Ch → 10

Haloalkanes And Haloarenes

Halo → It comes from halogens
→ Group - 17 elements are known as halogen
→ Group - 17 elements are denoted by X.
→ Group - 17 elements are found in diatomic form i.e; X_2
X_2 → 1 molecule of halogen contains 2 atoms of halogen

$X_2 = F_2, Cl_2, Br_2, I_2$

↓

Halogen → These are salt forming elements

→ Halogen are electronegative element

$X + e \rightarrow X^-$

V.e = 7

Halogen → common system - Halide
→ IUPAC system - Halide

Halogen (X)	common system (Halide)	IUPAC (Halo)
F	Fluoride	Fluoro
Cl	chloride	chloro
Br	Bromide	Bromo
I	Iodide	Iodo

✡ Alkane

→ It is saturated hydrocarbon
→ It is identified by the presence of single bond between two carbon atoms.

→ Saturated hydrocarbon is known as alkane.
Its general formula is C_nH_{2n+2}
where n = no. of carbon atoms

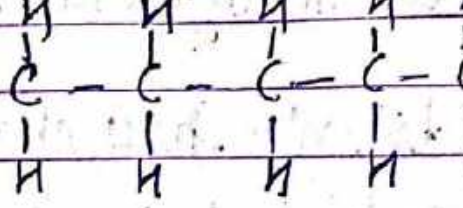
C_nH_{2n+2} → Alkane

Representation

a) Molecular formula
b) structural formula
c) condensed formula
d) Bond line formula

$n = 5$, C_5H_{12} → pentane

a) C_5H_{12} → Molecular

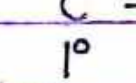
b)  → structural

c) $CH_3-CH_2-CH_2-CH_2-CH_3$
$CH_3-(CH_2)_3-CH_3$ → condensed

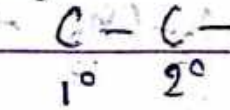
d)  → Bond line

* In alkane carbon occurs in three forms

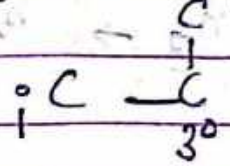
a) primary carbon (1° carbon)



b) secondary carbon (2° carbon)



c) Tertiary carbon (3° carbon)

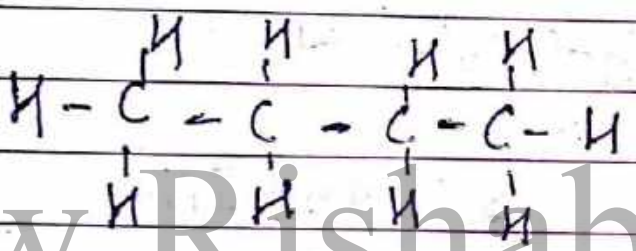


✡ Isomerism of alkanes

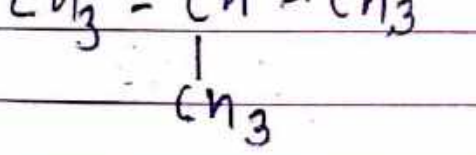
→ Alkane show chain isomerism.
It is due to different arrangement of C-atoms

→ First three alkane doesn't show chain isomerism

Butane C_4H_{10} → n-butane
→ iso-butane



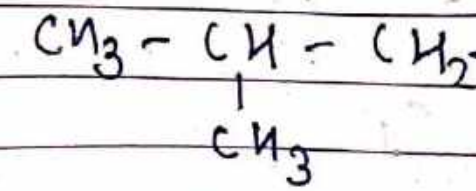
$CH_3-CH_2-CH_2-CH_3$ → n butane



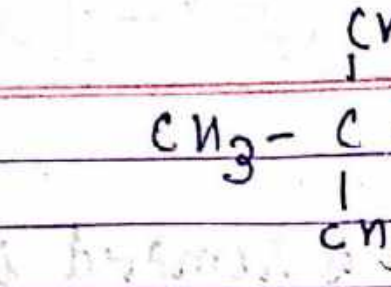
→ iso butane

C_5H_{12}

$CH_3-CH_2-CH_2-CH_2-CH_3$ → n pentane



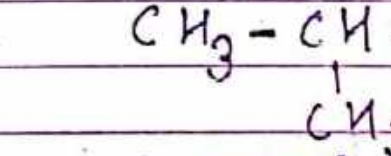
→ iso pentane



- Neo pentane

C_6H_{14}

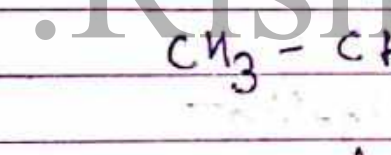
(i) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ → n-hexane

(ii) 

→ Isohexane

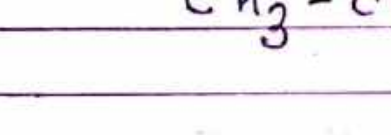
2-methyl pentane

~~$CH_3-CH-C-CH_2-CH_3$~~
~~CH3~~

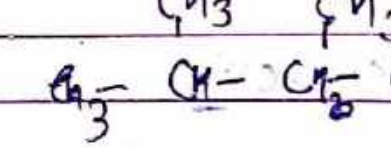
(iv) 

→ Neo hexane

2,2-dimethyl butane

(iii) 

3-methyl pentane

(v) 

2,3-dimethyl butane

☆ Alkyl Group

→ When 1- Hydrogen atom is removed from the alkane then alkyl group is formed.

$$C_nH_{2n+2} \xrightarrow{-H} C_nH_{2n+1}$$

Alkane → Alkyl

→ Alkyl group is denoted by (R-)

eg.

$$CH_4 \xrightarrow{-H} CH_3$$

Methane → methyl

$$C_2H_6 \xrightarrow{-H} C_2H_5$$

Ethane → Ethyl

$$CH_3-CH_3 \xrightarrow{-H} CH_3-CH_2-$$

Ethyl

Propane C_3H_8

$CH_3-CH_2-CH_3$ (1° 2° 1°)

→ $CH_3-CH_2-CH_2-$
primary alkyl or n-propyl

$CH_3-\underset{|}{CH}-CH_3$
Sec ~~alk~~ propyl
or Isopropyl

Page No.: 7
Date: / /

Butane C_4H_{10}

1) $CH_3-CH_2-CH_2-CH_3$ (1° 2° 2° 1°)

→ $CH_3-CH_2-CH_2-CH_2-$ n-butyl

→ $CH_3-CH_2-\underset{1}{CH}-CH_3$ Sec-butyl

$CH_3-\underset{1^\circ}{CH_2}-\underset{2^\circ}{CH_2}-\underset{1^\circ}{CH_3}-\underset{3^\circ}{\underset{H}{C}}-\underset{1^\circ}{CH_3} \xrightarrow{-H} CH_3-\underset{}{\overset{CH_3}{\underset{}{C}}}-CH_3$

Tertiary-butyl

$CH_3-\underset{3^\circ}{\underset{CH_3}{CH}}-\underset{1^\circ}{CH_3} \xrightarrow{-H} CH_3-\overset{CH_3}{\underset{}{CH}}-CH_2-$

iso-butyl

$CH_3-\underset{}{\overset{CH_3}{\underset{}{CH}}}-CH_2-CH_3 \xrightarrow{-H} CH_3-\overset{CH_3}{\underset{}{CH}}-CH_2-CH_2-$

Iso pentyl

$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{}{C}}}-CH_3 \xrightarrow{-H} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-$

Neo pentyl

$CH_3-\underset{3^\circ}{\underset{CH_3}{CH}}-CH_2-CH_3 \rightarrow CH_3-\overset{CH_3}{\underset{}{C}}-CH_2-CH_3$

Tert-pentyl

$CH_3-CH_2-CH_2-CH_2-CH_3 \rightarrow CH_3-CH_2-CH_2-\underset{1}{CH}-CH_3$

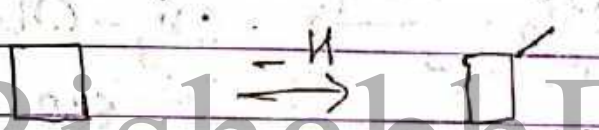
sec-butyl pentyl

* Alicylic organic compounds

cyclo + word root + p. suffix

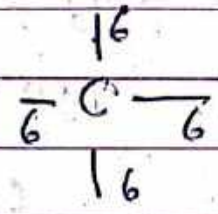
cyclopentane

cycloalkane $\xrightarrow{-H}$ Cycloalkyl



cyclobutyl

Geometry



No. of sigma bond = No. of hybrid orbital

H.O = 4

Hybridisation → sp^3

Geometry → Tetrahedral

Bond angle → 109.5° or 109°28'

* What is haloalkane?
→ It is halogen derivative of alkane.

$C_nH_{2n+2} \xrightarrow[+X]{-H} (C_nH_{2n+1})X$

Alkane — Haloalkane – IUPAC system
Alkyl halide – Common system

$R-H \xrightarrow[+X]{-H} R-X$

Alkane — Haloalkane, Alkyl halide

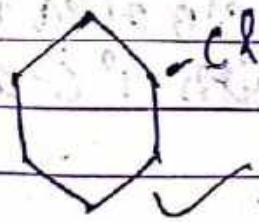
4/04/19

* Write the structural formula of the following organic compounds:

i) Sec-propyl chloride
ii) Tert-butyl bromide
iii) cyclo-hexyl chloride
iv) Neo-pentyl bromide.
v) Iso butyl chloride

→ i) $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$

ii) $CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

iii) 

iv) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-Br$

v) $CH_3-\underset{\underset{CH_3}{|}}{CH_2}-CH_2-Cl$

✱ Classification of haloalkane

→ on the basis of no. of halogen atoms. Haloalkanes are classified into 4 parts

i) Monohalogen derivative

$$CH_4 \xrightarrow[+X]{-H} CH_3 - X$$

ii) Dihalogen derivative

$$CH_4 \xrightarrow[+2X]{-2H} CH_2X_2$$

iii) Trihalogen derivative

$$CH_4 \xrightarrow[+3X]{-3H} CHX_3$$

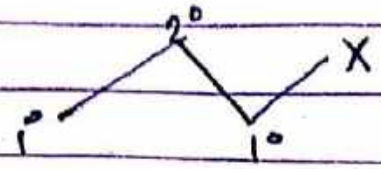
iv) Tetrahalogen derivative

$$CH_4 \xrightarrow[+4X]{-4H} C-X_4$$

* Classification of monohalogen derivative

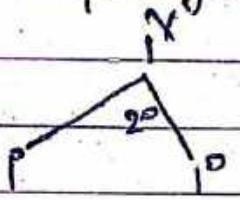
→ It is classified into three parts

i) primary alkyl halide or 1° halo alkane
- Halogen is bonded with 1° C-atom



$CH_3 - CH_2 - CH_2 - X$ → n-propyl halide

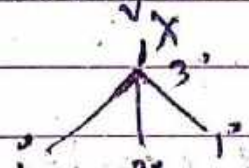
ii) secondary alkyl halide or 2° Haloalkane
→ Halogen is bonded with 2° of c-atom



$CH_3 - \underset{X}{CH} - CH_3$

→ iso-propyl halide
Sec-propyl halide

iii) Tertiary alkyl halide or 3° Haloalkane
→ Halogen is bonded with 3° of c-atom



$CH_3 - \underset{\underset{CH_3}{|}}{\overset{X}{\overset{|}{C}}} - CH_3$

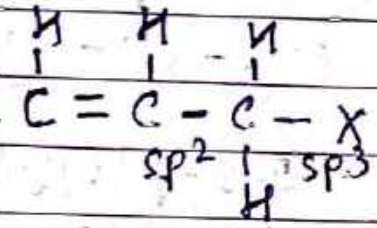
→ Tert-butyl halide

* classification based on hybridisation

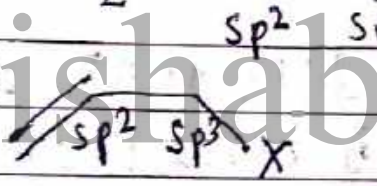
→ on the basis of hybridisation monohalogen derivative is classified ~~on the~~ into two parts.

i) Allylic halide
ii) vinyl halide

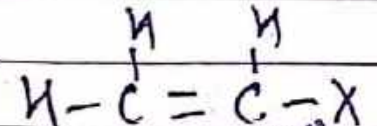
i) Allylic halide
⇒ When halogen atom is bonded with sp^3 hybridised carbon atom and next C-atom is sp^2 hybridised then it is known as allylic halide.



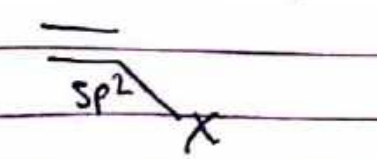
$CH_2 = CH - CH_2 - X$
$sp^2 \quad sp^3$



ii) vinyl halide
⇒ When halogen atom is bonded with sp^2 hybridised carbon atom then it is known as vinyl halide.



