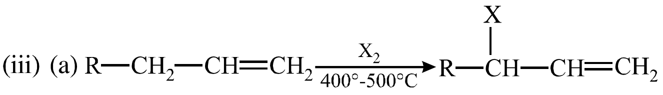
2. **Alkenes**



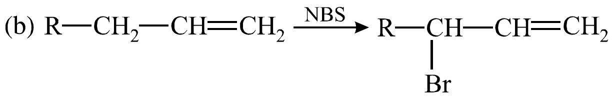
$$\text{(i)}\ R-CH=CH_2 + X_2 \xrightarrow{CCl_4} R-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH_2}}$$



$$\text{(ii)}\ R-CH=CH_2 + H-X \longrightarrow R-\underset{X}{\underset{|}{CH}}-CH_3$$

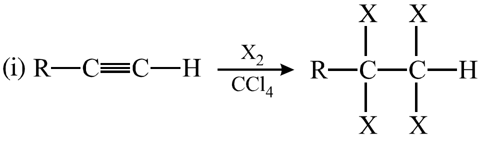


$$\text{(iii) (a)}\ R-CH_2-CH=CH_2 \xrightarrow[400°\text{-}500°C]{X_2} R-\overset{X}{\overset{|}{CH}}-CH=CH_2$$

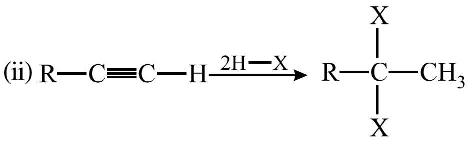


$$\text{(b)}\ R-CH_2-CH=CH_2 \xrightarrow{NBS} R-\underset{Br}{\underset{|}{CH}}-CH=CH_2$$

3. **Alkynes**



$$\text{(i)}\ R-C\equiv C-H \xrightarrow[CCl_4]{X_2} R-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-H$$



$$\text{(ii) } R—C≡C—H \xrightarrow{2H—X} R—\underset{X}{\overset{X}{C}}—CH_3$$

4. Alkyl Halides

(i) Finkelstein Reaction

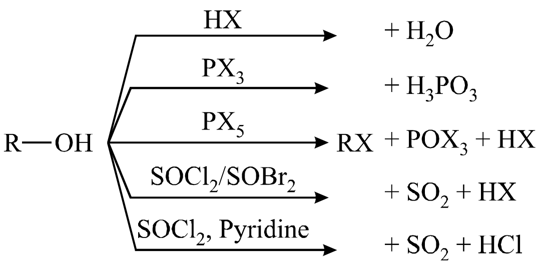
$$R—Br + NaI \xrightarrow{\text{acetone}} R—I + NaBr$$

$$R—Cl + NaI \xrightarrow{\text{acetone}} R—I + NaCl$$

(ii) Swartz Reaction

$$\begin{matrix} R—I \\ R—Br \\ R—Cl \end{matrix} + AgF \xrightarrow[\text{Polar aprotic}]{\text{DMSO}} R—F + \begin{matrix} AgI \\ AgBr \\ AgCl \end{matrix}$$

5. Alcohol



$$R—OH \xrightarrow{HX} RX + H_2O$$

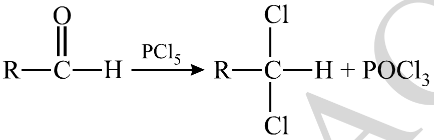
$$R—OH \xrightarrow{PX_3} RX + H_3PO_3$$

$$R—OH \xrightarrow{PX_5} RX + POX_3 + HX$$

$$R—OH \xrightarrow{SOCl_2/SOBr_2} RX + SO_2 + HX$$

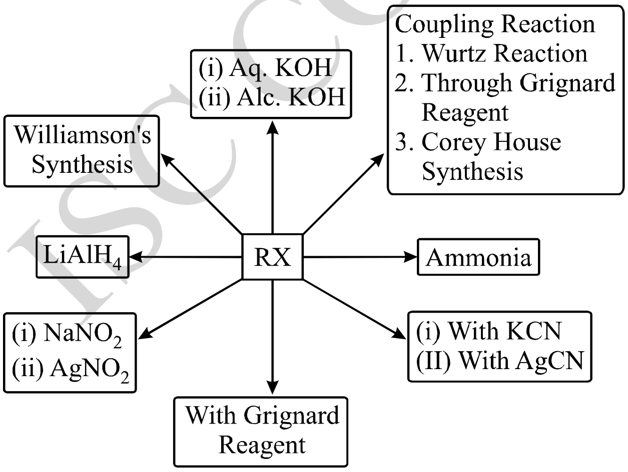
$$R—OH \xrightarrow{SOCl_2,\ \text{Pyridine}} RX + SO_2 + HCl$$

6. Carbonyl Compound



$$R—\overset{O}{\overset{\|}{C}}—H \xrightarrow{PCl_5} R—\underset{Cl}{\overset{Cl}{C}}—H + POCl_3$$

