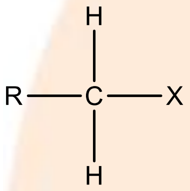
Revision Notes

Class - 12 Chemistry

Chapter 10 - Haloalkanes and Haloarenes

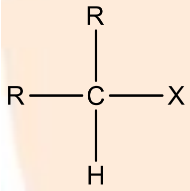
1. Introduction

The alkyl halides or halogenated alkanes are a group of compounds derived from alkanes that contain one or more halogens. They are commonly used as flame retardants, fire extinguishing agents, refrigerants, propellants, solvents, and drugs. Haloalkanes are roughly classified into three types based on the type of carbon atom to which the halogen atom is connected.



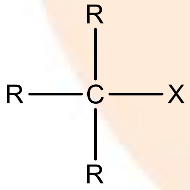
$R-\overset{H}{\underset{H}{C}}-X$

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.

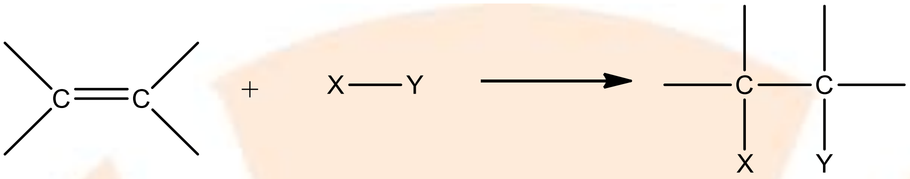
2. Reactions in organic chemistry

2.1 Depending on the reaction conditions and the attack reagents, various types of reactions can occur in organic compounds. There are 3 types of reactions in organic chemistry:

2.2 Addition Reaction

A new compound is formed by the reaction of two or more compounds. It is generally the attack of a reagent on a **π** bond.

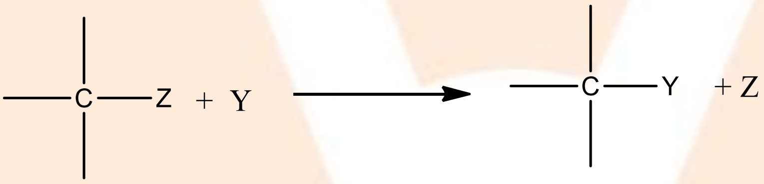
Example-1



2.3 Substitution Reaction

When a functional group attacks and replaces other functional group in a compound, the type of reaction is known as substitution reaction. The group which is replaced is called as the leaving group.

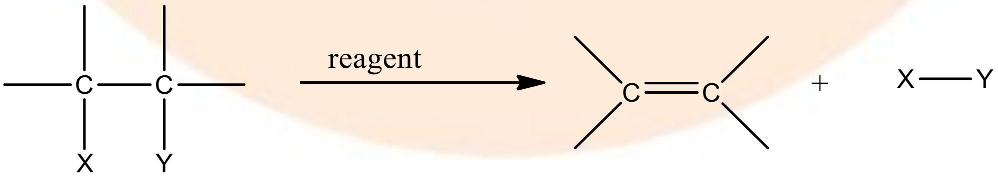
Example-2



2.4 Elimination Reaction

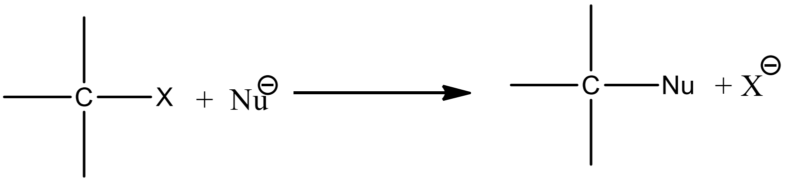
The reagent removes the groups (For example Hydrogen, Vicinal halides) present in ∝-β position to form an unsaturated compound.

Example-3



3. Nucleophilic substitutions reactions

Example-4

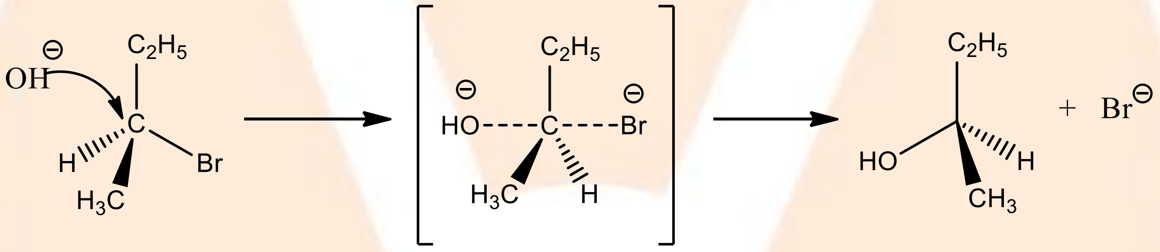


The replacement of halogen atom (leaving group) by the attacking nucleophile is called nucleophilic substitution reaction at sp^3 carbon. This reaction proceeds through two mechanism i.e. $\mathbf{S_N2}$ and $\mathbf{S_N1}$.

3.1 Substitution Nucleophilic Bimolecular - S_{N^2}

Example-5

Key Features of S_{N^2} Mechanism



Transition state

Note:

1. Single step reaction.
2. Rate=k [RX] [Nu]
3. No intermediate is formed. Reaction proceeds through one sp^3d transition state where one bond breaks and one is formed simultaneously.
4. Rearrangement is not observed.
5. Inversion of configuration is observed
6. Order of reactivity of alkyl halides:

$CH_3X > 1^\circ > 2^\circ > 3^\circ$

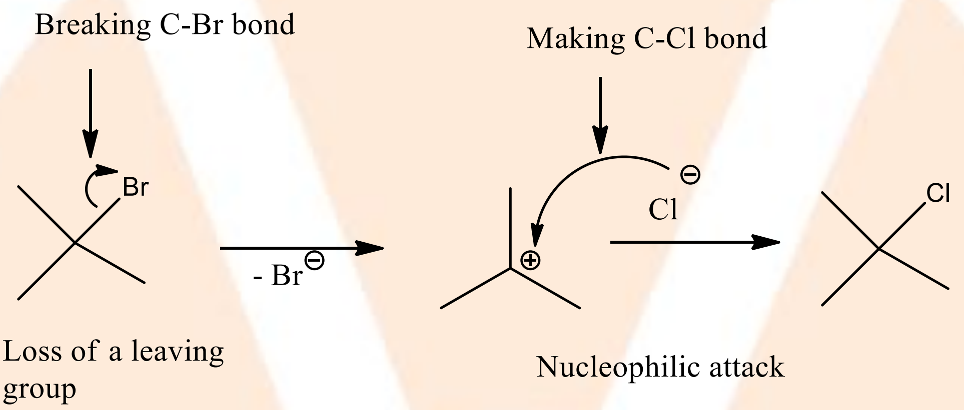
As the size increases steric hindrance increases, so there is difficulty in formation of transition state.

7. Favored by aprotic solvents.

3.2 Substitution Nucleophilic Unimolecular-S_{N^1}

Example -6

The S_N1 is a stepwise mechanism



Key features of S_{N^1} mechanism

1. It is a two-step reaction. First step involves formation of carbocation as well as its rearrangement such that carbocation is at most stable position, then nucleophile attacks the carbocation to form the final product which is the second step.

2. $Rate = k[RX]$

3. Intermediate is formed which is carbocation.

4. Rearrangement is commonly observed.

5. Racemic mixture is obtained.

6. Order of reactivity of alkyl halides:

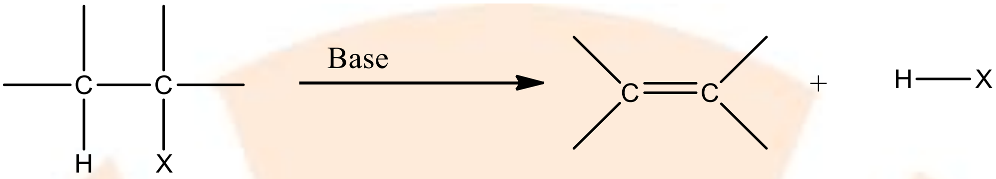
$3^\circ > 2^\circ > 1^\circ > CH_3X$

This can be attributed to the stability of the carbocation that is formed.

7. Favored by protic solvents.

4. Elimination Reactions

Example-7



The removal of adjacent hydrogen, a hydrogen and adjacent halide as well as vicinal halides to form unsaturated compound is generally called as elimination reaction. It proceeds via three kinds of mechanism.