$CH_2 = CH - X$
sp^2



Q. Identify allylic & and vinyl halide and also identify 1°, 2° and 3° haloalkane

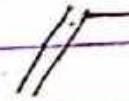
i)  → Allylic
2°

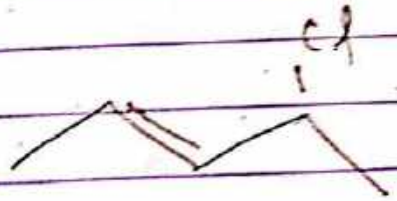
ii)  → Vinyl
2°

iii)  → ~~Vinyl~~ Allylic
~~2°~~ 1°

iv)  → Allylic
3°

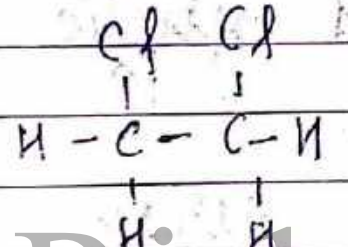
v)  → Vinyl
1°

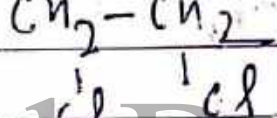
vi)  → Allylic
1°

vii)  → Allylic
→ 2°

* Dihalogen derivative is classified into two parts:
a) Vicinal dihalide
b) Gem dihalide

a) vicinal dihalide → when two same halogen atoms are present at the adjacent carbon atom, then it is known as vicinal dihalide.
e.g.

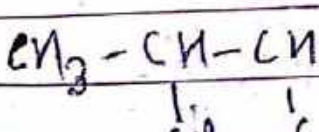




Ethylene dichloride

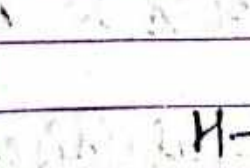
concept

The common name of vicinal dihalide is alkylene dihalide



propylene dichloride

5) Gem dihalide → When two same halogen atoms are present at the same C-atoms then it is known as gem dihalide

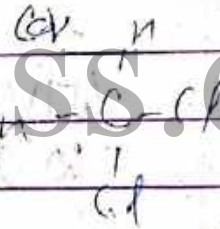


CH_3-CHBr_2
Ethylidenedibromide

Concept → The common name of gemdihalide is alkylidene dihalide

CH_2Cl_2

$CH_3-CH_2-CHCl_2$
propylidene dichloride



Trihalogen derivative
e.g. $CHCl_3$ – chloroform
$CHBr_3$ – Bromoform
CHI_3 – Iodoform

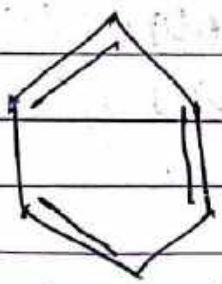
Tetrahalogen derivative
e.g.
CCl_4 – carbontetra chloride
CBr_4 – carbontetra bromide
CI_4 – carbon tetra iodide

☆ Aromatic organic compound

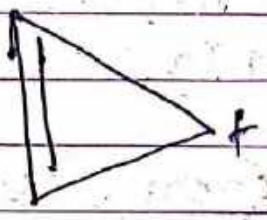
* concept for aromatic organic compound
→ Given organic compound should be cyclic/ closed chain.
→ carbon-atom should be sp^2 hybridised. Geometry should be triangular planar.
→ π-bond are in conjugated form
delocalized form
→ It obeys Huckle's rule
π-electron should be $(4n+2)\pi$

$(4n+2)\pi$
where $n = 0, 1, 2, 3, 4, \ldots$
$2\pi, 6\pi, 10\pi, 14\pi, 18\pi$

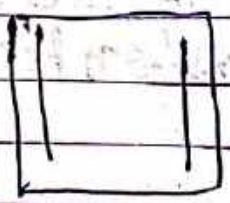
e.g.

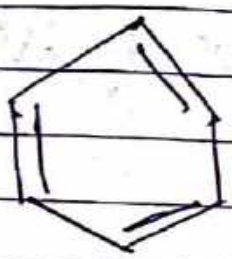


Aromatic

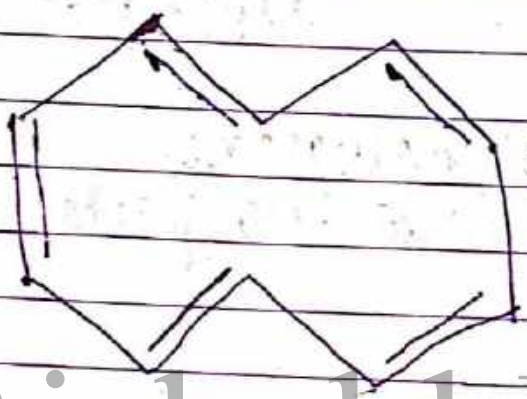


Aromatic

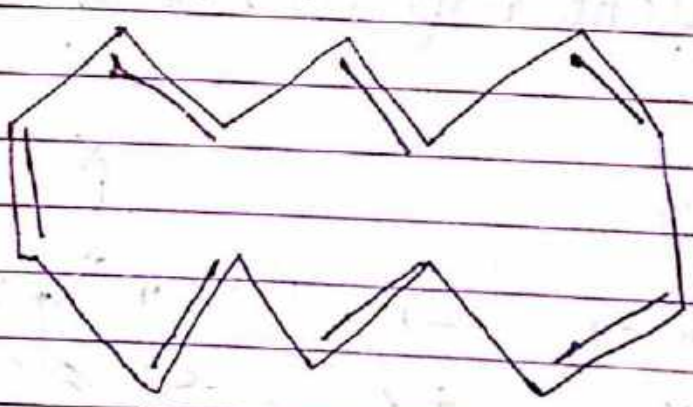




Aromatic compounds



Non-aromatic



Non-aromatic

8/04

Page No.: 17
Date: / /

✡ what is haloarene?

→ It is halogen derivative of arene (Benzene).

C_6H_6

arene or Benzene

$$C_6H_6 \xrightarrow[+X]{-H} C_6H_5X$$

arene

Haloarene - IUPAC system

Aryl halide - common system

✡ classification of haloarenes

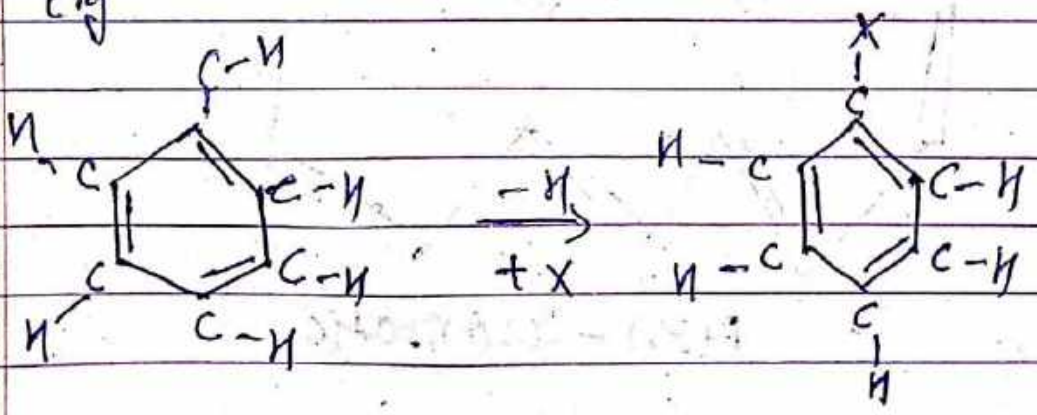
→ It is classified into two parts

a) Aryl halide

b) Aralkyl halide

a) Aryl halide → When halogen atom is direct bonded with benzene ring then it is known as 'aryl halide.

e.g

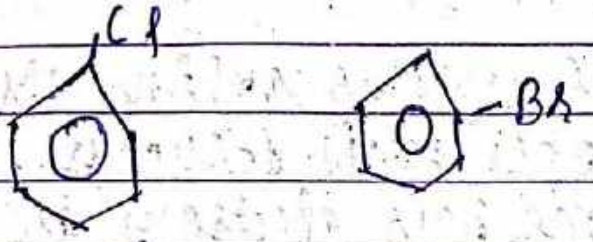
b) 

→ Aryl halide is further classified in two parts:

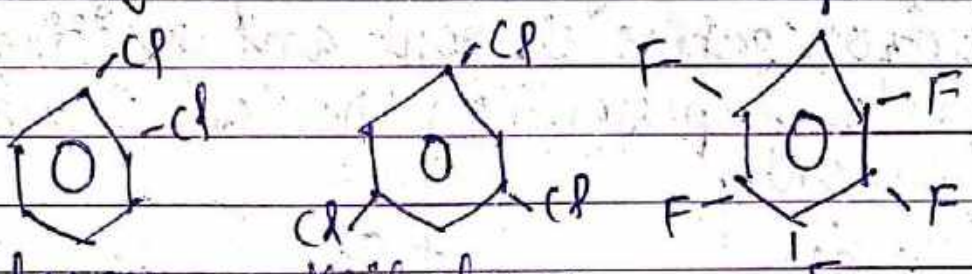
i) Monohalogen derivative

ii) polyhalogen derivative

i) Monohalogen derivative

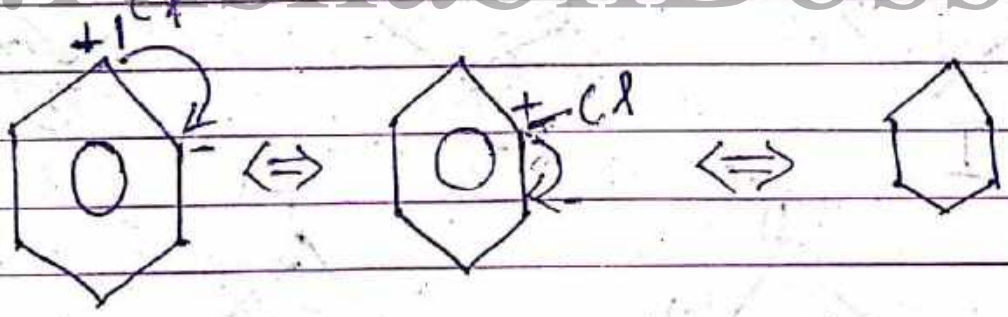
e.g 

ii) Polyhalogen derivative

eg 

Dihalogen Trihalogen Hexahalogen

* concept for ortho, meta and para

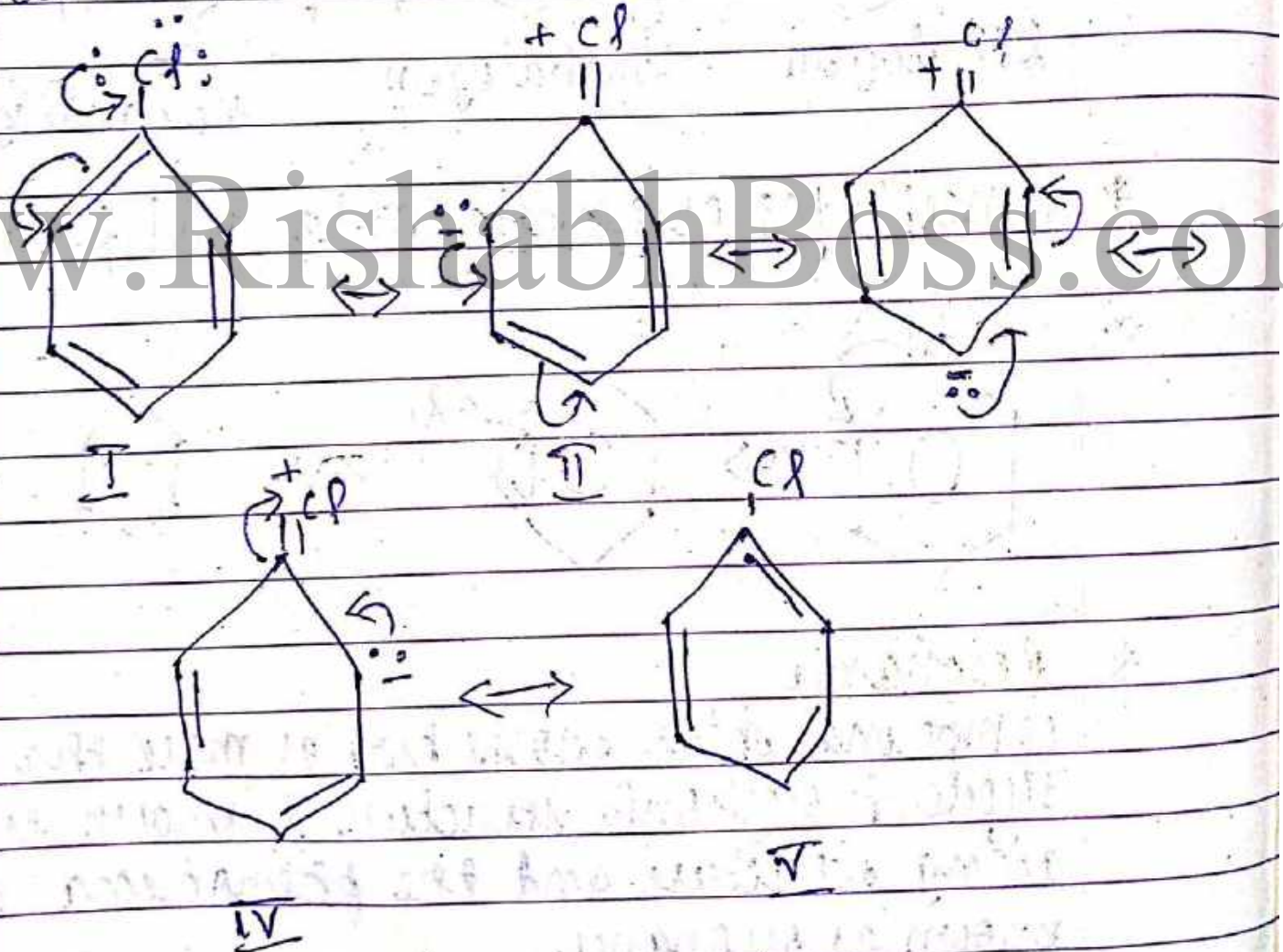


* Resonance

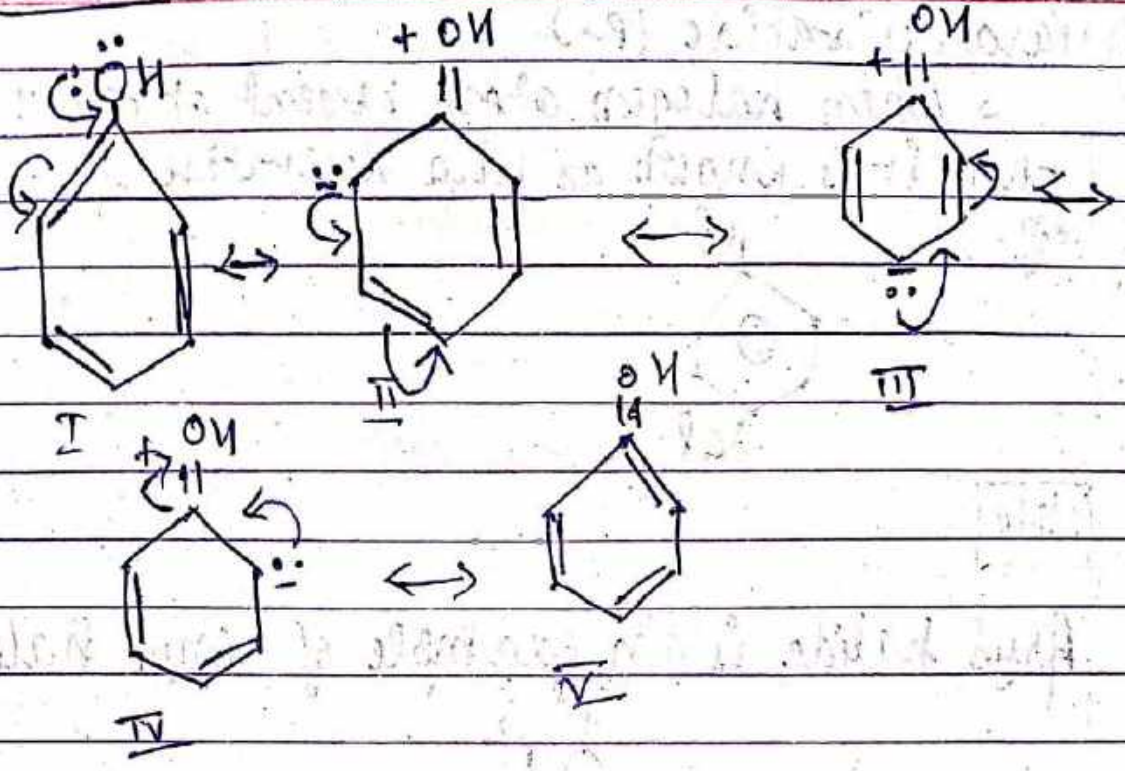
compound which shows two or more than two different electronic structure is known as resonating structure and the phenomena is known as resonance.

Some common points related with resonance

i) There is no change in the position of atom or group.
ii) Every Each and every resonanting structure should be be proper lewis structure.
iii) π-bond and lone pair electrons are delocalised.
iv) Negative charge should be present on the more electronegative element and positive charge (+) should be present on the less electronegative element.



8/04 **Phenol**



✡ Polyhalogen derivative

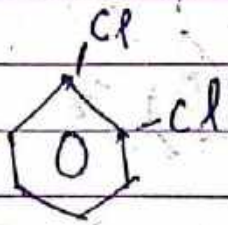
① Dihalogen derivative

It is classified into three parts

i) ortho derivative (O-)

→ when halogen atom present at the 2/6 position then it is known as ortho derivative

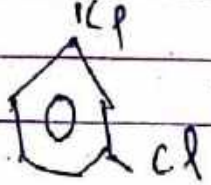
e.g



ii) Meta derivative (M-)

→ when halogen atom present at the 3/5 position then it is known as meta derivative.

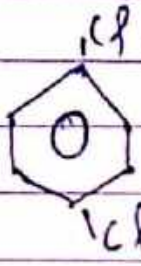
e.g



iii) Para derivative (p-)

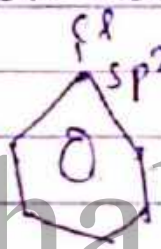
→ When halogen atom present at the 4 position then it is known as para derivative.

e.g.



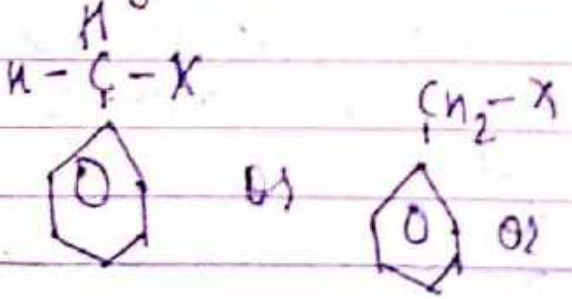
Note

Aryl halide is an example of vinyl halide



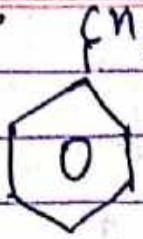
ii) Aralkyl halide → When halogen atom is bonded with side chain of benzene ring then it is known as aralkyl halide.

e.g

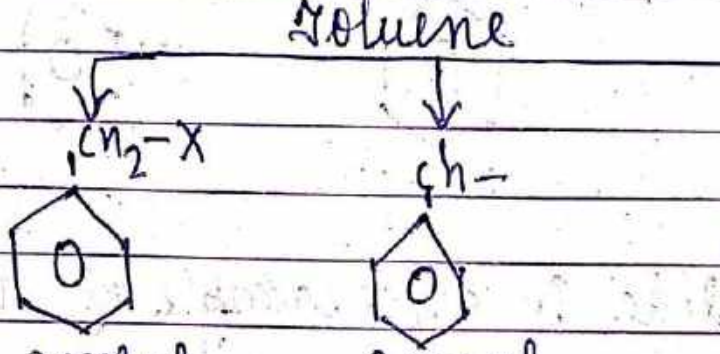


$C_6H_5CH_2-X$

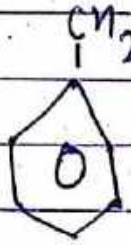
Concept

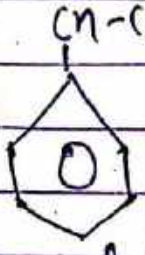


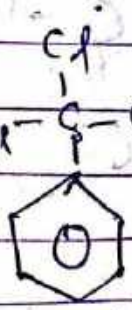
Toluene
Methyl benzene



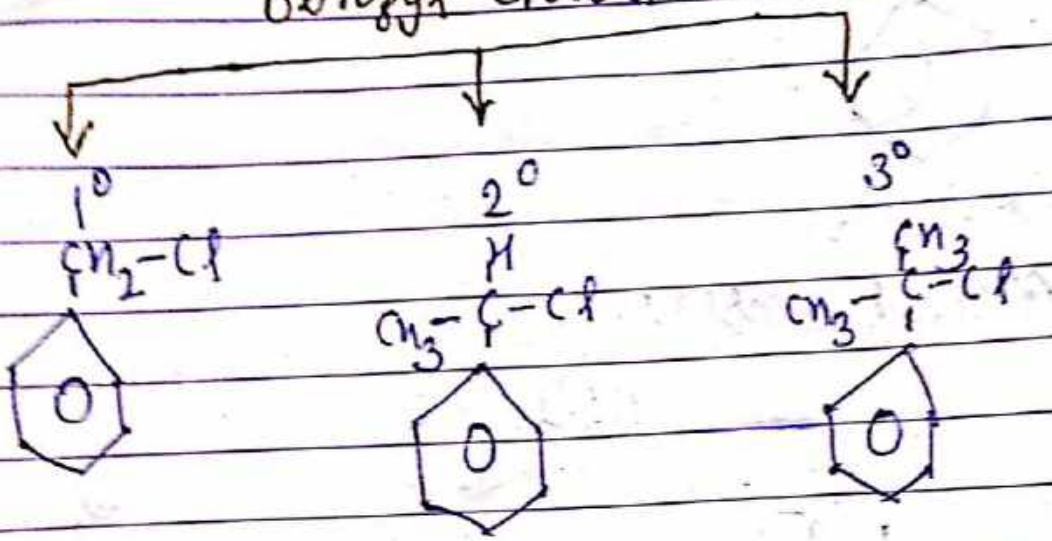
→ Alkyl halide is classified into three parts
i) Dihalogen Monohalogen derivative
ii) Dihalogen derivative
iii) Trihalogen derivative

i) e.g  → Benzyl chloride

ii) e.g 
Benzal dichloride

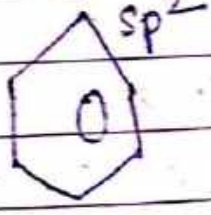
iii) e.g 
Benzo trichloride

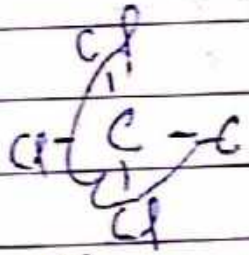
Benzyl chloride

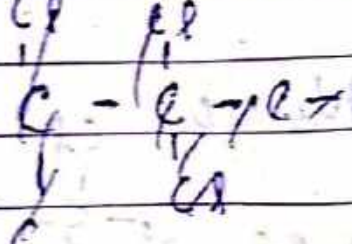


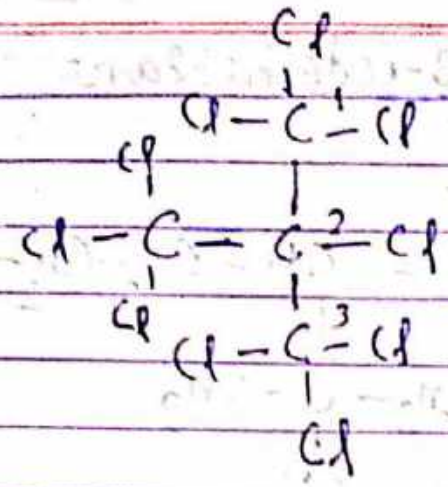
Note

Benzyl halide is an example of allylic halide.



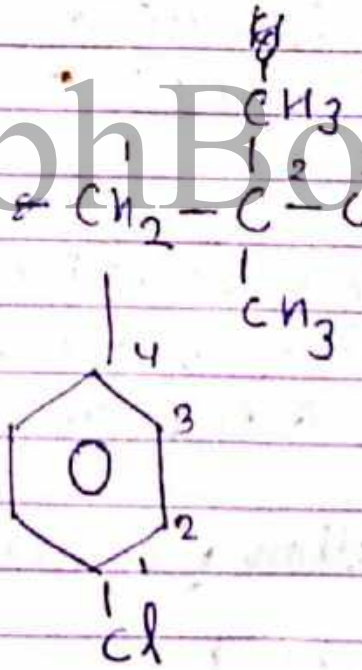






1,1,1,2,3,3,3-Heptachloro-2-(1,1,1-trichloro methyl) propane.

P-Cl $C_6H_4CH_2C(CH_3)_3$



1-Chloro-4-(2,2-dimethyl propyl) benzene

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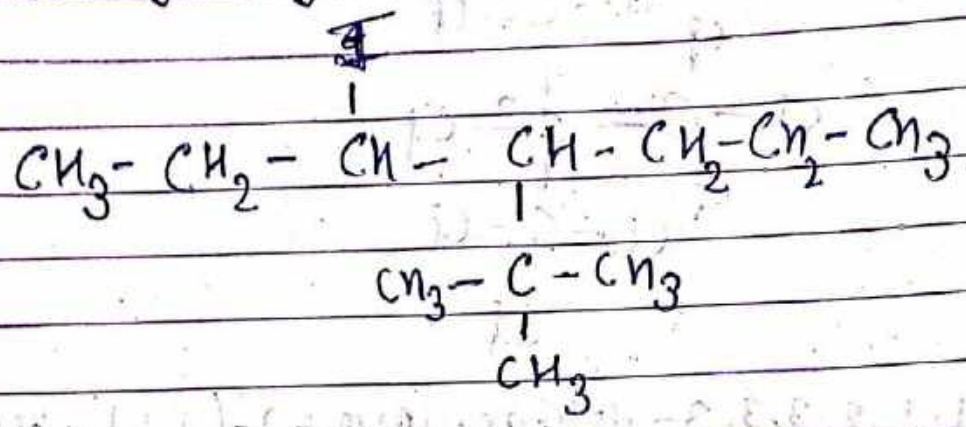
4-tertiary-butyl-3-iodo heptane



☆ Isomerism of haloalkane

Haloalkane shows three types of isomerism

i) chain isomerism
ii) position isomerism
iii) optical isomerism

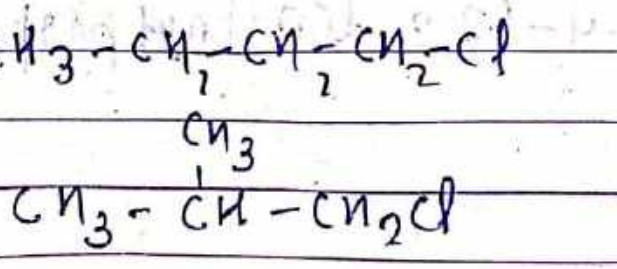
i) Chain isomerism

⇒ Such type of isomerism is due to different chain constituting by the carbon atom.