7.2 Reactions of Alkyl Halide



1. Coupling Reaction

(a) Wurtz Reaction

$$2RX + 2Na \xrightarrow{Et_2O} R—R + 2NaX$$

(b) Grignard Reagent

$$R—X + R—MgX \longrightarrow R—R + MgX_2$$

(c) Corey-House Synthesis

$$R—X + 2Li \longrightarrow R—Li + LiX$$

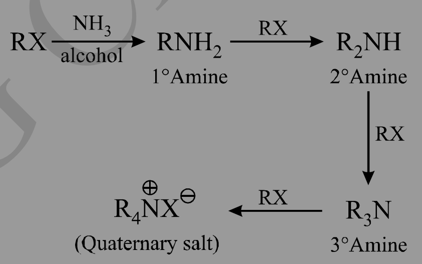
$$2R—Li + CuI \longrightarrow R_2CuLi + LiI$$

$$R_2CuLi + R'—X \longrightarrow R—R' + R—Cu + LiX$$

2. Ammonia

$$R—X + NH_3 \xrightarrow[\Delta]{C_2H_5OH} \underset{1° \text{ Amine}}{R—NH_2} + HX$$

Note.. If alkyl halide is in excess, then 2° and 3° amines and even quaternary salts are also formed.



This reaction is called Hofmann ammonolysis of alkyl halides.

3. KCN

$$R—X + KCN \longrightarrow R—CN + KX$$

4. AgCN

$$R—X + AgCN \longrightarrow R—\overset{\oplus}{N}≡\overset{\ominus}{C}$$

5. $NaNO_2$

$$R—X + NaNO_2 \longrightarrow R—O—N=O + NaX$$

6. $AgNO_2$

$$RX + AgNO_2 \longrightarrow R—NO_2 + AgX$$

7. $LiAlH_4$

$$R—X + LiAlH_4 \longrightarrow R—H$$

8. Williamson's Synthesis

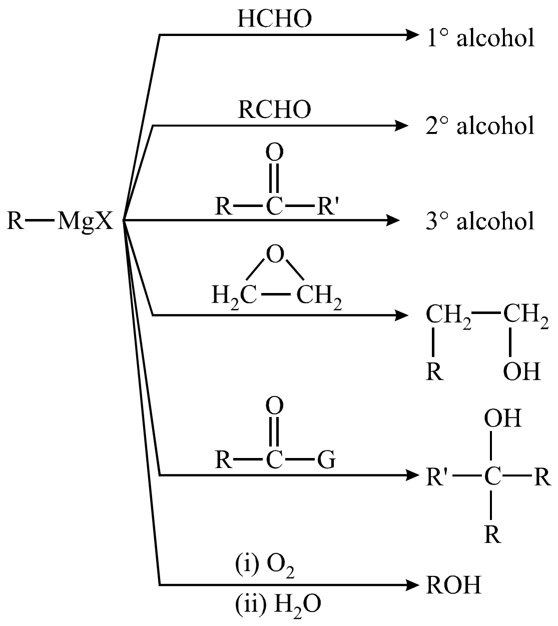
$$R—X + R'—O—Na \longrightarrow R—O—R'$$

9. Aq. KOH & Alc. KOH

$$R—X \xrightarrow{\text{aq. KOH}} R—OH$$

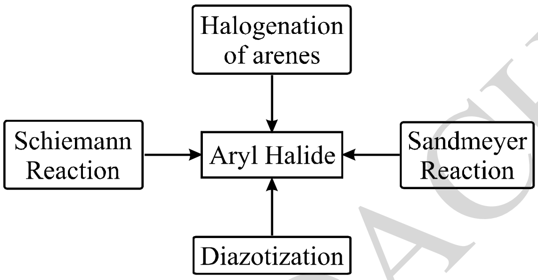
$$R—X \xrightarrow{\text{alc KOH}} \text{Alkene}$$

10. Reactions of R–MgX

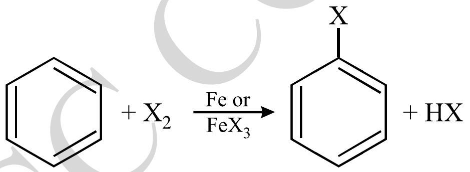


8. ARYL HALIDE/HALOARENES

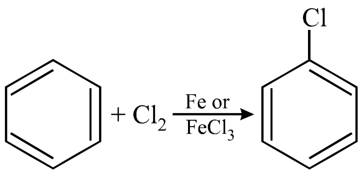
8.1 Preparation of Aryl Halide/Haloarenes