4.1 Elimination Bimolecular- E2

Example-8

Key Features of E2 Mechanism

1. Single step reaction.

2. Rate=k[RX]

3. Single transition state with no intermediate.

4. No rearrangement

5. Strong bases are generally used as reagents.

6. Order or reactivity of alkyl halides:

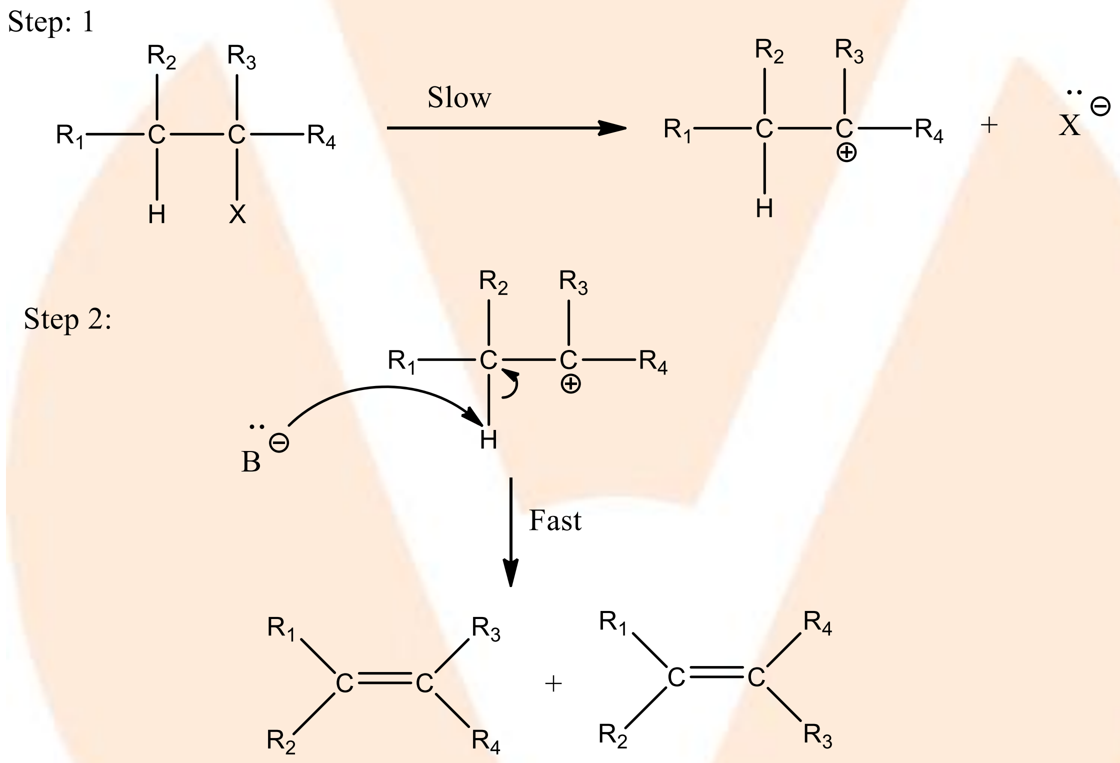
$3^\circ > 2^\circ > 1^\circ$

The number of alpha hydrogens will increase as we go from higher to lower alkene leading to alkene stability.

7. Favored by aprotic solvents.

4.2 Elimination Unimolecular-E1

Example-9



Key Features of E_1 Mechanism

1. It is a twostep reaction. First step involves formation of carbocation by loss of the leaving group and the second step is the deprotonation by using a nucleophilic base (generally weak).

2. $\text{Rate}=k[\text{RX}]$

3. Carbocation is formed as intermediate.

4. Rearrangement generally occurs until the carbocation is at its most stable position.

5. Observed in presence of weak bases.

6. Order or reactivity of alkyl halides:

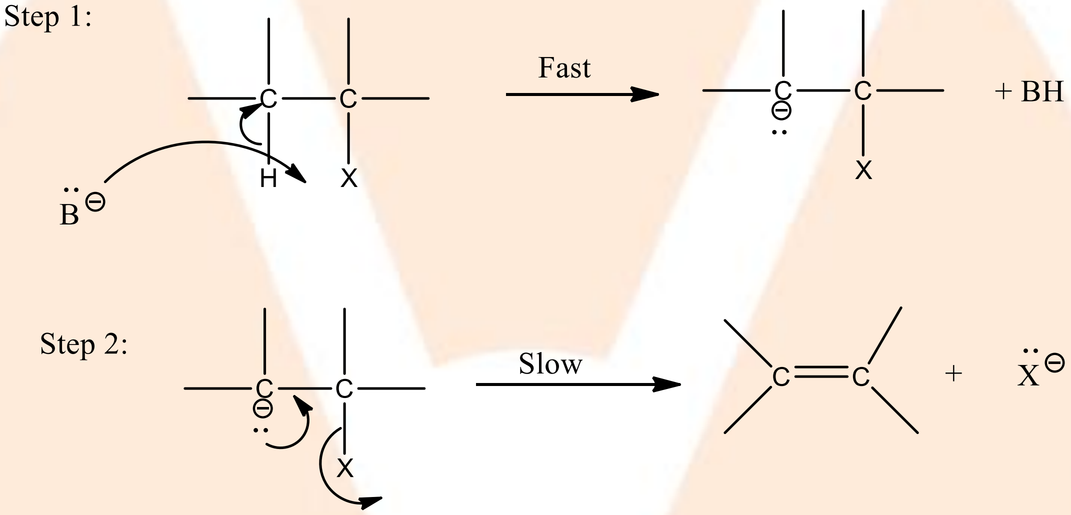
$3^{\circ} > 2^{\circ} > 1^{\circ}$

This can be attributed to the stability of carbocation formed as well as the stability of alkene formed.

7. Favored by protic solvents.

4.3 Elimination Unimolecular via Conjugate base E1cB

Example-10



Key Features of E1 Mechanism

1. It is a two-step reaction. First step is the formation of carbanion as intermediate and the second step is the loss of the leaving group.

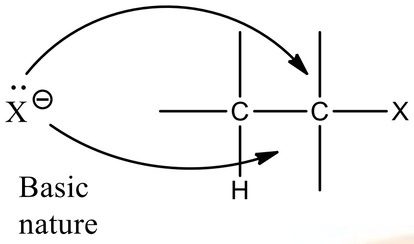
2. Rate=k[RX] [Base]

3. Carbanion is formed as intermediate.

4. Occurs when a poor leaving group is present.

5. Substitution and elimination

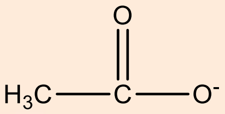
There is some similarity between a base and nucleophile such that a base can also be a nucleophile. To get more insight on how elimination and substitution compete, we will analyze the properties of bases and nucleophiles:



5.1 Nucleophilicity vs Basicity

a. In the case of the same attacking group nucleophilicity and basicity is considered to be the same. Eg:

$CH_3O^- > OH^- >$



$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O^-$

b. Neutral nucleophiles are weaker than negatively charged nucleophiles. Eg:

$OH^- > H_2O$ Or $NH_2^- > NH_3$

c. Since larger atoms are more polarizable, the reason being the less attraction from the nucleus due to large size are better nucleophiles but these nucleophiles will be weak bases as they cannot form a strong bond with hydrogen atoms leading to strong conjugate acid formation. Also contrary to this strong base is the better nucleophile if the size of attacking groups is the same. e.g.

Acidic Strength:

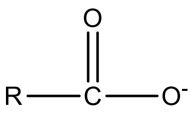
$CH_4 < NH_3 < H_2O < HF$

Basic Strength and Nucleophilicity:

${}^{0}CH_3 > {}^{0}NH_2 > {}^{0}OH > F^{0}$

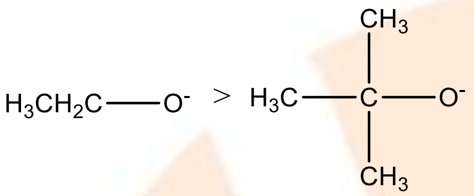
d. Nucleophilicity depends upon the nature of solvent if the sizes of attacking groups are different. However, Nucleophilicity is the same as basicity for gases.

e. With increase in stability of anion, nucleophilicity decreases.



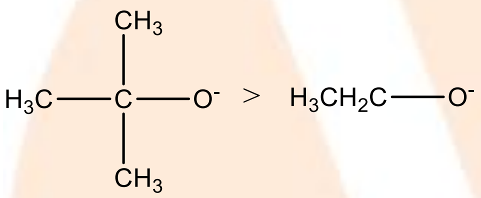
$R-C(=O)-O^-$ is a weaker nucleophile as it is resonance stabilized.

f. Nucleophilicity is controlled by steric factors



$H_3CH_2C-O^- > H_3C-C(CH_3)_2-O^-$

Nucleophilicity Order

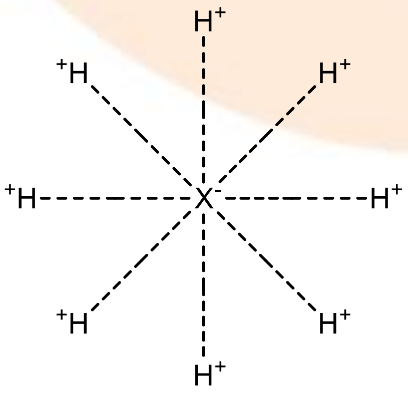


$H_3C-C(CH_3)_2-O^- > H_3CH_2C-O^-$

Basicity Order

g. A strong base can be converted into a good leaving group. e.g.: Groups containing Oxygen such as hydroxide can be converted into a good leaving group in weak acid medium as it gets protonated and thus become a good leaving group.

h. Protic solvent: These solvents have a hydrogen atom attached to an atom of a strong electro-negative element (e.g. Oxygen). Molecules of protic solvent can, therefore form hydrogen bonds to nucleophiles as:



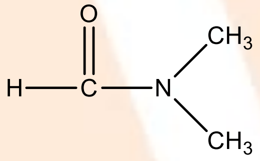
Small nucleophiles, which have a higher charge density than larger nucleophiles, are strongly solvated and this solvation prevents direct access to the nucleophilic center. Therefore, the smaller nucleophiles do not act as good nucleophiles like the larger nucleophiles. So, nucleophilicity is the opposite of basicity in protic solvents.

$$F^{-} \quad Cl^{-} \quad Br^{-} \quad I^{-}$$

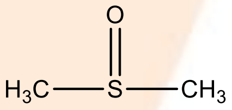
$$\xleftarrow[\text{increasing basicity}]{\hspace{5cm}}$$

$$\xrightarrow[\text{incresing nucleophilicity}]{\hspace{8cm}}$$

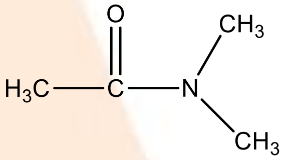
i. Aprotic solvents: Polar solvents that do not have H-atom, thus they are not able to form Hydrogen Bond. E.g.