⇒ There is no change in the position of halogen atom

ii) Only skelton of carbon atoms are changed

e.g C_4H_9Cl



$C_5H_{11}Br$

$CH_3-CH_2-CH_2-CH_2-CH_2Br$ n-Propylbromide

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-Br$ Sec-propyl Bromide

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-Br$

(ii) Position isomerism

→ Such type of isomerism is due to different position occupied by the halogen atom in the same chain of carbon atom.

ex → $C_5H_{11}Br$

$CH_3-CH_2-CH_2-CH_2-CH_2-Br$

$CH_3-CH_2-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3$

$CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH-CH_3$

* Mixture of chain and position isomerism
→ Such type of isomerism is due to skeleton of carbon atoms are changed along with position of halogen atom.

ex → $C_5H_{11}Br$

$CH_3CH_2CH_2CH_2CH_2-Br$

$CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2-CH_2-Br$

$CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2-Br$

H.W Write all the possible isomers of $C_5H_{11}Br$ (write their IUPAC name) identify 1°, 2° and 3° haloalkane

→ $\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-Br$

1-Bromopentane (1°)

$CH_3-CH_2-\underset{\underset{Br}{|}}{C}H-CH_3$

2-Bromopentane (2°)

$CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_3$ $CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}H-CH_2-CH_3$

i) $CH_3-CH_2-CH_2-CH_2-CH_2-Br$

1-Bromopentane (1°)

ii) $CH_3-CH_2-CH_2-\underset{Br}{CH}-CH_3$

2°-Bromopentane (2°)

iii) $CH_3-CH_2-\underset{Br}{CH}-CH_2-CH_3$

3-Bromopentane (3°)

iv) $CH_3-\underset{CH_3}{CH}-CH_2-CH_2-Br$

→ 1-Bromo-3-methylbutane (1°)

v) $CH_3-\underset{CH_3}{CH}-\underset{Br}{CH}-CH_3$

→ 2-Bromo-3-methylbutane (2°)

vi) $CH_3-\underset{Br}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_3$

→ 2-bromo-2-methylbutane (3°)

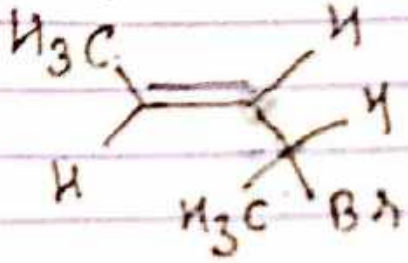
vii) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-Br$

→ 1-Bromo-2-methyl butane (1°)

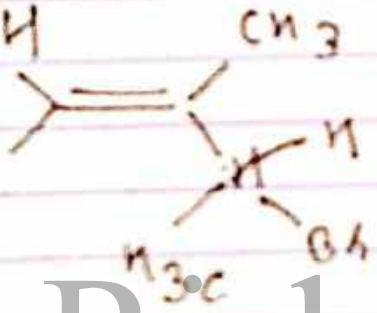
viii) $CH_3-\underset{\underset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-Br$

→ 1-Bromo-2,2-dimethyl propane (1°)

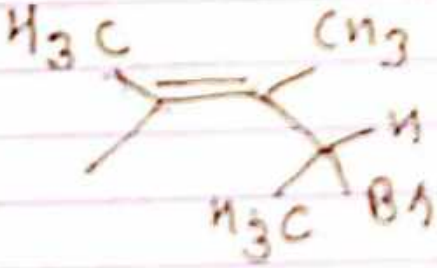
Example 10.2

i) 

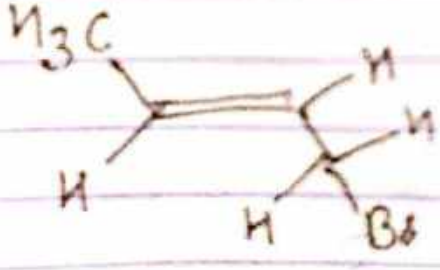
→ 4-Bromopent-2-ene.

ii) 

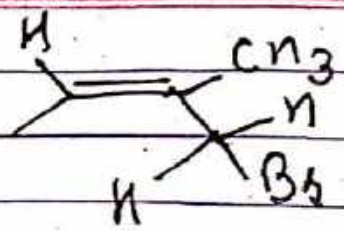
→ 4-Bromo-3-methylbut-1-ene

iii) 

→ 4-Bromo-3-methylpent-2-ene

iv) 

→ 4-Bromobut-2-ene

vi) 

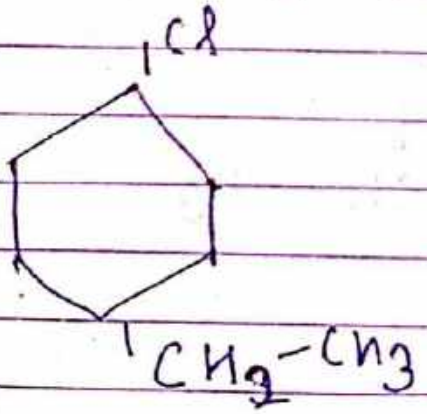
→ 3-Bromo-2-methylpropene

10.1 Write structures of the following compounds:

i) 2-chloro-3-methylpentane

→ $CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

ii) 1-chloro-4-ethylcyclohexane

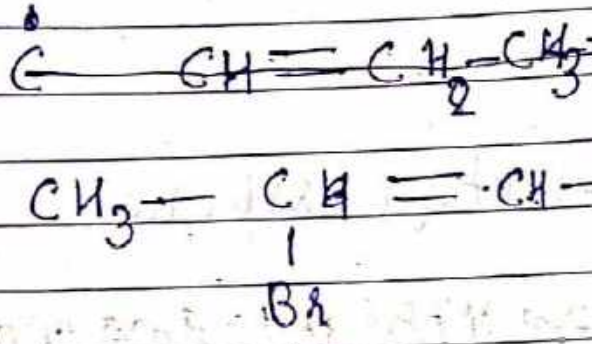
→ 

iii) 4-Tert-Butyl-3-iodoheptane

→ $CH_3-CH_2-\underset{I}{\underset{|}{CH}}-\underset{C(CH_3)_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

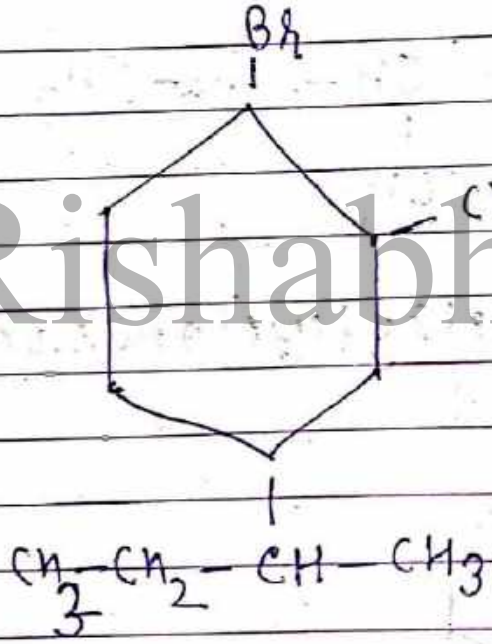
iv) 1,4-Dibromobut-2-ene

→



v) 1-Bromo-4-sec.-butyl-2-methyl benzene.

→



✡ Method of preparation
Haloalkane

1. From alkene
conversion of alkene to haloalkane

Alkene
→ It is due to presence of double bond between two carbon atoms.
⇒ There are two types of alkene.
a) Symmetrical alkene. → Same C-atoms around double bond.
ex → $CH_2 = CH_2$ (proper ethene)
b) unsymmetrical alkene → different no. of C-atoms around double bond
ex →
$CH_3 - CH = CH_2$ (propene)

✡✡ concept for π-bond

→ It is a weak bond.
→ π-bonds are delocalised
→ 2 σ-bond unite to form 1 π-bond
→ 1 π-bond breaks into to 2 σ-bond
→ 1 + and 1 -ve combine to form 1 π-bond

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* Shifting of π-bond

a) Symmetrical alkene

In this case, π-bond shifts in either direction

eg.

$$CH_2 = CH_2 \longrightarrow \overset{\oplus}{C}H_2 - \overset{\ominus}{C}H_2$$

$$CH_2 = CH_2 \longrightarrow \overset{\ominus}{C}H_2 - \overset{\oplus}{C}H_2$$

b) unsymmetrical alkene.

→ In this case, π-bond shifts in the direction of inductive effect.

ex→

$$CH_3 - CH = CH_2 \rightarrow CH_3 - \overset{\oplus}{C}H - \overset{\ominus}{C}H_2$$

Note

In organic reaction

Substrate + Reagent → Product

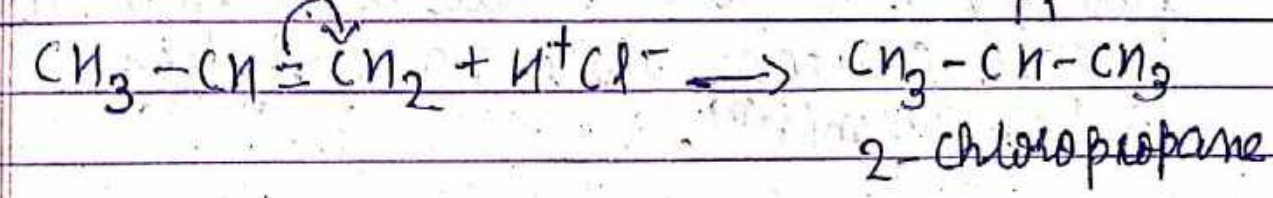
↓ ↓

alkene + Halogen acid → Halo alkane

Halogen acid (HX)

$H^+X^- = H^+Cl^-$ H^+Br^- H^+I^-

⇒ Above reaction is an example of electrophilic addition reaction. It completes into three step. It can be understood with the help of following example



$$CH_3-CH=CH_2 + H^+Cl^- \longrightarrow CH_3-\underset{Cl}{CH}-CH_3$$

2-chloropropane

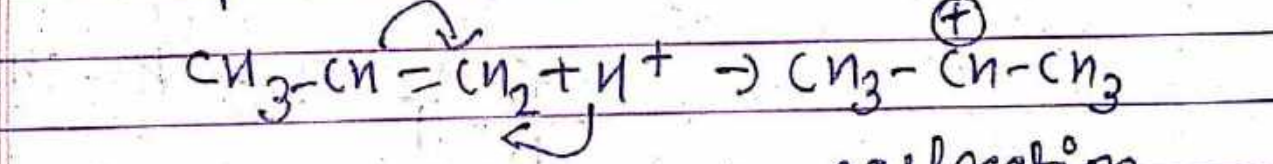
✡ Mechanism

Step I: Formation of electrophile

$$H-Cl \longrightarrow H^+ + Cl^-$$

Electrophile, Nucleophile

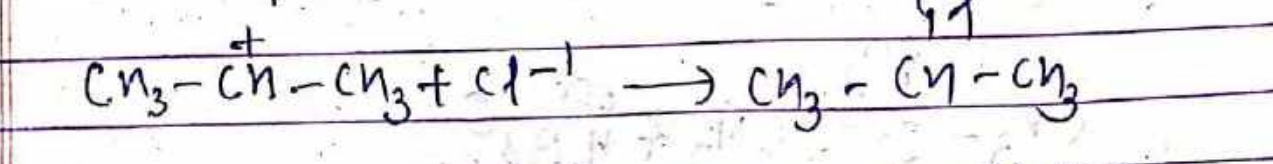
Step II: Electrophile attacks on substrate molecule



$$CH_3-CH=CH_2 + H^+ \rightarrow CH_3-\overset{\oplus}{C}H-CH_3$$

carbocation

Step III: Nucleophile attacks on carbocation



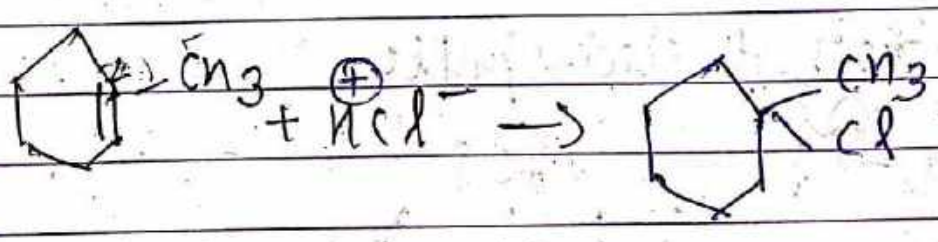
$$CH_3-\overset{+}{C}H-CH_3 + Cl^- \longrightarrow CH_3-\underset{Cl}{CH}-CH_3$$

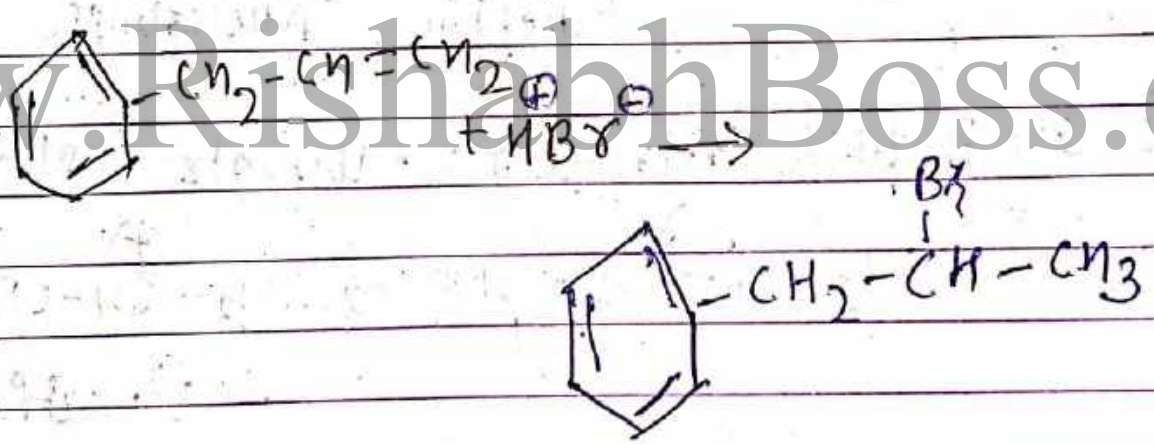
2-chloropropane

☆ Markonikoff's Markownikoff's rule

→ When an unsymmetrical reagent is added to the unsymmetrical alkene then -ve part of the reagent is added to that double bonded C-atom where no. of hydrogen atom is less or minm.