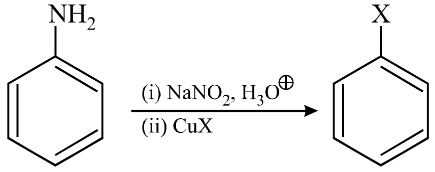
(a) Halogenation of Arenes



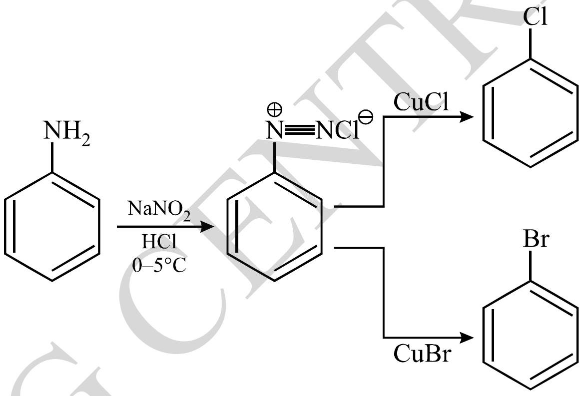
Example - 14



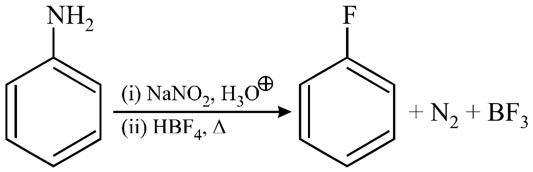
(b) Sandmeyer Reaction



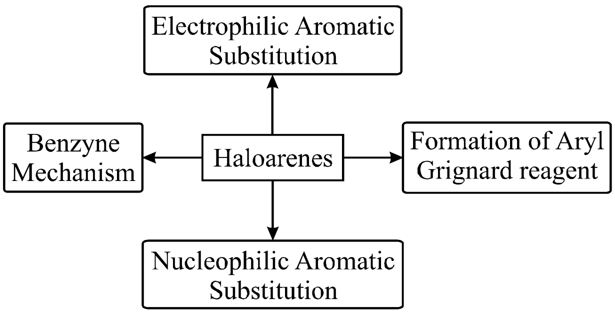
(c) Diazotization



(d) Schiemann Reaction

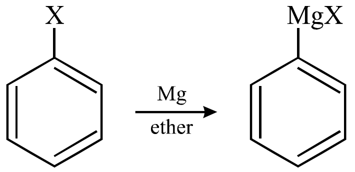


8.2 Reactions of Aryl Halide/Haloarenes



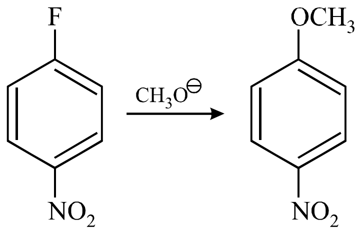
(a) Electrophilic Aromatic Substitution Reaction : Halogens are weakly deactivating and ortho/para directing.

(b) Formation of Aryl Grignard Reagent :



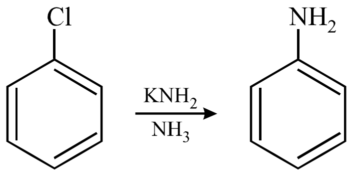
Reactivity order : Ar–I > Ar–Br > Ar–Cl > Ar–F

(c) S_NAr – Aromatic Nucleophilic Substitution Reaction



(d) Benzyne Mechanism (Elimination Addition Mechanism)

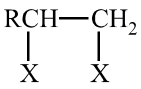
Strong bases such as Na, K and amide react readily with aryl halides.



9. REACTIONS OF SPECIAL ALKYL HALIDES

9.1 Di-Halides

$RCHX_2$ Alkylidene Dihalides or Geminal Dihalides



$\underset{X}{RCH}-\underset{X}{CH_2}$ Alkylene Dihalides or Vicinal (1, 2) Dihalides

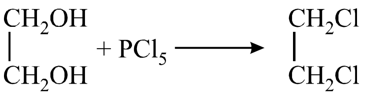
9.1.1 Preparation

(a) Alkenes and Alkynes Halogenation of Alkenes & Alkynes

$CH_2{=}CH_2 + X_2 \longrightarrow CH_2X-CH_2X$ Vicinal Dihalide

$CH{\equiv}CH + 2HX \longrightarrow CH_3CHX_2$ Geminal Dihalide

(b) PCl_5 with Diols & Carbonyl Compounds



$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + PCl_5 \longrightarrow \begin{matrix}CH_2Cl\\ |\\ CH_2Cl\end{matrix}$$ Vicinal Dihalide

$CH_3CHO + PCl_5 \longrightarrow CH_3CHCl_2$ Gem Dihalide

9.1.2 Properties

(a) Alcoholic KOH : (Dehydrohalogenation)

$XCH_2CH_2X \xrightarrow[KOH]{Alcoholic} CH{\equiv}CH$

$CH_3CHX_2 \xrightarrow[KOH]{Alcoholic} CH{\equiv}CH$

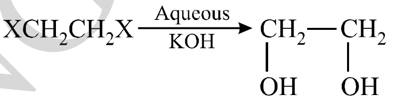
(b) Zinc Dust : (Dehalogenation)