N, N-Dimethyl formamide
(DMF)

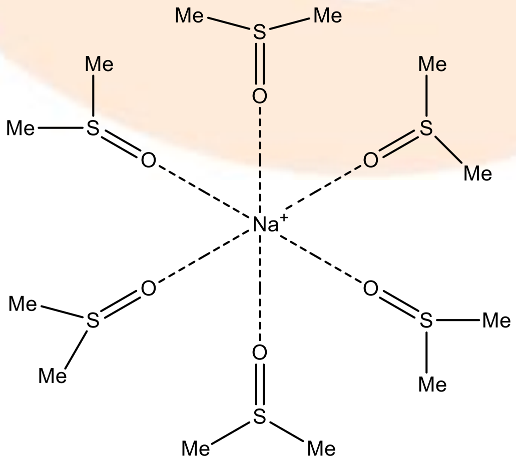


Dimethyl sulphoxide
(DMSO)



Dimethyl acetamide
(DMA)

These solvents dissolve ionic compounds and solvate the cations.



5.2 Saytzeff vs. Hoffmann Rule

According to position of double bond, two types of alkenes are formed and the rule that controls the position of bond are known as Saytzeff and Hoffman rule.

5.2.1 Saytzeff's Rule/Zaitsev Rule

According to this rule more stable alkene is formed, thus leading to formation of more substituted products. This reaction is said to be thermodynamically controlled

5.2.2 Hoffmann Rule

According to this less stable alkene should be formed, thus leading to formation of less substituted product. Here the product is formed by removal of more acidic β hydrogen, thus the reaction is said to be kinetically controlled.

5.3 Effect of Temperature

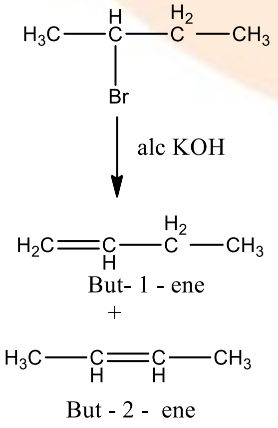
High temperature favours elimination while low temperature favours substitution reaction.

6. Stereochemistry

6.1 Regioselectivity

It is the preference of bond formation at a particular position or direction out of all the positions or directions that are present.

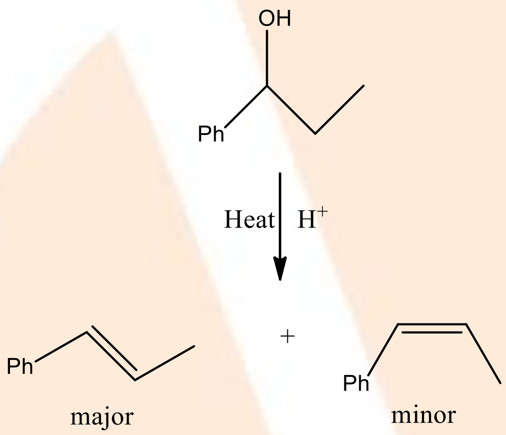
Example-11



6.2 Stereoselectivity

Stereoselective reactions are those reactions where the final product is a mixture of stereoisomers out of which one is the major and other is the minor product according to the reaction conditions. Either the pathway of lower activation energy (kinetic control) is preferred or the more stable product (thermodynamic control).

Example-12

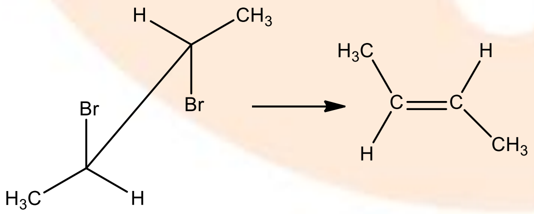


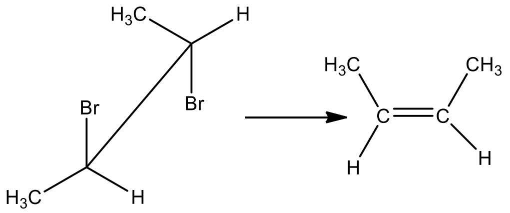
6.3 Stereospecificity

In this type of reactions, the initial reactant isomer decides the outcome of the reaction i.e. the final product is specified by the stereochemistry of the reactant.

The reaction gives a different diastereomer of the product from each stereoisomer of the starting material.

Example-13



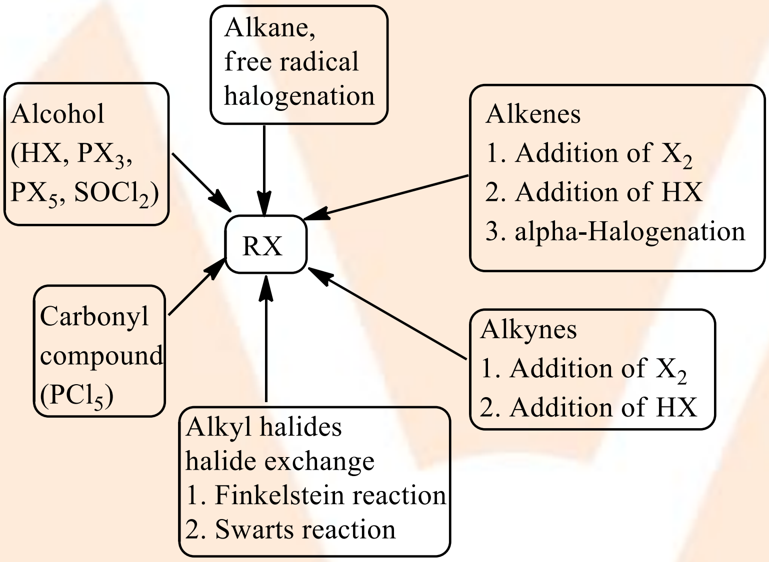


6.4 Chemoselectivity

If more than one type of functional groups are present, then the reagent attacks exclusively on a specific group leaving others as it is. Thesetypes of reactions are known as chemoselective reactions.

7. Alkyl Halides

7.1 Preparation of Alkyl Halides

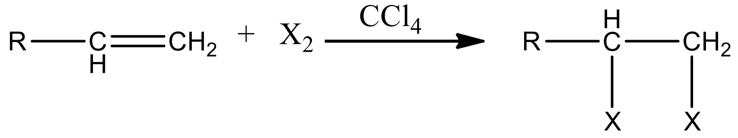


1. Alkanes

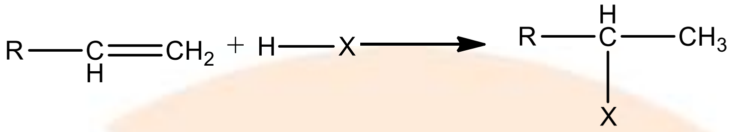
$$RH \xrightarrow{Cl_2} RCl + HCl$$

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

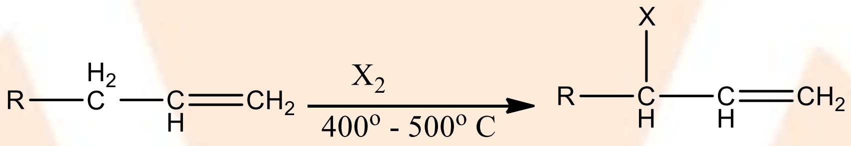
2. Alkenes

(i) 

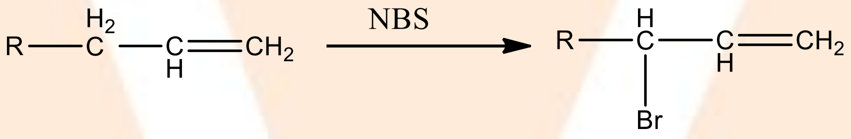
$$R\text{-}CH{=}CH_2 + X_2 \xrightarrow{CCl_4} R\text{-}CH(X)\text{-}CH_2X$$

(ii) 

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

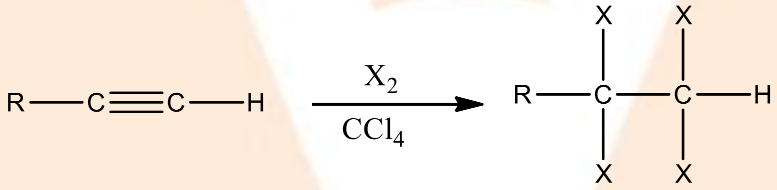
(iii) 

$$R\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow[400^o - 500^o\ C]{X_2} R\text{-}CH(X)\text{-}CH{=}CH_2$$

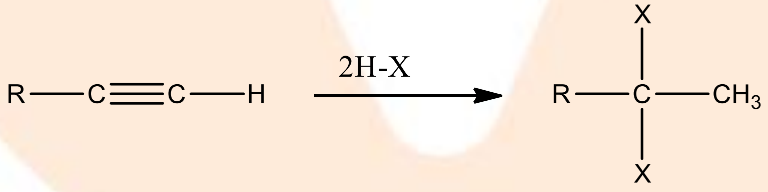


$$R\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow{NBS} R\text{-}CH(Br)\text{-}CH{=}CH_2$$

3. Alkynes



$$R\text{-}C{\equiv}C\text{-}H \xrightarrow[CCl_4]{X_2} R\text{-}CX_2\text{-}CX_2\text{-}H$$



$$R\text{-}C{\equiv}C\text{-}H \xrightarrow{2H\text{-}X} R\text{-}CX_2\text{-}CH_3$$