Gives product of the following reactions

1. 

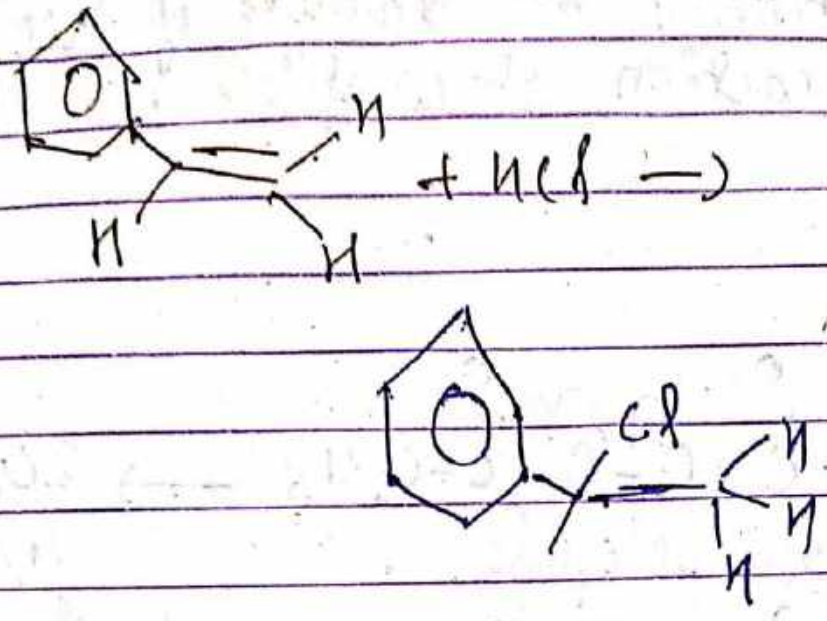
2. 

3. $(CH_3)_2C=CH_2 + HBr \rightarrow$

$$CH_3-\overset{CH_3}{\underset{|}{C}}=CH_2 + \overset{\oplus}{H}\overset{\ominus}{Br}$$

$$\Rightarrow CH_3-\overset{CH_3}{\underset{Br}{\overset{|}{\underset{|}{C}}}}-CH_3 = (CH_3)_2\overset{Br}{\overset{|}{C}}-CH_3$$

1.



* Ethene to Ethyl chloride

→ $CH_2 = CH_2 + HCl \longrightarrow CH_3 - CH_2 - Cl$

* Propene to chloropropane
* Markownikoff's rule with example

* Antimarkownikoff's rule (kharash effect)

→ When unsymmetrical reagent is added to unsymmetrical alkane in presence peroxide then -ve parts of reagent is added to that double bond carbon atom where no. of hydrogen atom is maximum.

ex:-

$CH_3 - CH = CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3 - CH_2 - CH_2 - Br$

substrate (↓) reagent (↓) Product (↑)

1-Bromo propane

→ Above reaction is an example of free radical addition reaction. It complete in three steps:-

Mechanism

Step1. $C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2C_6H_5-\overset{O}{\overset{\|}{C}}-O$

Benzoyl peropide — free radical

$C_6H_5-\overset{O}{\overset{\|}{C}}-O + H-Br \rightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-OH + Br$

Benzoic acid — new free radical

Step2. Br free radical attacks on substrate molecule

$CH_3-CH=CH_2 + Br \rightarrow$

→ $CH_3-\overset{Br}{CH}-CH_2$ (2° free radicals (less stable))

→ $CH_3-CH-CH_2-Br$ (2° free radicals (More stable))

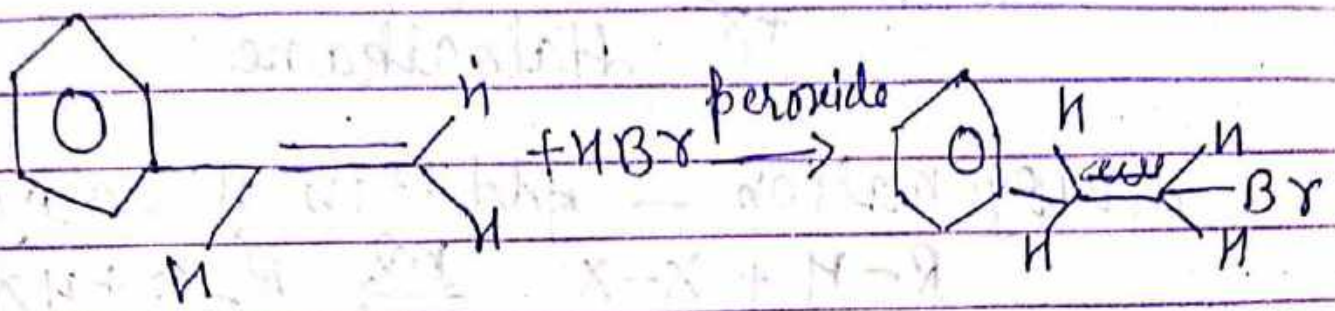
Step3. For motion of product

$CH_3-CH-CH_2-Br + H-Br \rightarrow CH_3-CH_2-CH_2-Br + Br$

1- Bromo propane

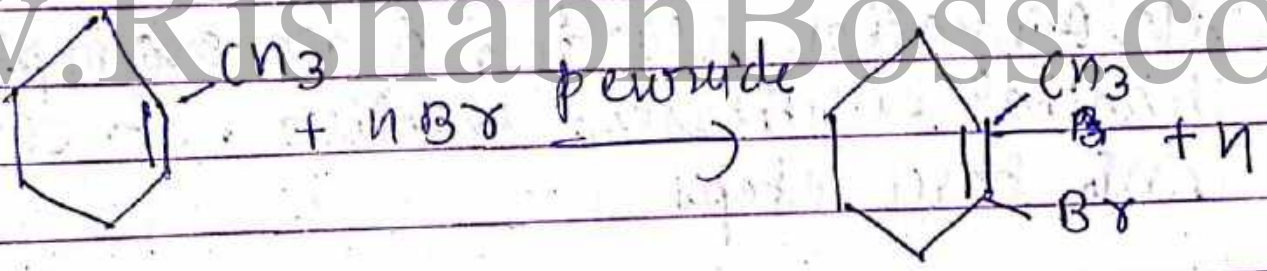
Q. Write product of the following compounds

i)

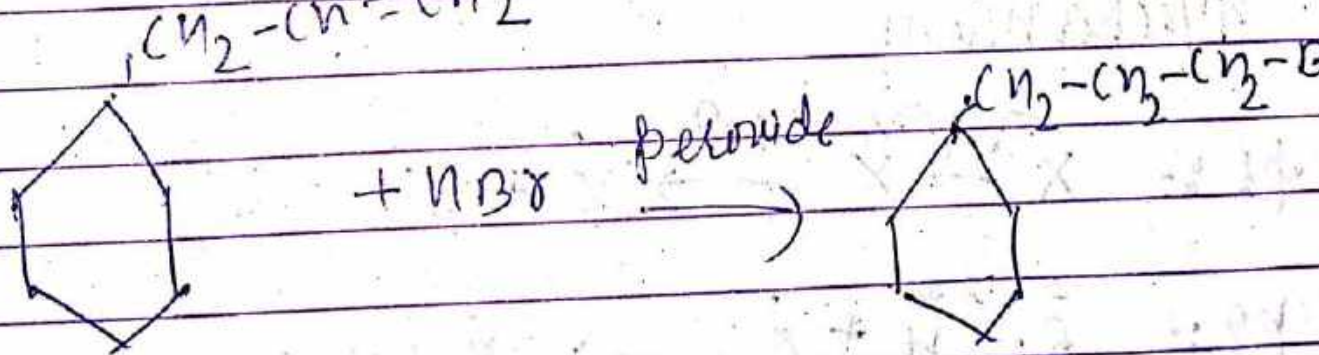


ii) $CH_3-CH_2-CH=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3-CH_2-CH_2-CH_2-Br$

iii)



iv)



Alkane to Haloalkane

$$R-H \xrightarrow[+X]{-H} R-X$$

Haloalkane

Halogenation — Addition of halogen

$$R-H + X-X \xrightarrow{h\nu} R-X + HX$$

→ By the halogenation of alkane in the presence of sunlight then it forms haloalkane.

→ Halogenation reaction is an example of free radical substitution reaction. It completes into three steps

Mechanism

Step 1 :- $X-X \xrightarrow{h\nu} \dot{X} + \dot{X}$

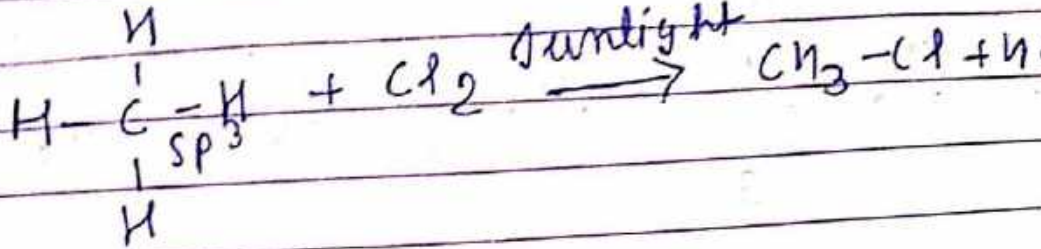
Step 2 :- $R-H + \dot{X} \longrightarrow \dot{R} + HX$

Alkyl free radical

Step 3 :- $\dot{R} + \dot{X} \longrightarrow R-X$

product

* Halogenation reaction is a chain reaction

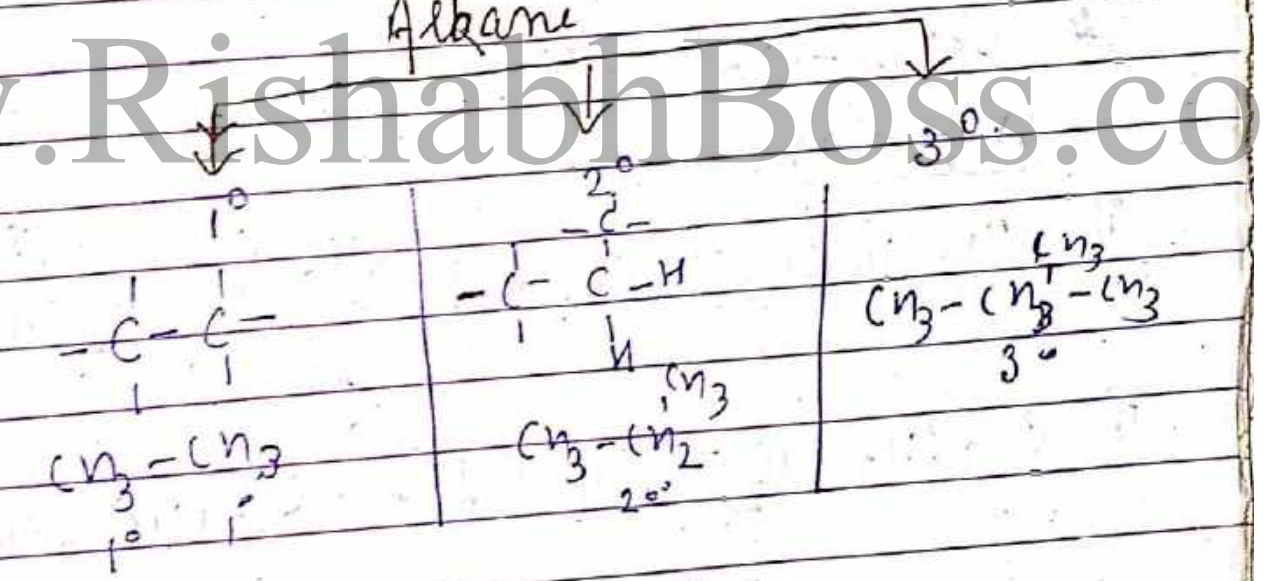


$$CH_3-Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

Alkane

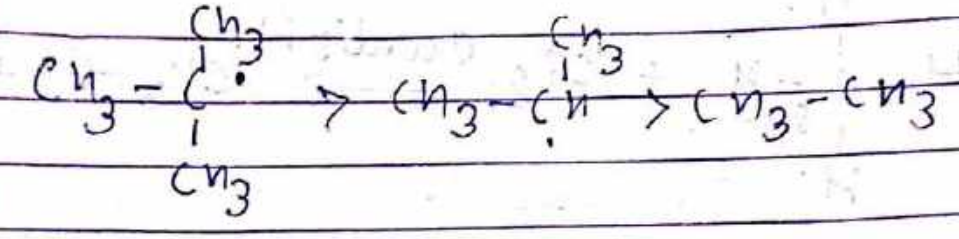


Order of displace of H-atom

$3^\circ C-H > 2^\circ C-H > 1^\circ C-H$

* Halogenation reaction is an example of free radical substitution reaction.