$XCH_2CH_2X \xrightarrow[Alcohol]{Zn} CH_2{=}CH_2$

$CH_3CHX_2 \xrightarrow[Alcohol]{Zn} CH_2{=}CH_2$

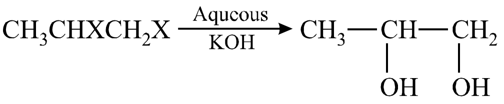
(c) Action of aq. KOH : (Alkaline Hydrolysis)

(i) Vicinal Dihalides



$XCH_2CH_2X \xrightarrow[KOH]{Aqueous} \underset{OH}{CH_2}-\underset{OH}{CH_2}$

Ethylene Glycol

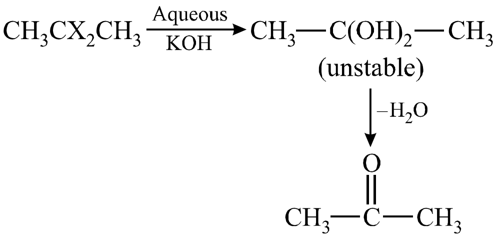


$CH_3CHXCH_2X \xrightarrow[KOH]{Aqucous} CH_3-\underset{OH}{CH}-\underset{OH}{CH_2}$

Propan-1, 2-diol

(ii) Gem Dihalides

$CH_3CHX_2 \xrightarrow[KOH]{Aqueous} \underset{(unstable)}{CH_3CH(OH)_2} \xrightarrow{-H_2O} CH_3CHO$



$$CH_3CX_2CH_3 \xrightarrow[KOH]{Aqueous} \underset{(unstable)}{CH_3-C(OH)_2-CH_3} \xrightarrow{-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Acetone

Note.. The above reaction is used to distinguish between gem and vicinal dihalides.

9.2 TRI-HALIDES & TETRA-HALIDES

$CHCl_3$ Chloroform (liquid)	$CHBr_3$ Bromoform (liquid)
$CHCl_3$ Iodoform (yellow solid)	CCl_4 Carbon Tetrachloride (liquid)

9.2.1 CHLOROFORM : $CHCl_3$

(A) Preparation

(i) Ethyl Alcohol : (using $NaOH/Cl_2$ or $CaOCl_2$)

$$NaOH + Cl_2 \longrightarrow NaOCl + HCl \ ; \ NaOCl \longrightarrow [O]$$

$$C_2H_5OH \xrightarrow[{[O]}]{Cl_2} CH_3CHO \xrightarrow{Cl_2} \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

Ca (OH)$_2$

$$CCl_3CHO + \underset{\text{Slaked Lime}}{Ca(OH)_2} \longrightarrow \underset{\text{Chloroform}}{2CHCl_3} + Ca(HCOO)_2$$

NaOH

$$CH_3CHO + 3Cl_2 \longrightarrow CCl_3CHO \xrightarrow{\text{Hydrolysis}}$$

$$\underset{\text{Chloralhydrate}}{CCl_3CH(OH)_2} \xrightarrow{NaOH} CHCl_3 + HCOONa + H_2O$$

Note.. Pure form of chloroform is prepared from chloral by treating it with NaOH.

(ii) Methyl Ketones

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{CCl_3COCH_3} \xrightarrow{Ca(OH)_2} CHCl_3 + (CH_3COO)_2Ca$$

(iii) Carbon Tetrachloride

$$CCl_4 + 2[H] \xrightarrow[HCl]{Fe + H_2O} CHCl_3 + HCl$$

(iv) Chlorination of Methane at 370ºC

$$CH_4 + 3Cl_2 \xrightarrow[\text{Diffused Sunlight}]{370°C} CHCl_3 + 3HCl$$

(B) Reactions

(i) Oxidation

Chloroform in presence of light and air (O_2) forms a highly posionous gas, Phosgene.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

Note.. 1% ethanol is added and then chloroform is stored in brown bottles, filled upto brim to stop the above decompostition.

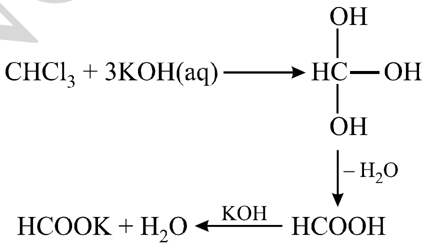
(ii) Carbylamine Reaction

$$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3H_2O + 3\,KCl$$

$$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5NC + 3\,H_2O + 3\,KCl$$

Isocyanides (carbylamines) have a very disagreable smell, so the above reaction is used as a test of chlororom and test of 1º (aliphatic and aromatic) amines.