4. Alkyl Halides

(i) Finkelstein Reaction

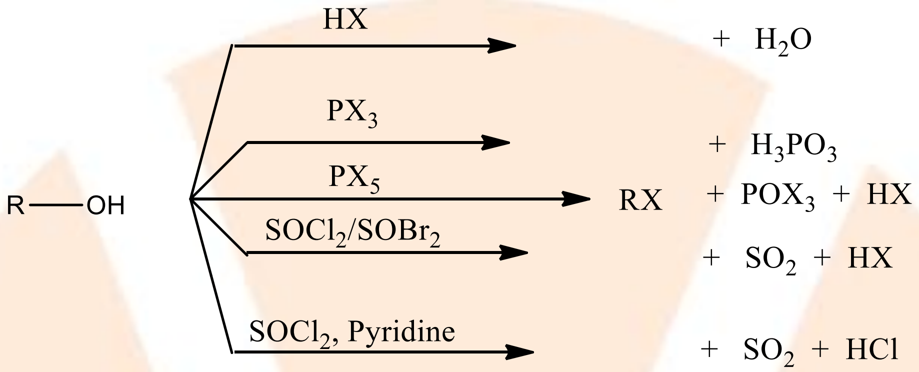
$R\text{-}Br + NaI \xrightarrow{acetone} R\text{-}I + NaBr$

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

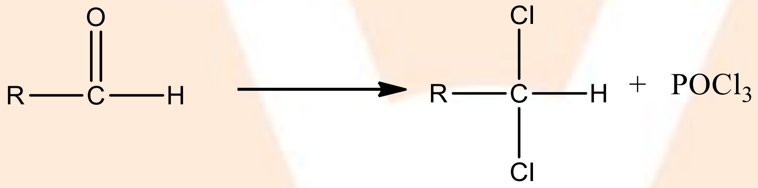
(ii) Swartz Reaction

$$R\text{-}I/Br/Cl + AgF \xrightarrow{DMSO} R\text{-}F + AgI/Br/Cl$$

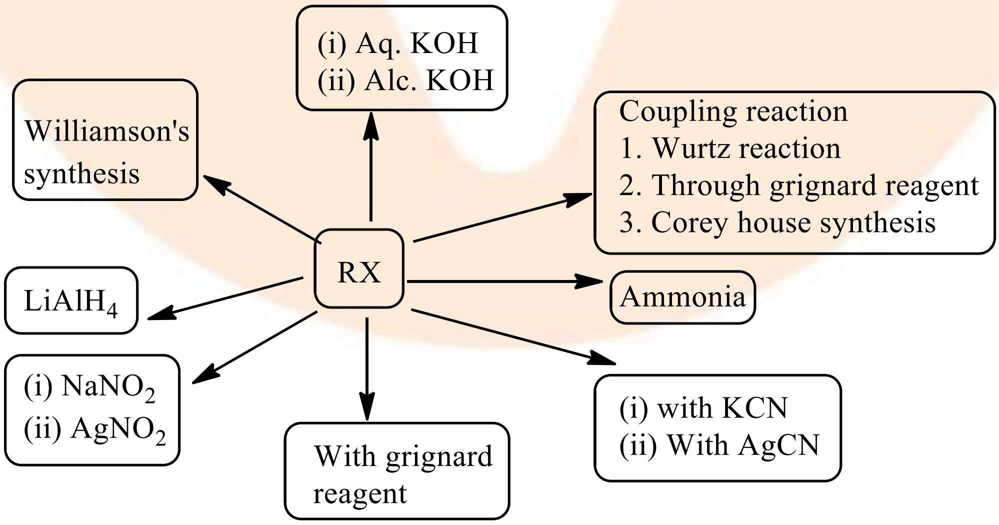
5. Alcohol



6. Carbonyl Compound



7.2 Reactions of Alkyl Halide



1. Coupling Reaction

(a) Wurtz Reaction

$$2\,RX + 2Na \xrightarrow{Et_2O} R\text{-}R + 2\,NaX$$

(b) Grignard Reagent

$$R\text{-}X + R\text{-}MgX \rightarrow R\text{-}R + MgX_2$$

(c) Corey-House Synthesis

$$R\text{-}X + 2\,Li \rightarrow R\text{-}Li + LiX$$

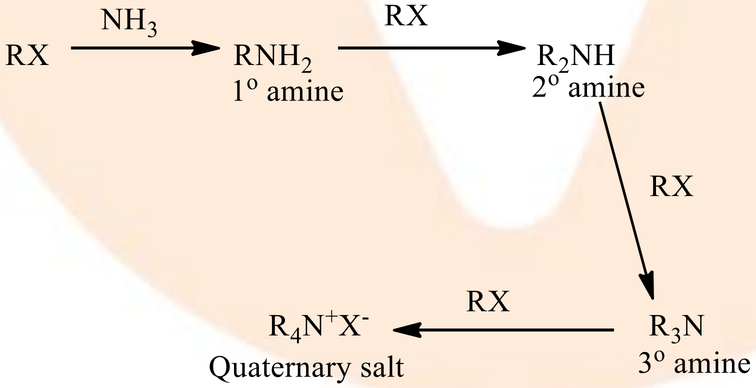
$$2\,R\text{-}Li + CuI \rightarrow R_2CuLi + LiI$$

$$R_2CuLi + R'\text{-}X \rightarrow R\text{-}R' + R\text{-}Cu + LiX$$

2. Amine Substitution

$$R\text{-}X + NH_3 \xrightarrow[\Delta]{C_2H_5OH} R\text{-}NH_2 + HX$$

Note: If alkyle 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

$$R\text{-}X + KCN \rightarrow R\text{-}CN + KX$$

4. AgCN

$\text{R-X} + \text{AgCN} \rightarrow \text{R-N} \equiv \text{C}$

5. NaNO$_2$

$\text{R-X} + \text{NaNO}_2 \rightarrow \text{R-O-N=O} + \text{NaX}$

6. AgNO$_2$

$\text{RX} + \text{AgNO}_2 \rightarrow \text{R-NO}_2 + \text{AgX}$

7. LiAlH$_4$

$\text{R-X} + \text{LiAlH}_4 \rightarrow \text{R-H}$

8. Williamson's Ether Synthesis

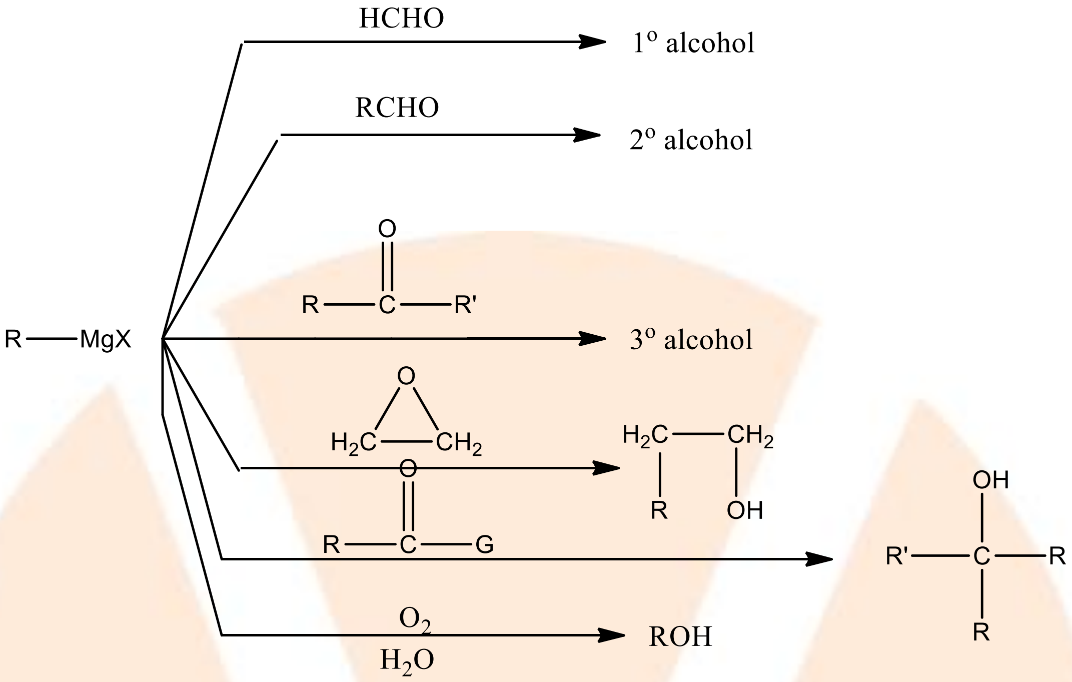
$\text{R—X} + \text{R'—O—Na} \longrightarrow \text{R—O—R'}$

9. Aq. KOH and Alc. KOH

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

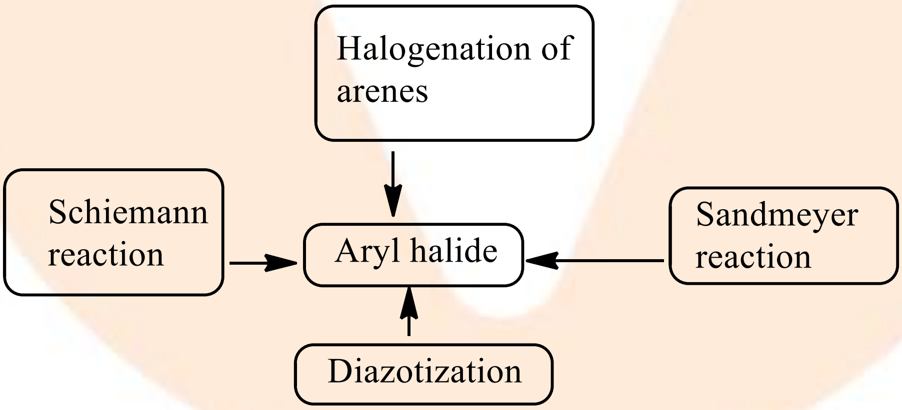
$\text{R-X} \xrightarrow{\text{alc. KOH}} \text{alkene}$