- Order of stability of free radical



* Write possible monohalogen derivative

→ $CH_3-CH_2-CH_3 + Cl_2 \xrightarrow{h\nu}$ a) $CH_3-CHCl-CH_3 + HCl$

b) $CH_3-CH_2-CH_2-Cl + HCl$

* $C_5H_{12} + Cl_2 \xrightarrow{h\nu}$

n-pentane

i) $CH_3CH_2CH_2CH_2CH_3 + Cl_2 \xrightarrow{h\nu} CH_3CH_2\underset{Cl}{CH}-CH_2-CH_3 + HCl$

ii) $CH_3CH_2CH_2CH_2CH_3 + Cl_2 \xrightarrow{h\nu} CH_3\underset{Cl}{CH}CH_2CH_2CH_3 + HCl$

iii) $C_5H_{12} + Cl_2 \xrightarrow{h\nu} CH_3CH_2CH_2CH_2CH_2-Cl + HCl$

2 & 0 butane (4 product)

i) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3 + Cl_2 \xrightarrow{h\nu} CH_3-\underset{Cl}{\underset{|}{C}}(CH_3)-CH_2-CH_3 + HCl$

ii) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3 + Cl_2 \xrightarrow{h\nu} CH_3-\underset{CH_3}{\underset{|}{C}}-CH_2-CH_2-Cl + HCl$

iii) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3 + Cl_2 \xrightarrow{h\nu} CH_3-CH(CH_3)-\underset{Cl}{\underset{|}{CH}}-CH_3 + HCl$

iv)

Neo-pentane [1 product]

$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 + Cl_2 \rightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{CH_2Cl}{\overset{|}{C}}}}-CH_3$$

Dihalogen derivative

$CH_3-CH_2-CH_3 + 2Cl_2 \xrightarrow{h\nu}$

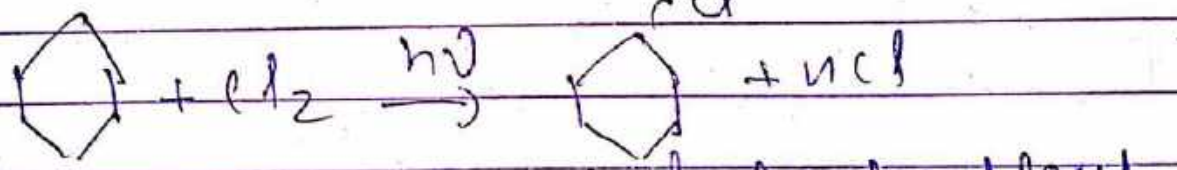
a) $CH_3-CH_2-CHCl_2 + 2HCl$

b) $CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3 + 2HCl$

c) $CH_3-\underset{\underset{Cl}{|}}{CH}-\overset{\overset{Cl}{|}}{CH_2} + 2HCl$

d) $\underset{\underset{Cl}{|}}{CH_2}-CH_2-\overset{\overset{Cl}{|}}{CH_2} + 2HCl$

$C_5H_{10} + Cl_2 \xrightarrow{h\nu} C_5H_9Cl + HCl$



cyclopentane — cyclo pentyl chloride

sp^3 (-C) — 25%.

sp^2 (=C) — 33.33%.

sp (≡C) — 50%.

Maximum the S-character more will be electronegativity

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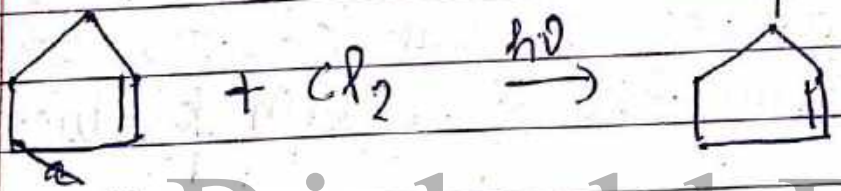
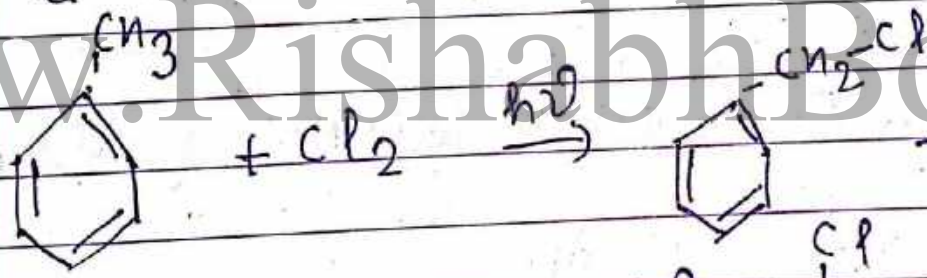
* Allylic substitution
→ When H-atom is displaced from the sp^3 hybridised C-atom and next C-atom is sp^2 hybridised then it is known as allylic substitution.

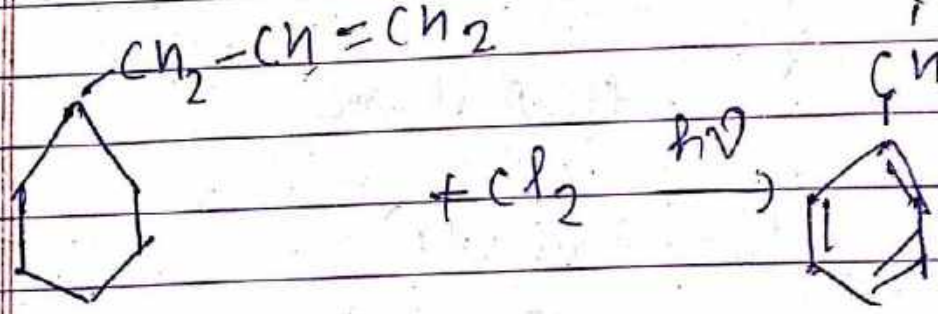
• Order of displacement
sp^3 C-H > sp^2 C-H > sp C-H

* Give product

i) 

ii) 

iii) $CH_3-CH=CH_2 + Cl_2 \xrightarrow{h\nu} \underset{Cl}{CH_2}-CH=CH_2 + HCl$

iv) 

✡ Formation of vicinal dihalide

Eg. →

$$CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} \underset{\text{Ethylene dibromide}}{CH_2(Br)-CH_2(Br)}$$

Eg →

$$CH_3-CH=CH_2 + Br_2 \xrightarrow{CCl_4} \underset{\text{propylene dibromide}}{CH_3-CH(Br)-CH_2(Br)}$$

By the addition of halogen in alkene in the presence of CCl_4 then it forms vicinal dihalide.

In this reaction 1 π-bond breaks into 2 σ-bond and shifts at the adjacent C-atom where halogen atom combines to form product

✡ Alcohol to Haloalkane

Alcohol → It is hydroxy derivative of haloalkane

$$\underset{\text{Alkane}}{R-H} \xrightarrow[+OH]{-H} \underset{\text{Alcohol}}{R-OH}$$

$$\underset{\text{Alcohol}}{R-OH} \xrightarrow[+X]{-OH} \underset{\text{Haloalkane}}{R-X}$$

(1) By using halogen acid (HX)

$$\overset{+}{H}X^- = \overset{+}{H}Cl^- \quad \overset{+}{H}Br^- \quad \overset{+}{H}I^-$$

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order of nucleophilic power

$Cl^- < Br^- < I^-$

Pattern

$$R-OH + H-X \xrightarrow{\text{D.A}} R-X + H_2O$$

Alcohol — Halogen acid — Haloalkane

☆ Mechanism

Step 1 $H-\ddot{X} \longrightarrow H^+ + \ddot{X}^-$

Step 2 $R-\ddot{O}-H + H^+ \longrightarrow R-\overset{\oplus}{O}(H)-H \longrightarrow R^+ + H_2O$ (Nucleophile)

Step 3. $R^+ + X^- \rightarrow R-X$

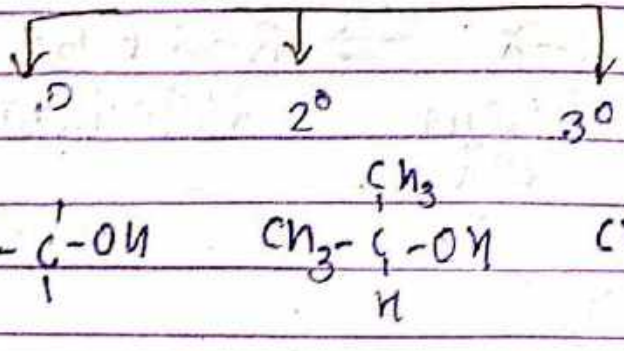
HX	D.A (Dehydrating agent)
HCl	anhydrous $ZnCl_2$
HBr	conc. H_2SO_4
HI	H_3PO_4 (phosphoric acid)

☆ Ethanol to ethyl chloride

$$CH_3-CH_2-OH + HCl \xrightarrow[ZnCl_2]{\text{anhydrous}} CH_3CH_2Cl + H_2O$$

When alcohol is treated with halogen acid in the presence of dehydrating agent is then known as haloalkane is formed.

Alcohol

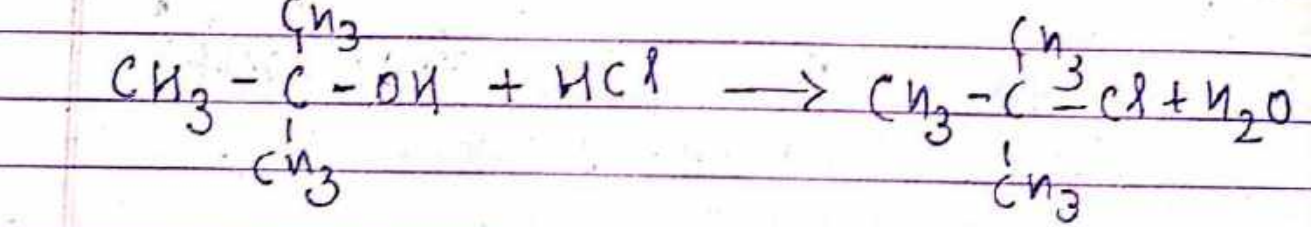


* Order of reactivity

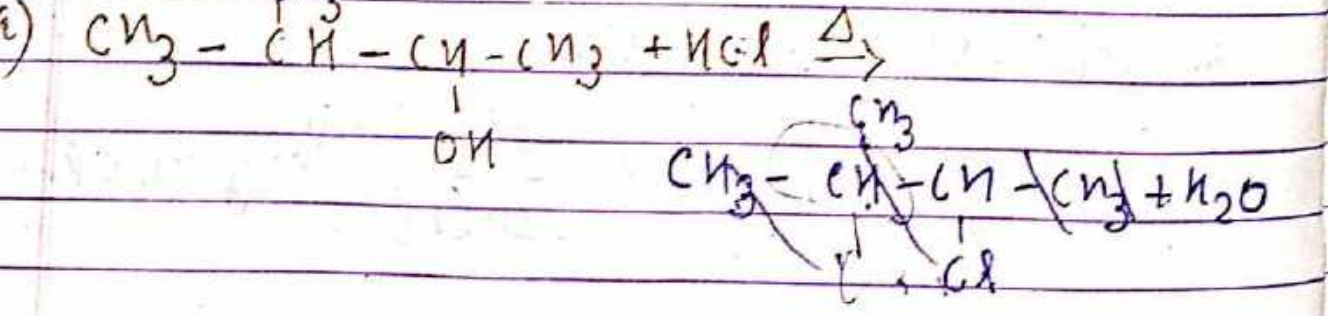
1° alcohol < 2° alcohol < 3° alcohol

It is due to C-OH bond is more polar in case 3° alcohol due to +I effect.