(iii) Hydrolysis



$$CHCl_3 + 3KOH(aq) \longrightarrow HC(OH)_3 \xrightarrow{-H_2O} HCOOH \xrightarrow{KOH} HCOOK + H_2O$$

(iv) Formation of Acetylene

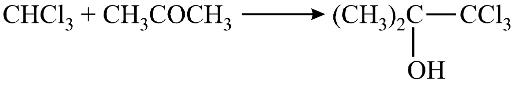
$$2CHCl_3 + 6Ag \longrightarrow \underset{\text{Acetylene}}{CH\equiv CH} + 6AgCl$$

(v) Formation of Chloropicrin

$$CHCl_3 + HNO_3 \longrightarrow CCl_3NO_2$$

Chloropicrin
(an insecticide)

(vi) Formation of Chloretone



$$CHCl_3 + CH_3COCH_3 \longrightarrow (CH_3)_2C(OH)-CCl_3$$

Chloretone
(a hypnotic medicine)

9.2.2 IODOFORM : CHI_3

(A) Preparation :

$$C_2H_5OH + 3I_2 + 3Na_2CO_3 \;\big\downarrow\; \underset{\substack{\text{yellow}\\\text{solid}}}{CHI_3\downarrow} + 3HCOONa + 3NaI + 2CO_2\uparrow$$

$$CH_3COCH_3 + 3I_2 + 2Na_2CO_3 \;\big\downarrow\; CHI_3\downarrow + 2NaI + CH_3COONa + H_2O + 2CO_2\uparrow$$

Note.. This reaction is known as Iodoform reaction or **Iodoform test.** Since the iodoform is a yellow colored solid, so the iodoform reaction is used to test ethyl alcohol, acetaldehyde, sec. alochols of $R(CH_3)CHOH$ (methyl alkyl carbinol) and methyl ketones ($RCOCH_3$), because all these form iodoform. The side product of the iodoform reaction, sodium carboxylate is acidified to produce carboxylic acid (RCOOH).

9.2.3 CARBON TETRACHLORIDE : CCl_4

(A) Preparation :

(i) $\underset{\text{excess}}{CH_4 + 4Cl_2} \xrightarrow[\text{diffused}]{hv} CCl_4 + 4HCl$

(ii) $CS_2 + 3Cl_2 \xrightarrow[Fe/I_2]{AlCl} CCl_4 + S_2Cl_2$

S_2Cl_2 is separated by fractional distillation. It is then treated with more CS_2 to give CCl_4. C washed with NaOH and distilled to obtain pure CCl_4.

$$2S_2Cl_2 + CS_2 \longrightarrow CCl_4 + 6S$$

(iii) $CH_3CH_2CH_3 + Cl_2 \xrightarrow[\text{70-100 atm}]{400°C} CCl_4 + HCl + C_2Cl_6$

Note.. CCl_4 is a colourless and poisonuous liquid which is insoluble in H_2O. It is a good solvent for grease and oils. CCl_4 is used in fire extingusher for electric fires as Pyrene. It is also an insecticide for hookworms.

(B) Reactions :

(i) Oxidation

$$CCl_4 + \underset{\text{Steam}}{H_2O} \xrightarrow{500°C} COCl_2 + 2HCl$$

(ii) Reduction

$$CCl_4 + 2[H] \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

(iii) Hydrolysis

$$\begin{tikzcd} CCl_4 + 4KOH(aq) \arrow[r] & C(OH)_4 \arrow[d, "2H_2O"] \\ K_2CO_3 + H_2O & CO_2 \arrow[l, "2KOH"'] \end{tikzcd}$$

(iv) Action of HF

$$CCl_4 + 4HF \xrightarrow{SbF_6} \underset{\text{Freon}}{CCl_2F_2} + 2HCl$$

9.2.4 VINYL CHLORIDE : $CH_2 = CHCl$

Vinyl group $CH_2 = CH–$

(A) Preparation

(i) $CH\equiv CH + HCl \longrightarrow CH_2{=}CHCl$

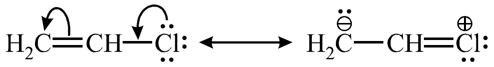
(ii) $\underset{\text{Vicinal Dihalides}}{CH_2ClCH_2Cl} \xrightarrow{KOH(alc.)} CH_2{=}CHCl + KCl + H_2O$

(iii) $CH_2{=}CH_2 + Cl_2 \xrightarrow{600°C} CH_2{=}CHCl + HCl$

(B) Reaction

(i) $CH_2{=}CHCl + \text{alc. KOH} \longrightarrow \underset{\text{Acetylene}}{CH\equiv CH} + HCl$

Halogen atom is vinyl chloride is quite stable and does not respond to nucleophilic substitution reactions easily. It is due to resonance stabilisation of vinyl chloride.



9.2.5 ALLYL CHLORIDE : $H_2C = CHCH_2Cl$

(A) Preparation

(i) $\underset{\text{Propene}}{H_2C{=}CHCH_3} + Cl_2 \xrightarrow{500–600°C} CH_2{=}CHCH_2Cl$

(ii) $\underset{\text{Allyl Alcohol}}{H_2C{=}CHCH_2OH} + PCl_5 \longrightarrow H_2C{=}CHCH_2Cl + POCl_3 + HCl$

(B) Reactions

(i) Addition Reactions

$$CH_2{=}CH{-}CH_2Cl + Cl_2 \longrightarrow CH_2ClCHClCH_2Cl$$

$$CH_2{=}CH{-}CH_2Br + HBr \longrightarrow \underset{\text{1, 2-Dibromopropane}}{CH_3CHBrCH_2Br}$$

The addition follows Markonikov's rule. However in presence of peroxides, 1, 3-dibromopropane is formed.