10. Reactions of R-MgX

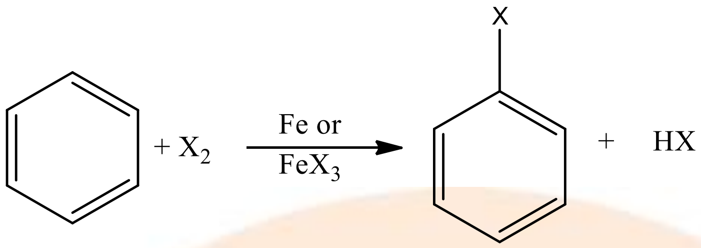


8. ArylHalide/Halorenes

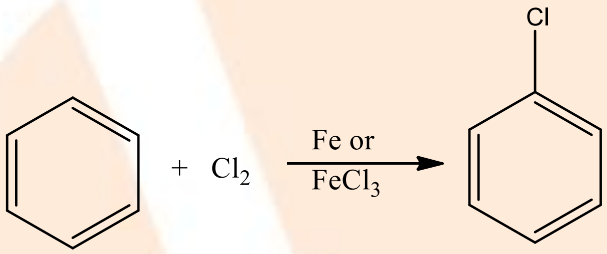
8.1 Preparation of Aryl Halide/Halorenes



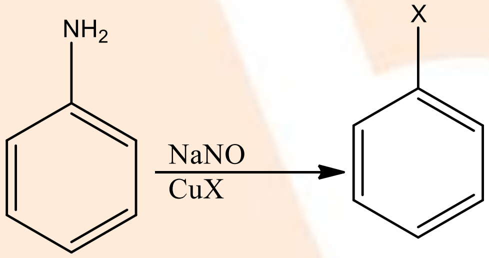
(a) Halogenation of Arenes



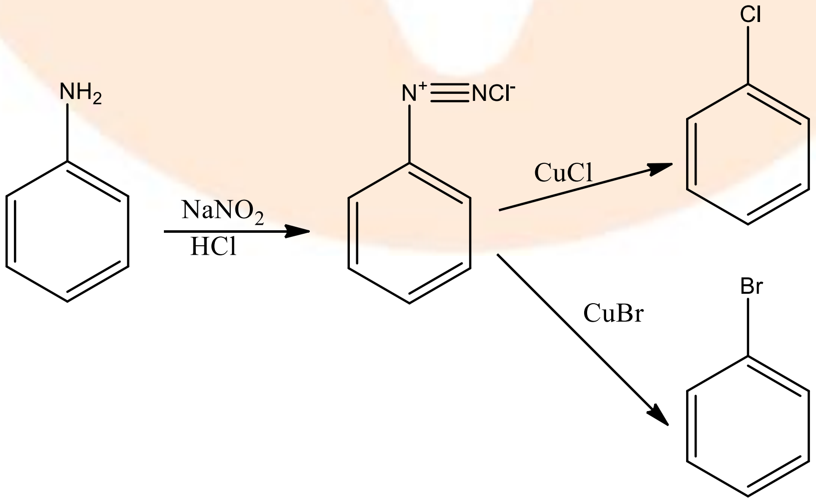
Example-14



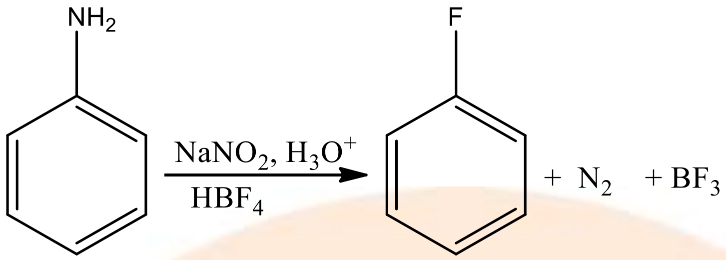
(b) Sandmeyer Reaction



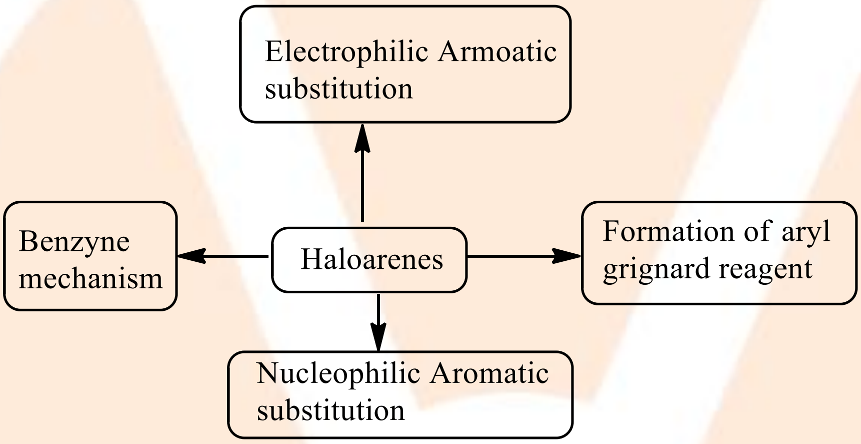
(c) Diazotiation



(d) Schiemann Reaction

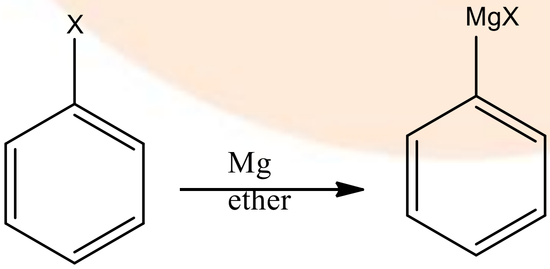


8.2 Reactions of Aryl Halide/Haloaranes

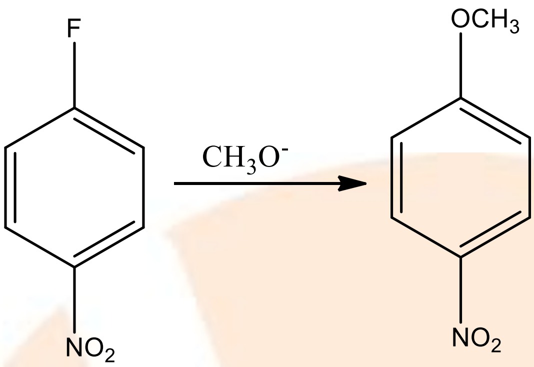


Electrophilic Aromatic Substitution Reaction: Halogens are weakly deactivating as they have strong induction effect and weak mesomeric effect. They are ortho/para directing.

(a) Formation of Aryl Grignard Reagent:

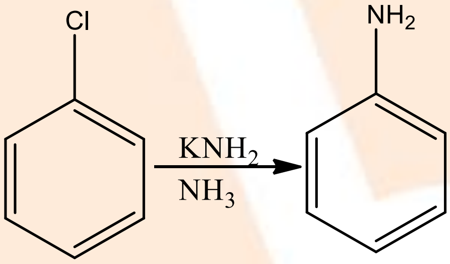


(b) S_NAr - Aromatic Nucleophilic Substitution Reaction



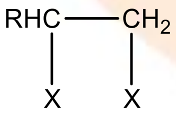
(c) Benzyne Mechanism(Elimination Addition Mechanism)

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



9. Reactions of Special Alkyl Halides

9.1 Di-Halides

$RCHX_2$	Alkyidene Dihalides or Geminal Dihalides
 $\underset{X}{RHC}-\underset{X}{CH_2}$	Alkylene Dihalides or Vicinal(1,2) Dihalides

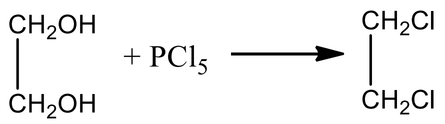
9.1.1 Preparation of:

(a) Halogenation of Alkenes and Alkynes

$CH_2=CH_2 + X_2 \rightarrow CH_2X\text{-}CH_2X$ (Vicinal Dihalide)

$CH\equiv CH + 2HX \rightarrow CH_3CHX_2$ (Geminal Dihalide)

(b) PCl_5 with Diols and Carbonyl Compounds



$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} + PCl_5 \longrightarrow \begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

Vicinal Dihalide

$CH_3CHO + PCl_5 \longrightarrow CH_3CHCl_2$ Gem Dihalide

9.1.2 Properties of some more reagents

(a) Alcoholic KOH: (Dehydrohalogenation)

$$XCH_2CH_2X \xrightarrow[\text{KOH}]{\text{alcoholic}} CH \equiv CH$$

$$CH_3CHX_2 \xrightarrow[\text{KOH}]{\text{alcoholic}} CH \equiv CH$$

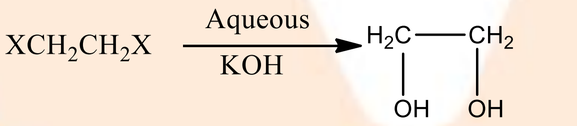
(b) Zinc Dust: (Dehalogenation)

$$XCH_2CH_2X \xrightarrow[\text{Zn}]{\text{alcohol}} CH_2{=}CH_2$$

$$CH_3CHX_2 \xrightarrow[\text{Zn}]{\text{alcohol}} CH_2{=}CH_2$$

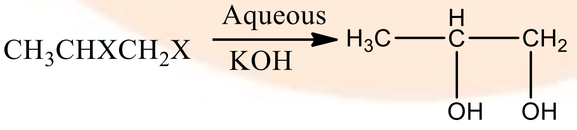
(c) Action of aq. KOH: (Alkaline Hydrolysis)