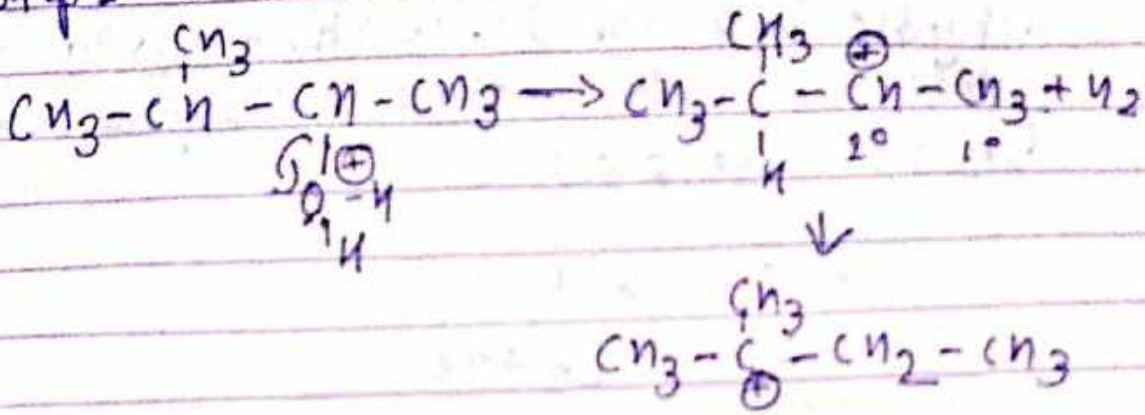
* Tert-butyl alcohol to Tert-butyl chloride



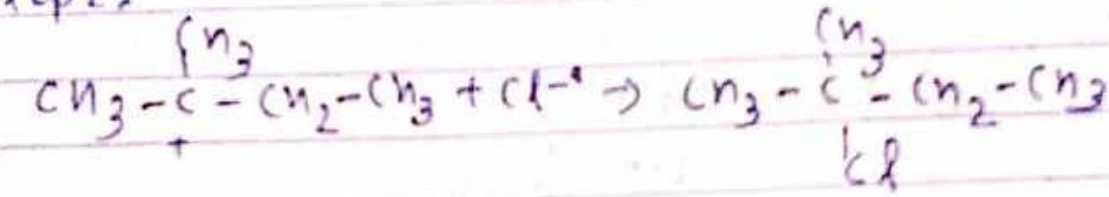
* Complete the reaction

a) 

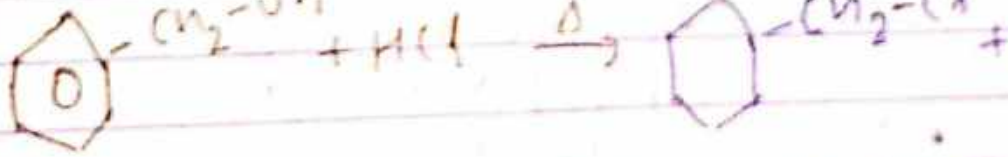
Step 1.



Step 2.



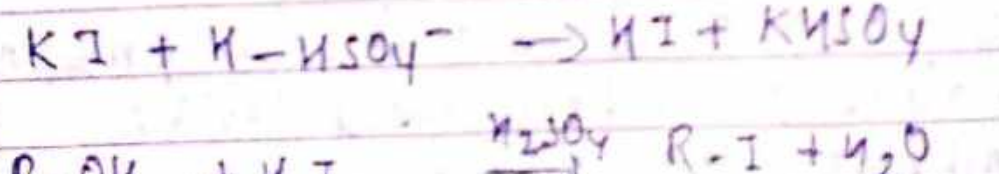
b) 

c) 

Q. Why is sulphuric acid not used during the reaction of alcohol with KI.

LECTURER

→



-> H_2SO_4 act as oxidising agent along with dehydrating agent. So that H_2SO_4 oxidises iodide ion into iodine. Therefore, reaction does not take place

$$H-I \rightarrow H^+ + I^-$$
$$2I^- \rightarrow I_2 + 2e$$

2. Alcohol to haloalkane using phosphorus halide

P → Tricovalency
Pentacovalency

Phosphorous combines with halogen to forms two types of halide

a) trihalide
b) pentahalide

=) $P_4 + 6X_2 \rightarrow 4PX_3$
phosphorus trihalide

=) $P_4 + 10X_2 \rightarrow 4PX_5$
phosphorus pentahalide

* using trihalide

When alcohol is treated with phosphorous trihalide then it forms haloalkane and phosphorous acid as biproduct

$$3R-OH + PX_3 \rightarrow 3R-X + H_3PO_3$$
Alcohol Haloalkane Phosphorous acid

$3CH_3-CH_2-OH + PCl_3 \rightarrow$

$3CH_3-CH_2-Cl + H_3PO_3$

* using phosphorous penta-halide

$PX_5 = PCl_5, PBr_5, PI_5$

PCl_5 - phosphorous pentachloride

$$\underset{\text{Alcohol}}{R-OH} + PCl_5 \rightarrow \underset{\text{Alkyl chloride}}{R-Cl} + \underset{\text{Phosphorous oxychloride}}{POCl_3} + HCl$$

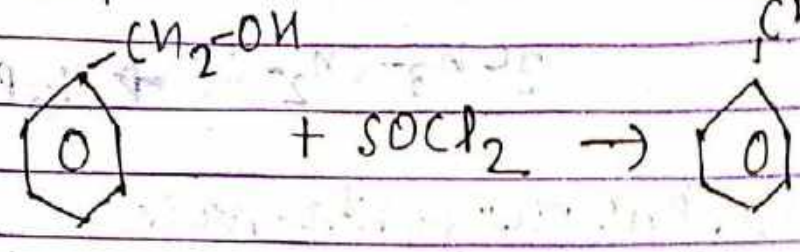
$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + PCl_5 \rightarrow \underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl} + POCl_3 + HCl$$

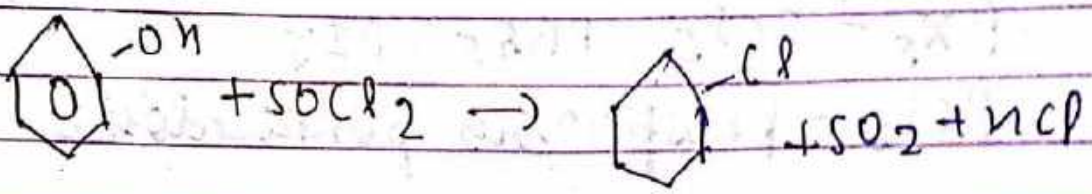
* using thionyl chloride ($SOCl_2$)

$$\underset{\text{Alcohol}}{R-OH} + SOCl_2 \rightarrow \underset{\text{Alkyl chloride}}{R-Cl} + SO_2 + HCl$$

Above reaction is good method for the preparation of alkyl chloride because SO_2 and HCl are in gaseous phase and it escape from the product so that pure alkyl chloride is formed.

* complete the reaction

i) 

ii) 

iii) $CH_3-CH_2-OH + SOCl_2 \rightarrow CH_3-CH_2-Cl + SO_2 + HCl$

* Halide exchange

$X + e^- \rightarrow X^-$

Halogen Halide

$X^- = F^-, Cl^-, Br^-, I^-$

Order of Nucleophile

$F^- < Cl^- < Br^- < I^-$

a) Finklestein reaction

$RX + NaI \rightarrow R-I + NaX$

($X = Cl/Br$) Iodoalkane

When chloro/bromo alkane is treated with sodium iodide (NaI) then iodoalkane is formed. It is known as finkelstein reaction

* complete the reaction

i) $CH_3-CH_2-Cl + NaI \rightarrow CH_3-CH_2-I + NaCl$

ii) $CH_3-CH_2-Br + NaI \rightarrow CH_3-CH_2-I + NaBr$

b) Swarts Reaction

$$R-X + AgF \rightarrow R-F + AgX$$

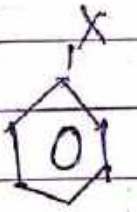
X = Cl/Br Fluoroalkane

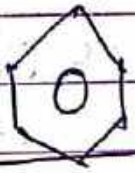
When chloro or bromo alkane is treated with silver fluoride (AgF) then it forms fluoroalkane. It is known as Swarts reaction.

Ex:-

$CH_3-CH_2-Cl + AgF \rightarrow CH_3-CH_2-F + AgCl$

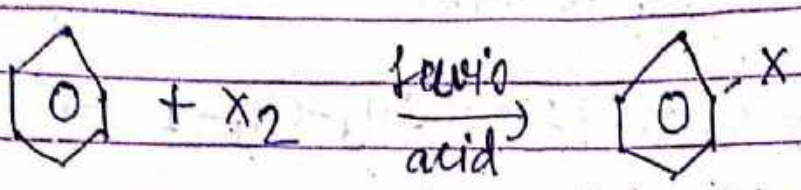
Haloarenes

Aryl halide – 

Aralkyl halide – 

* Method of preparation of aryl halide

⇒ By the halogenation of arene in the presence of lewis acid, aryl halide is formed

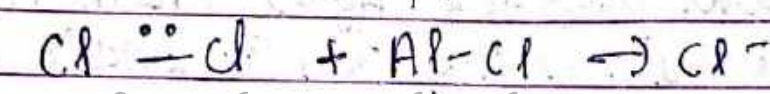


Aryl halide or Halobenzene

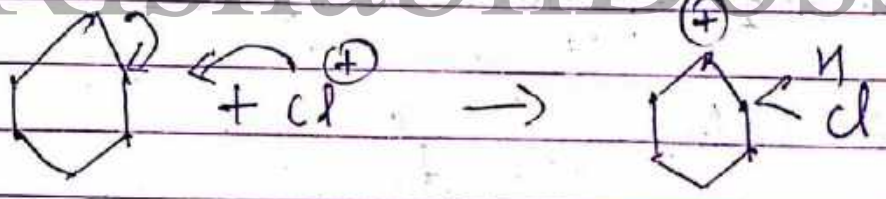
Above reaction is an example of electrophilic substitution reaction. It completes into three steps. It can be understood as.

Mechanism

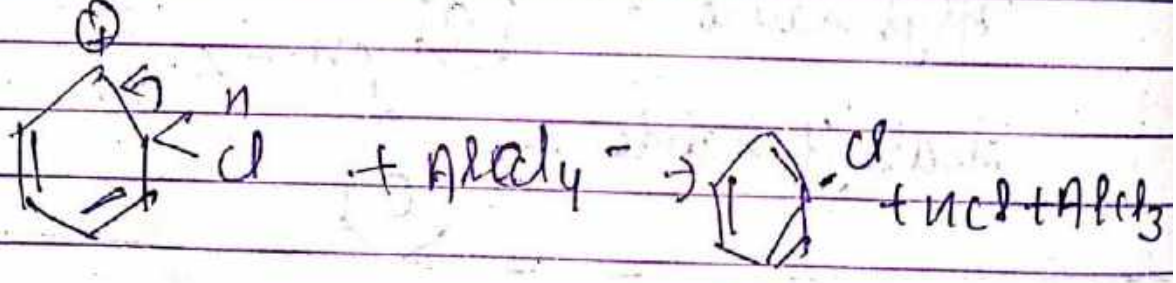
Steps



Step 2.



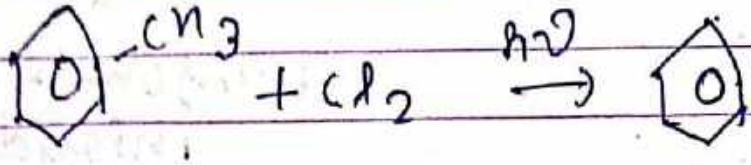
Step 3.



Chlorobenzene

* Formation of aralkyl halide

By the halogenation of alkyl benzene in the presence of sunlight arakyl halide is formed.

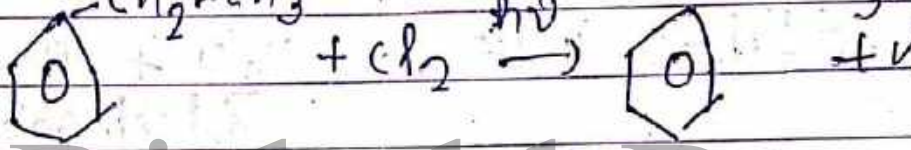


Toluene

Benzyl chloride
(Allylic halide)

order of displacement of H-atoms

$3^\circ C-H > 2^\circ C-H > 1^\circ C-H, Cl$

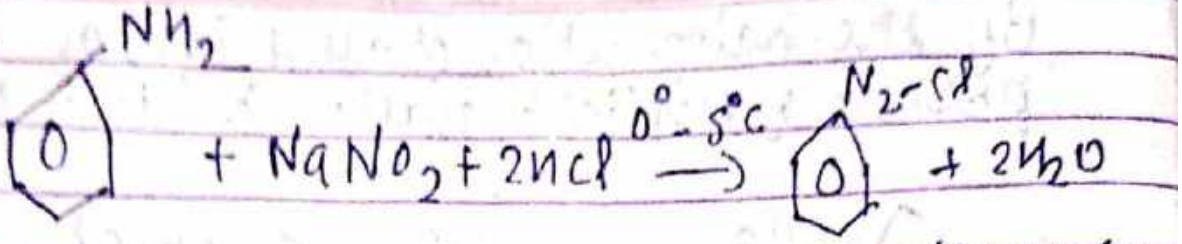


1-Chloro-1-phenylethane

* Aniline to aryl halide
It takes place in two steps

Step 1. Aniline to Diazonium salt
Step 2. Diazonium salt to aryl halide

1- Aniline to Diazonium salt
→ When aniline is treated with sodium nitrite ($NaNO_2$) and HCl at 0-5°C temperature then it form diazonium salt.