(ii) Nucleophilic Substitution Reactions

Since in allyl chloride, there is no resonance (unlike in vinyl chloride), nucleophilic substitution reactions take place with ease.

$$CH_2{=}CH{-}CH_2Cl \xrightarrow{KOH(aq)} CH_2{=}CHCH_2OH + KCl$$

$$CH_2{=}CH{-}CH_2Cl \xrightarrow{NH_3} CH_2{=}CH{-}CH_2NH_2 + HCl$$

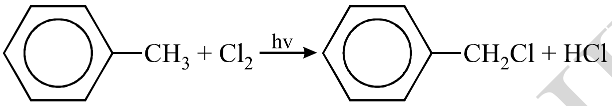
$$CH_2{=}CHCH_2Cl \xrightarrow{KCN} CH_2{=}CH{-}CH_2CN + KCl$$

$$CH_2{=}CHCH_2Cl + Mg \xrightarrow[\text{ether}]{\text{dry}} \underset{\text{Grignard Reagent}}{CH_2{=}CHCH_2MgCl}$$

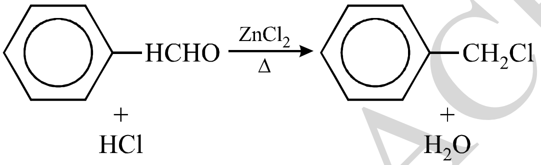
9.2.6 Benzyl Chloride : $C_6H_5CH_2Cl$: $PhCH_2Cl$

(A) Preparation

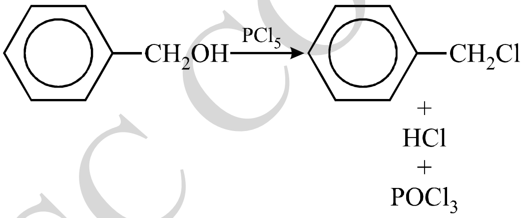
(i)



(ii)



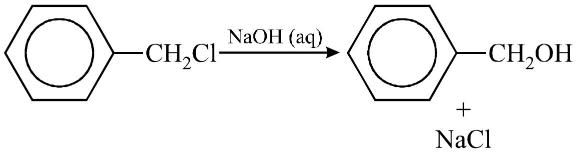
(iii)



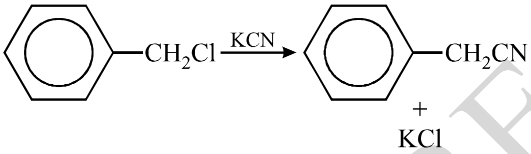
(B) Reactions

The main reactions are like those of Alkyl Halides (since there is no resonance in benzyl chloride and intermediate benzyl carbonium ion is stable supporting S_N1 substitution). Nucleophillic substitution reactions occur with ease unlike in case of aryl halides (due to resonance in aryl halides).

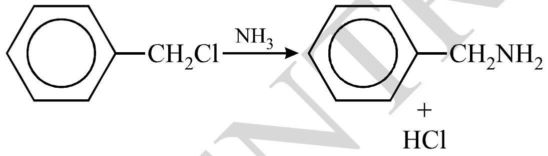
(i)



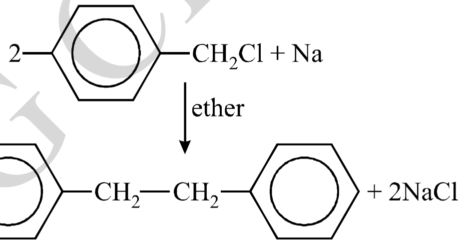
(ii)



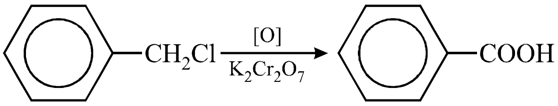
(iii)



(iv) Wurtz Reaction



(v) Oxidation



10. CHEMISTRY OF GRIGNARD REAGENT : R–Mg–X

10.1 Preparation

$$RX + Mg \xrightarrow[\text{ether}]{\text{reflux in}} \underset{\text{Alkyl Magnesium Halide}}{R{-}Mg{-}X}$$

Note... In Grignard reagent, we can have phenyl or alkenyl or alkynyl or aromatic group instead of R. All the reactions will remain same.