(i) Vicinal Dihalides



$$XCH_2CH_2X \xrightarrow[\text{KOH}]{\text{Aqueous}} \begin{array}{cc} H_2C & CH_2 \\ | & | \\ OH & OH \end{array}$$

Ethylene Glycol

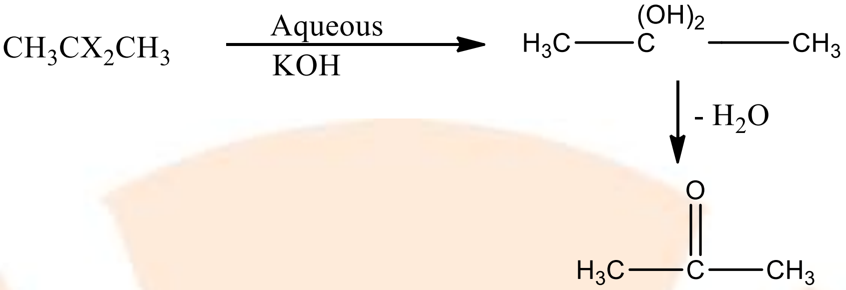


$$CH_3CHXCH_2X \xrightarrow[\text{KOH}]{\text{Aqueous}} H_3C-\overset{H}{C}-CH_2 \quad (\text{OH on } C, \text{ OH on } CH_2)$$

Propan-1,2-diol

(ii) Gem Dihalides

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



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

9.2 Tri- Halides and Tetra-Halides

$CHCl_3$ Chloroform (liquid)	$CHBr_3$ Bromoform (liquid)
CHI_3 Iodoform (yellow solid)	CCl_4 Carbon tetrachloride (liquid)

9.2.1 Chloroform: $CHCl_3$

(a) Preparation of chloroform

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

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

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

$Ca(OH)_2$

$CCl_3CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + Ca(HCOO)_2$

NaOH

$CH_3CHO + 3Cl_2 \rightarrow CCl_3CHO \xrightarrow{\text{Hydrolysis}} CCl_3CH(OH)_2$

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

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

(ii) Methyl Ketones

$CH_3COCH_3 + 3Cl_2 \rightarrow CCl_3COCH_3 \xrightarrow{Ca(OH)_2} CHCl_3 + (CH_3COO)_2Ca$

(iii) Carbon Tetrachloride

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

(iv) Chlorination of Methane (Reaction Temperature = $370^{\circ}C$)

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

(b) Reactions

(i) Oxidation

Chloroform in presence of light and air (O_2) froms a highly poisonousgas, Phosgene.

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

To prevent the decomposition of chloroform 1% ethanol is added and chloroform is stored in brown bottle.

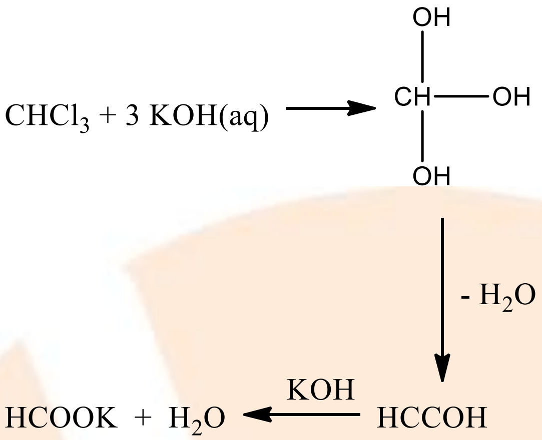
(ii) Carbylamine Reaction

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

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

This reaction is used as a test of primary aliphatic as well as secondary amines since carbylamines gives a pungent odour.

(iii) Hydrolysis



9.2.2 Iodoform: CHI_3

(a) Preparation

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

$$CH_3COCH_3 + 3I_2 + 3Na_2CO_3 \longrightarrow \underset{\text{yellow solid}}{CHI_3\downarrow} + 3CH_3COONa + 3NaI + 2CO_2\uparrow$$

Note- This above reaction is an important reaction used in practical chemistry which is known as Iodoform reaction. Iodoform is a yellow coloured solid. It is used to identify groups connected with $R-CH_3$ type of group such as ethyl alcohol, acetaldehyde, secondary alcohol, 2-ketones, $R(CH_3)CHOH$ (methyl alkyl carbinol) and methyl ketones ($RCOCH_3$), because all these form iodoform. The minor product of the iodoform reaction, sodium carboxylate is acidified to produce carboxylic acid (RCOOH).

9.2.3 Carbon Tetrachloride : CCl_4

(a) Preparation:

$$CH_4 + 4Cl_2 \xrightarrow[\text{diffused}]{\text{hv}} CCl_4 + 4HCl$$

$$CS_2 + 3Cl_2 \xrightarrow[\text{Fe/I}_2]{\text{AlCl}} CCl_4 + S_2Cl_2$$

Dfractional distillation is used to separate S_2Cl_2 . It is then treated with more CS_2 to give CCl_4. C washed with $NaOH$ and distilled to obtain pure CCl_4.

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

$$CH_3CH_2CH_3 + Cl_2 \xrightarrow[\text{70-100atm}]{400^oC} CCl_4 + HCl + C_2Cl_6$$

Note CCl_4 is a colourless and poisonous liquid which is insoluble in H_2O

It is a good solvent for grease and oils. CCl_4 is used in fire extinguisher for electric fires as Pyrene. It is also an insecticide for hookworms.

(b) Reactions:

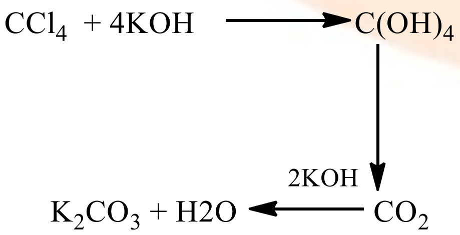
(i) Oxidation

$$CCl_4 + H_2O \xrightarrow{500^oC} COCl_2 + 2HCl$$

(ii) Reduction

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

(iii) Hydrolysis



(iv) Action of HF

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

9.2.4 Vinyl Chloride: $CH_2{=}CHCl$

Vinyl group $CH_2{=}CH-$

(a) Preparation

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

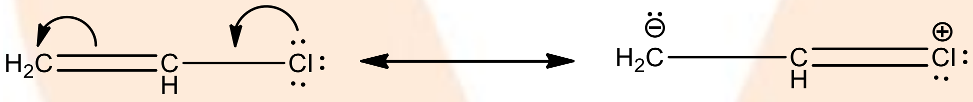
(ii) $ClCH_2CH_2Cl \xrightarrow{KOH(alc.)} CH_2{=}CHCl + KCl + H_2O$

(iii) $CH_2{=}CH_2 + Cl_2 \xrightarrow{600^oC} CH_2{=}CHCl + HCl$

(b) Reaction

$CH_2{=}CHCl + alc.KOH \rightarrow CH \equiv CH + HCl$

Vinyl Chloride is stable due to extended resonance of double bond with the halogen atom, So it does not undergo nucleophilic substitution.



9.2.5 Allyl chloride : $H_2C{=}CHCH_2Cl$

(a) Preparation

(i) $H_2C{=}CHCH_3 + Cl_2 \xrightarrow{500\text{-}600^oC} CH_2{=}CHCH_2Cl$

(ii) $CH_2{=}CHCH_2OH{+}PCl_5 \rightarrow CH_2{=}CHCH_2Cl + POCl_3{+}HCl$

(b) Reactions

(i) Addition Reactions

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

$CH_2{=}CH\text{-}CH_2Br + HBr \rightarrow CH_3CHBrCH_2Br$

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.

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

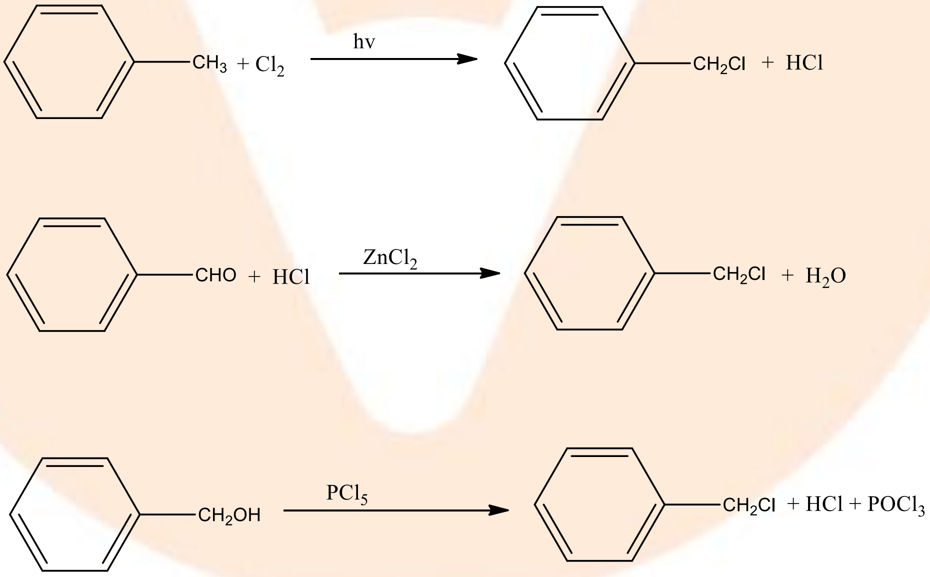
$$CH_2{=}CH\text{-}CH_2Cl \xrightarrow{NH_3} CH_2{=}CHCH_2NH_2 + HCl$$

$$CH_2{=}CH\text{-}CH_2Cl \xrightarrow{KCN} CH_2{=}CHCH_2CN + KCl$$

$$CH_2{=}CH\text{-}CH_2Cl + Mg \xrightarrow{\text{Dry ether}} CH_2{=}CHCH_2MgCl$$