10.2 Reactions

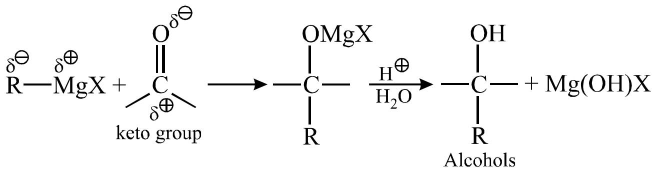
(A) Grignard reagent as a base reacts with compounds containing active H to give alkanes.

$$R{-}MgI + HOH \longrightarrow RH + Mg(OH)\,I$$

$$R{-}MgI + R'O{-}H \longrightarrow RH + Mg(OR')\,I$$

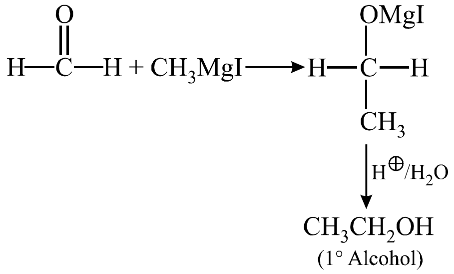
$$R{-}MgI + R'NH{-}H \longrightarrow RH + Mg(NHR')\,I$$

(B) Grignard reagent acts as a strong nucleophile and shows nucleophillic additions to give various products. Alkyl group being electron rich (carbonian) acts as nucleophile in Grignard Reagent.



$$\overset{\delta\ominus}{R}{-}\overset{\delta\oplus}{MgX} + \underset{\delta\oplus}{\overset{O^{\delta\ominus}}{\overset{\|}{C}}} \longrightarrow {-}\underset{R}{\overset{OMgX}{C}}{-} \xrightarrow[H_2O]{H^{\oplus}} {-}\underset{R}{\overset{OH}{C}}{-} + Mg(OH)X$$

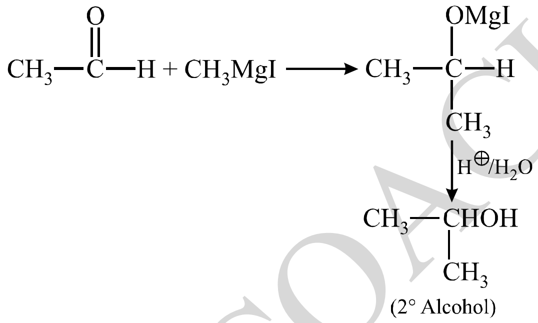
Example - 15



$$H{-}\overset{O}{\overset{\|}{C}}{-}H + CH_3MgI \longrightarrow H{-}\underset{CH_3}{\overset{OMgI}{C}}{-}H \xrightarrow{H^{\oplus}/H_2O} CH_3CH_2OH$$

(1° Alcohol)

Example - 16



$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}H + CH_3MgI \longrightarrow CH_3{-}\underset{CH_3}{\overset{OMgI}{C}}{-}H \xrightarrow{H^{\oplus}/H_2O} CH_3{-}\underset{CH_3}{CHOH}$$

(2° Alcohol)

Example - 17

$$(CH_3)_2C{=}O + CH_3MgI \longrightarrow (CH_3)_3C{-}OMgI \xrightarrow{H^{\oplus}/H_2O} (CH_3)_3C{-}OH$$

(3° Alcohol)

Note...

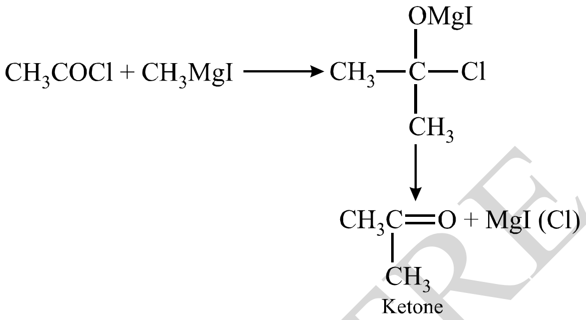
$HCHO + RMgX \longrightarrow$ 1° alcohol

$R'CHO + RMgX \longrightarrow$ 2° alcohol

$R'COR' + RMgX \longrightarrow$ 3° alcohol

(C) Acid Chloride

Example - 18



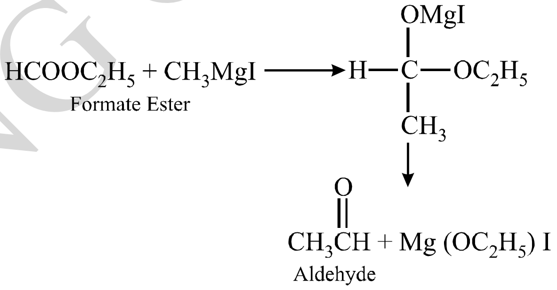
$$CH_3COCl + CH_3MgI \longrightarrow CH_3{-}\underset{CH_3}{\overset{OMgI}{C}}{-}Cl \longrightarrow \underset{CH_3}{CH_3C}{=}O + MgI\,(Cl)$$

Ketone

Ketones (acetone) formed further reacts with Grignard reagent to form 3° alcohols (tert. butyl alcohol). However, with 1 : 1 mole ratio of acid halide and Grignard Reagent, one can prepare ketones.

(D) Esters

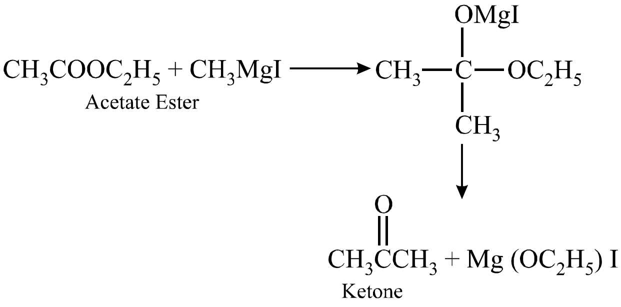
Example - 19



$$\underset{\text{Formate Ester}}{HCOOC_2H_5} + CH_3MgI \longrightarrow H{-}\underset{CH_3}{\overset{OMgI}{C}}{-}OC_2H_5 \longrightarrow \underset{\text{Aldehyde}}{CH_3\overset{O}{\overset{\|}{C}}H} + Mg\,(OC_2H_5)\,I$$

The aldehydes react further with CH_3MgI to give 2° alcohol, if present in excess. But 1 : 1 mole ratio of reactants will certainly give aldehydes.

Example - 20

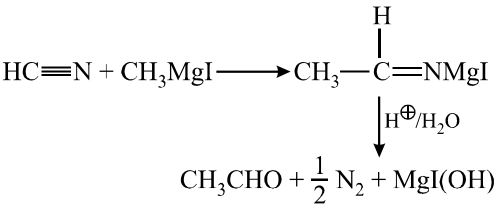


$$\underset{\text{Acetate Ester}}{CH_3COOC_2H_5} + CH_3MgI \longrightarrow CH_3{-}\underset{CH_3}{\overset{OMgI}{C}}{-}OC_2H_5 \longrightarrow \underset{\text{Ketone}}{CH_3\overset{O}{\overset{\|}{C}}CH_3} + Mg\,(OC_2H_5)\,I$$

The ketones react further with CH_3MgI to give 3° alcohol, if present in excess. But 1 : 1 mole ratio of reactants will certainly give ketones.

(E) Cyanides

Example - 21



$$HC\equiv N + CH_3MgI \longrightarrow CH_3-\overset{H}{\overset{|}{C}}=NMgI \xrightarrow{H^{\oplus}/H_2O} CH_3CHO + \frac{1}{2}N_2 + MgI(OH)$$

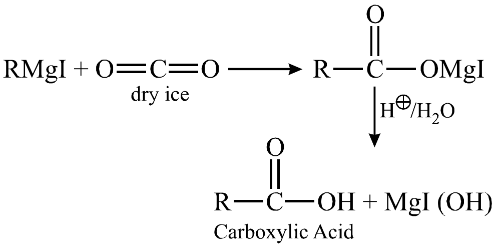
Example - 22

$$CH_3C\equiv N + CH_3MgI \longrightarrow (CH_3)_2C=N-MgI$$

$$\Big\downarrow H^{\oplus}/H_2O$$

$$(CH_3)_2C=O + \frac{1}{2}N_2 + MgI(OH)$$

(F) CO_2



$$RMgI + \underset{\text{dry ice}}{O=C=O} \longrightarrow R-\overset{O}{\overset{\|}{C}}-OMgI \xrightarrow{H^{\oplus}/H_2O} \underset{\text{Carboxylic Acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + MgI\,(OH)$$

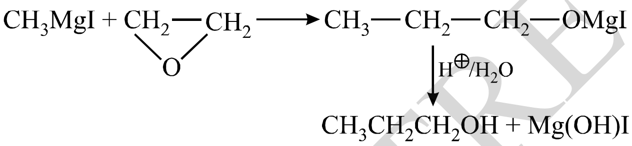
(G) Oxygen

$$RMgI + O_2 \xrightarrow[-75°]{\text{ether}} R-O-OMgI$$

$$\Big\downarrow H^{\oplus}/H_2O$$

$$\underset{\text{Alkyl Peroxides}}{R-O-O-H} + MgI(OH)$$

(H) Ethylene Oxide (Oxiranes)



(I) Alkynes

$$CH_3C\equiv C-H + CH_3MgI \longrightarrow CH_3C\equiv C-MgI + CH_4$$

$$CH_3C\equiv C-MgI + CH_3I \longrightarrow CH_3C\equiv C-CH_3 + MgI_2$$

(J) Alkyl Halides

$$R-MgI + CH_3CH_2Br \longrightarrow CH_3CH_2R + Mg(Br)I$$

$$CH_3MgBr + \underset{\text{Alkyl Bromide}}{CH_2=CHCH_2Br} \longrightarrow CH_2CH_2R + MgBr_2$$

(K) Inorganic Halides

$$4C_2H_5MgBr + 2PbCl_2 \longrightarrow \underset{\text{Tetraethyl Lead}}{(C_2H_5)_4Pb}$$

$$\Big\downarrow$$

$$Pb + 4MgBr(Cl)$$