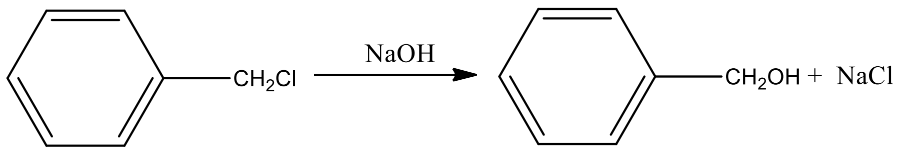
9.2.6 Benzyl Chloride: $C_6H_5CH_2Cl$: $PhCH_2Cl$

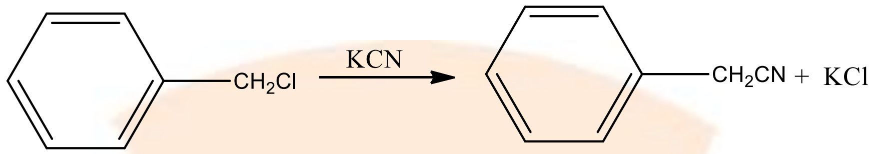
(a) Preparation

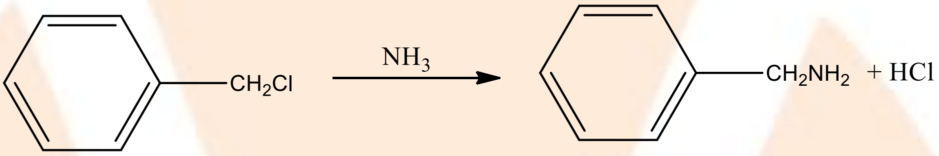


(b) Reactions

Benzyl halide undergo unimolecular nucleophilic substitution as the carbocation i.e. formed by loss of Chlorine is highly stable due to extended resonance, so the nucleophilic substitution easily takes place when compared to aryl halides.

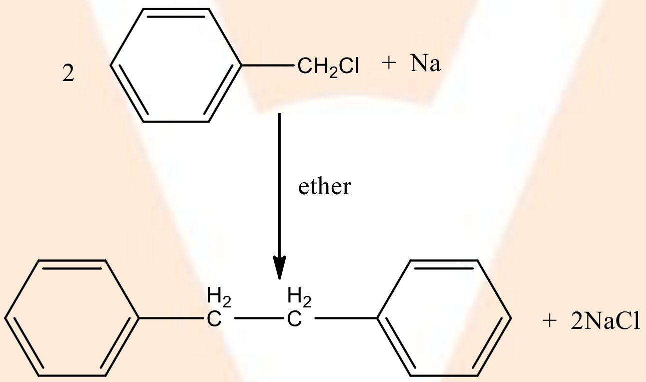




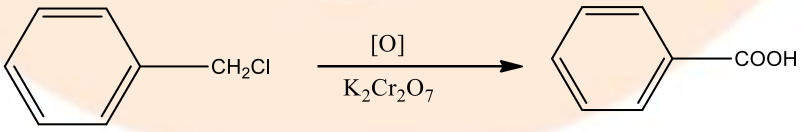


(i) Wurtz Reaction

Proceeds via free radical mechanism.



(ii) Oxidation



10. Chemistry of Grignard Reagent: R-Mg-X

10.1 Preparation

$$\mathrm{RX + Mg \xrightarrow[\text{ether}]{\text{reflux in}} R\text{-}Mg\text{-}X}$$

Note: In preparation of Grignard reagent we can have any hydrocarbon group, it will not effect the reaction mechanism

10.1 Reactions

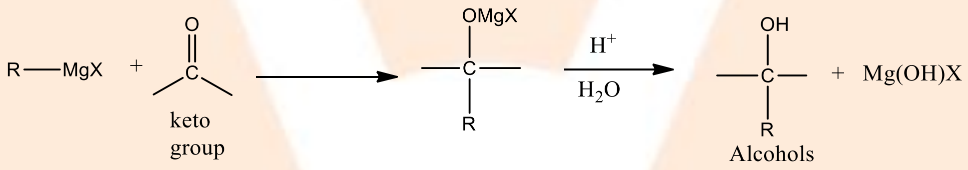
(a) Grignard reagent as a base reacts with compounds containing active H to give alkanes.

$$\text{R-MgI} + \text{HOH} \rightarrow \text{RH} + \text{Mg(OH)I}$$

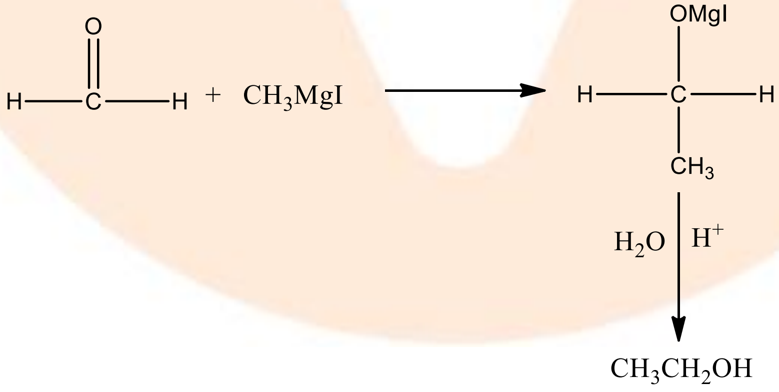
$$\text{R-MgI} + \text{R'OH} \rightarrow \text{RH} + \text{Mg(OR')I}$$

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

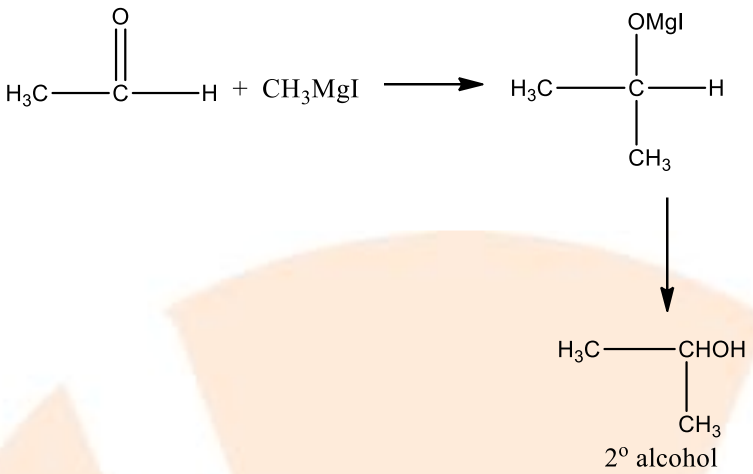
(b) Grignard reagent acts a strong nucleophile and shows nucleophilic additions to give various products. Alkyl group being electron rich (carbonian) acts as nucleophile in Grignard reagent.



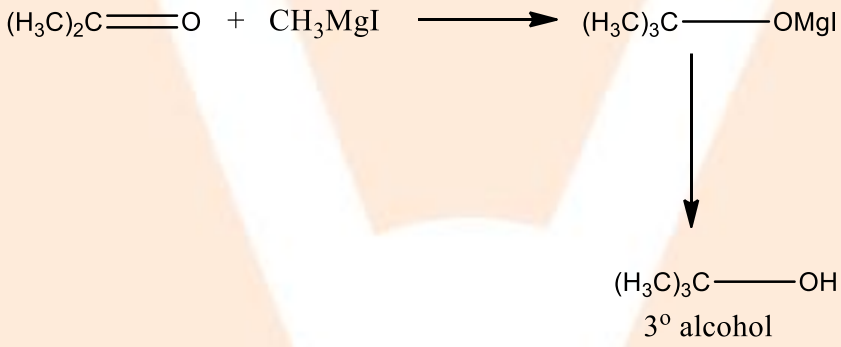
Example-15



Example-16

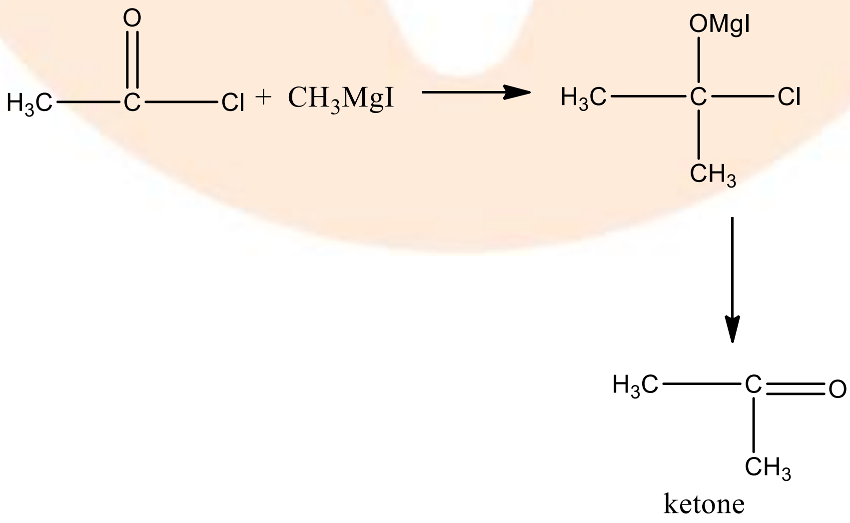


Example-17



(c) Acid Chloride

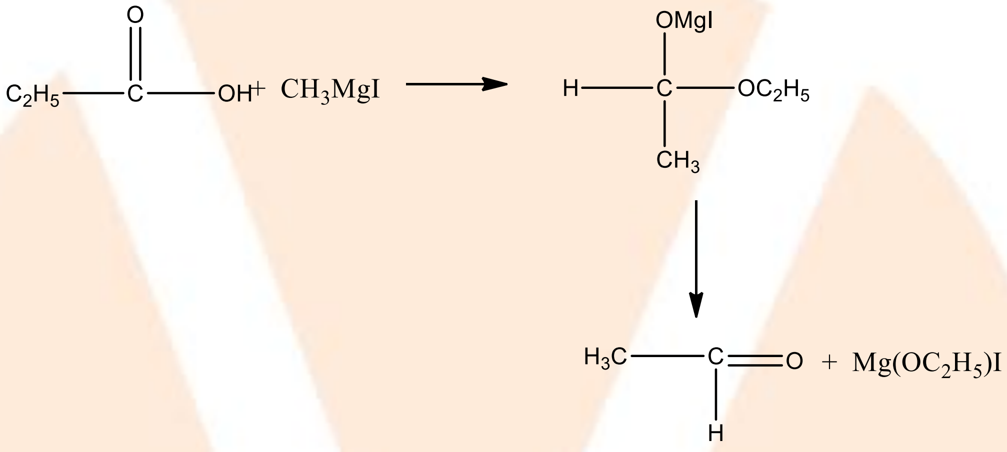
Example-18



Ketones (acetone) fromed further reacts with Grignard reagent to from 3° alcohols (tert. Butyl alcohol). However, with 1:1 mole ratio of acid halide andGrignard Reagent, one can prepare ketones.

(d) Esters

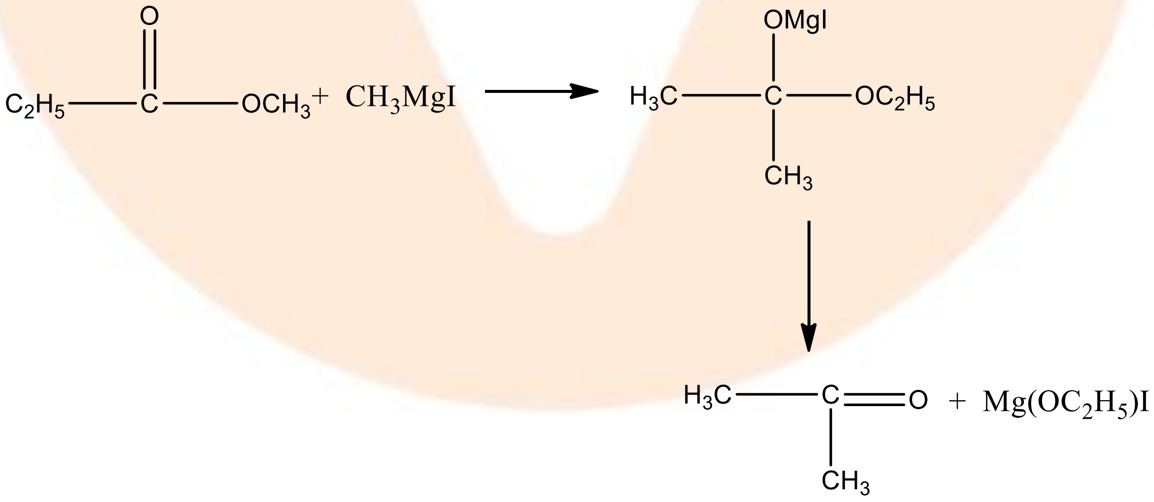
Example-19



Aldehyde

The further reaction of aldehyde with CH_3MgI will give secondary alcohol as the final product.

Example-20

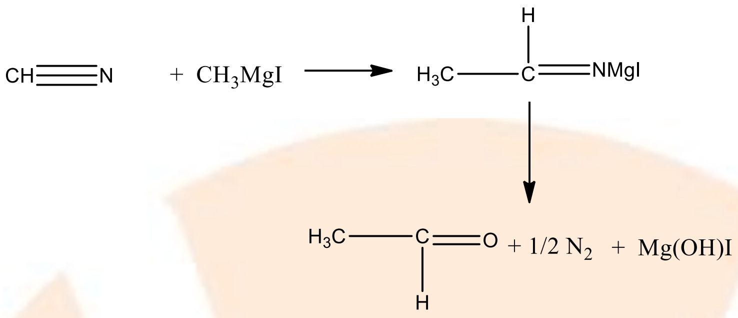


Ketone

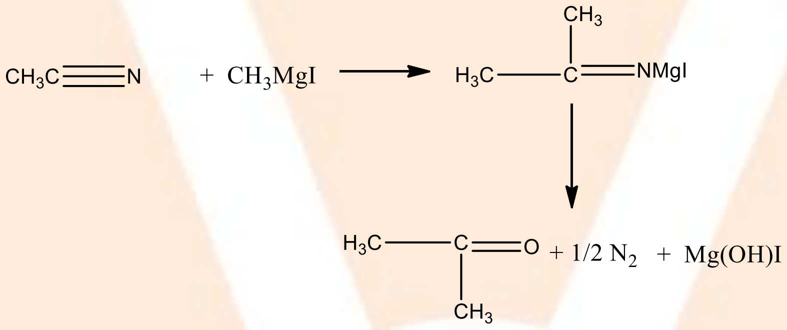
The ketones react further with CH_3MgI to give 3° alchohol, if present in excess. But 1:1 mole ratio of reactants will certainly give ketones.

(e) Cyanides

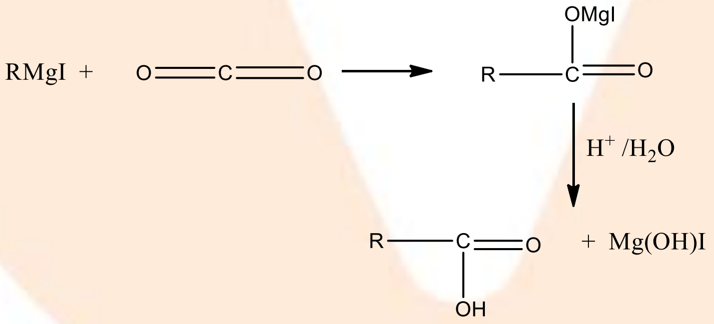
Example-21



Example-22

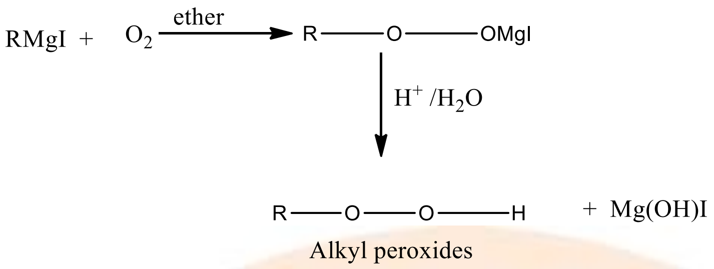


(a) CO_2

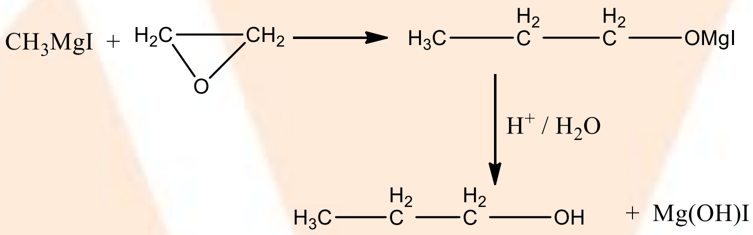


Carboxylic acid

(b) Oxygen



(c) Ethylene Oxide (Oxiranes)



(d) Alkynes

$$CH_3C\equiv C\text{-}H + CH_3MgI \rightarrow CH_3C\equiv C\text{-}MgI + CH_4$$

$$CH_3C\equiv C\text{-}MgI + CH_3I \rightarrow CH_3C\equiv C\text{-}CH_3 + MgI_2$$

(e) Alkyl Halides

$$R\text{-}MgI + CH_3CH_2Br \rightarrow CH_3CH_2R + Mg(Br)I$$

$$CH_3MgBr + CH_2{=}CHCH_2Br \rightarrow CH_3CH_2R + MgBr_2$$

(f) Inorganic Halides

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

$$\downarrow$$

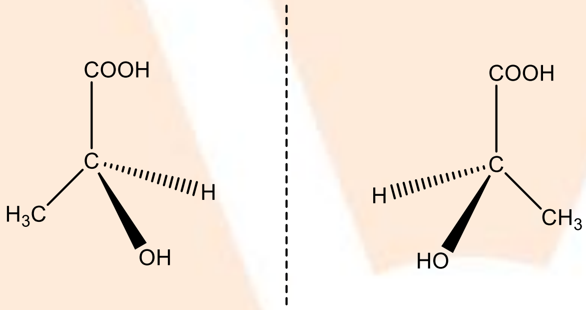
$$Pb + 4\ MgBr(Cl)$$

11. Some Important Concepts in Organic Chemistry:

- **Optical Activity:** The property due to which some compounds are able to rotate the plane of plane-polarised light when it is passed through their solution.

- **chirality and enantiomers:** The compounds when they are optically active are known as chiral molecule and they exist in pair such that they are mirror images of each other also known as enantiomers. If a mixture have enantiomers in equal quantity, then the mixture will have zero optical rotation and such mixtures are known as **racemic mixtures** and process of making such mixtures is known as **racemisation**.

Eg:



- **Retention:** The property due to which some elements are able to maintain both their absolute and relative configuration and position in space. In simple word the configuration of the stereocenter remains unchanged.

- **Inversion:** Here the absolute and relative configurations becomes reverse of each other which means their symmetry becomes different than what was it before.