Benzene diazonium chloride (diazonium salt)

Mechanism

Step 1 $NaNO_2 + H^+Cl^- \rightarrow NaCl + HNO_2$

Nitrous acid

$H-O-N=O + H^+ \rightarrow H_2O + N^+=O$

Electrophile

Step 2. $Ar-\ddot{N}H_2 + N^+=O \rightarrow Ar-\overset{H}{\underset{|}{N}}-N=O \rightarrow Ar-N-N^+-OH$

$Ar-N-N^+-OH \rightarrow Ar-N=N-OH + H^+$

Step 3. $Ar-N=N-OH + HCl \rightarrow Ar-N=N-Cl + H_2O$

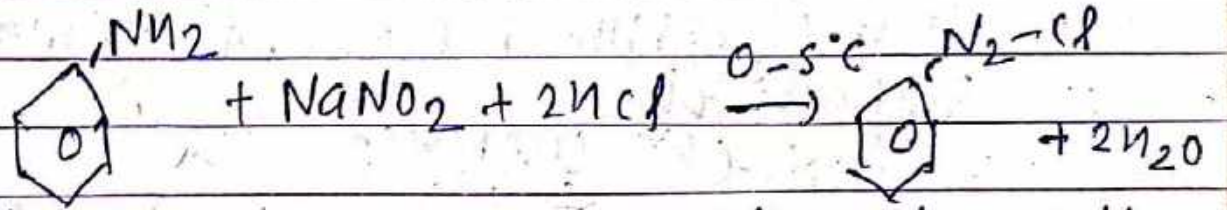
$-N_2-Cl$

Benzendiazonium chloride

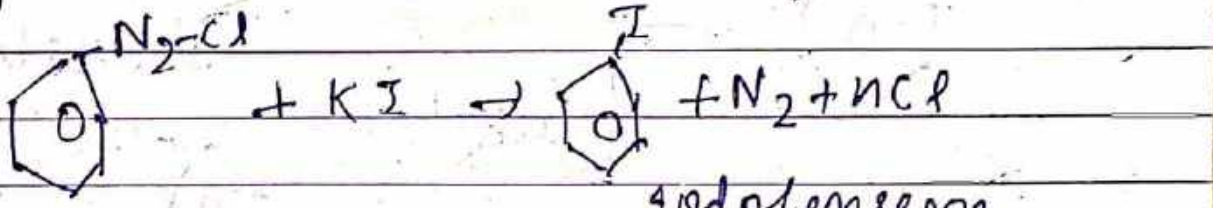
Step II Diazonium salt to Aryl halide

* Formation of iodobenzene

Aniline to iodobenzene

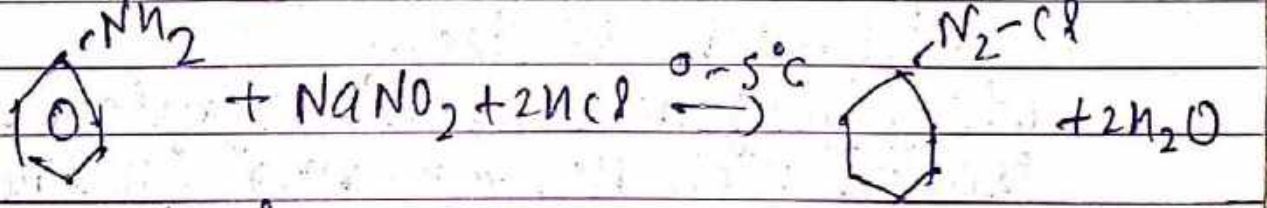


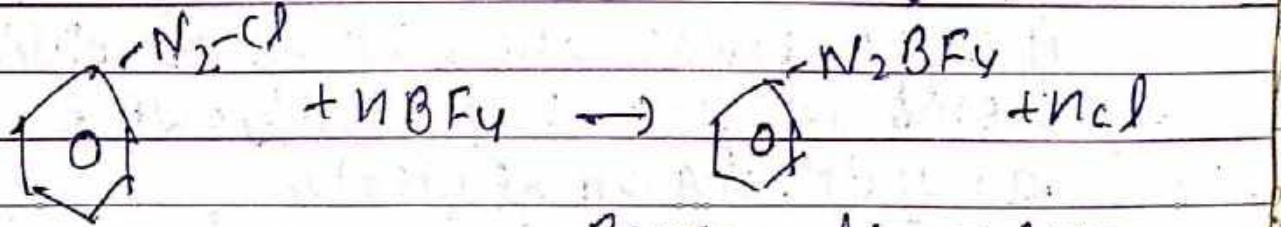
Aniline Diazonium salt



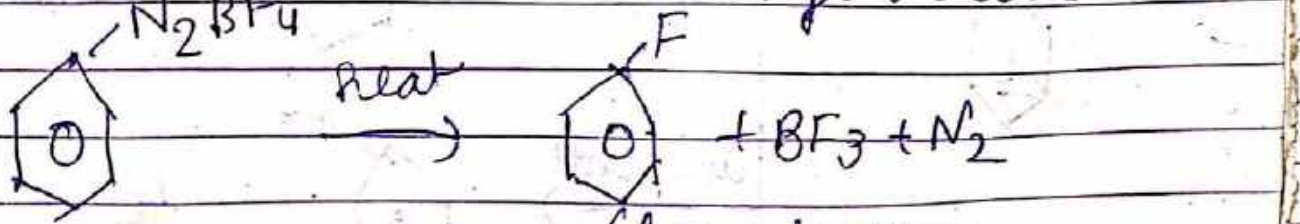
Iodobenzene

* Aniline to fluorobenzene





Benzene diazonium fluoroborate

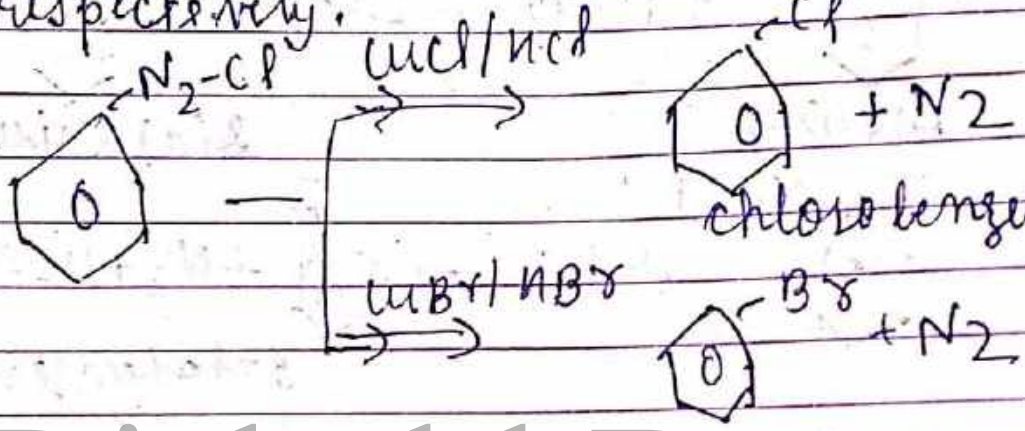


Fluorobenzene

✡ Formation of chloro and bromo benzene

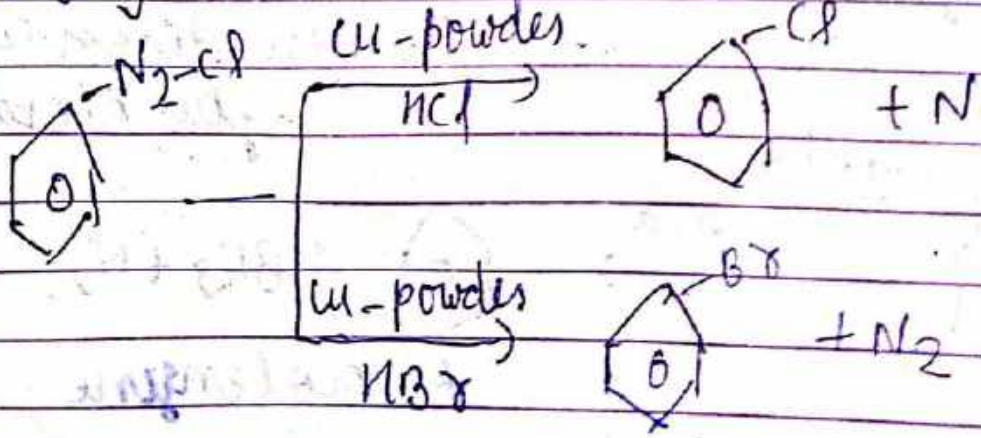
a) Sandmeyes reaction

⇒ When benzene diazonium chloride is treated with CuCl/HCl and CuBr/HBr then it forms chloro and bromo benzene respectively.



b) Gattermann Reactions

⇒ When benzene diazonium chloride is treated with HCl and HBr in the presence of coppes powdes then it forms chloro and bromo benzene respectively. It is known as Gattermann reactions.



✱ Physical properties of Haloalkanes and haloarenes

1. Physical state → lower member of haloalkane like CH_3Cl, CH_3Br, C_2H_5Cl etc. are found in gaseous phase.
But higher member of haloalkane are found in liquid / solid phase.

2. Solubility → Haloalkane is polar in nature but it is insoluble in water. It is due to alkyl group is hydrophobic in nature and it does not form hydrogen bond.

lower member of haloalkanes are partially soluble in water.
Haloalkanes are completely soluble in non-polar solvent like benzene, ethers, CCl_4 etc.

3. Melting and boiling point

$$R-H \xrightarrow[+X]{-H} R-X$$

Alkane — Non-polar (weak-vandaal force)

Haloalkane — polar (dipole-dipole interaction)

The melting and boiling point of haloalkane is maximum than comparable molecular mass of alkane. It is due to dipole-dipole interaction takes place in haloalkane while weak vandaal force takes place in alkane.

* The M.P and B.P of haloalkane depends upon molecular mass and surface area.

→ If the molecular mass of haloalkane increases then their M.P and B.P also increases.

ex:- $CH_3Cl < CH_3-CH_2-Cl < CH_3-CH_2-CH_2-Cl$

$CH_3Cl < CH_3Br < CH_3I$

$-CH_3-Cl < CH_2Cl_2 < CHCl_3 < CCl_4$

→ In case of isomeric haloalkane when the branching increases then M.P and B.P decreases. It is due to surface area decreases as result vandaal force of attraction decreases.

ex:- C_3H_7Cl — Propyl chloride

$CH_3-CH_2-CH_2-Cl$ — n-propyl chloride

$CH_3-\underset{Cl}{CH}-CH_3$ — Isopropyl chloride

$CH_3-CH_2-CH_2-CH_2-Cl > CH_3-\underset{CH_3}{CH}-CH_2-Cl > CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl$

* Arrange in increasing b.p

i) Bromomethane, Bromoform, chloromethane, Dibromomethane

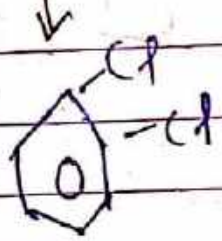
→ CH_3Br ; CBr_3 , CH_3Cl , CH_2Br_2

$CBr_3 > CH_2Br_2 > CH_3Br > CH_3Cl$

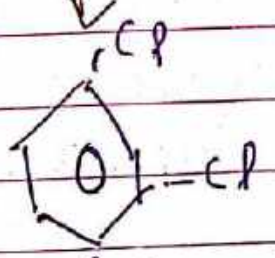
ii) 1-Chloropropane, Isopropyl chloride, 1-Chloro-butane

→ $CH_3-CH_2-CH_2Cl$ (II) $CH_3-\underset{Cl}{CH}-CH_3$ (I) $CH_3-CH_2-CH_2-CH_2Cl$ (III)

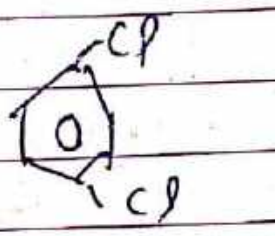
Dihaloarenes



O-isomes



m-isomes



p-isomes

The b.p of dihaloarenes are approx same but the M.P of p-isomes is maximum than O and m-isomes.

It is due to p-isomes is symmetrical in nature It fits into crystal lattice and form closed-packed structure so that p-isomes has

has max m.p than o and m- isomes

* chemical properties of haloalkane and haloarens

→ Haloalkanes shows four types of chemical reactions :-

i) SN reaction - Nucleophilic substitution reaction
ii) Elimination reaction
iii) Reaction with metal
iv) Reduction

i) SN reaction

→ Those chemical reactions in which atom or group of the substrate molecule is displaced by the atom or group of the reagent molecule then it is known as substitution reaction.

If the substitution reaction takes place by the nucleophile then it is known as nucleophilic substitution reaction (SN reaction).

Substrate + Reagent → Product

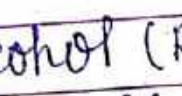
$R-X + NH^- \rightarrow \underset{\text{Product}}{R-NH^-} + X^-$

* Nucleophile
Nucleus loving species are known as nucleophile.

* Identification
→ Negatively charged species are known as nucleophile
ex → $-OH$, $-OR$, CN^-, NO_2^-, Cl^-, Br^-, F^-, I^-

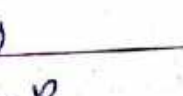
→ Neutral molecule in which central atom has lone pair electron act as nucleophile.
ex.- Water (H_2O), Ammonia (NH_3)

Alcohol (R-OH)



Ethes

Amine



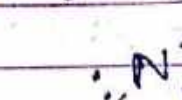
→ All lewis base (L.P donor) act as nucleophile

* Ambident nucleophile

→ The nucleophile which having two different donor site act as ambident nucleophile.

$-NO_2^-$ is an example of ambident nucleophile

donor site (Nitrite)



Donor Nitro

CN^- is ambident nucleophile
Cyanide - carbon donor site
Isocyanide - Nitrogen donor site

1. Displacement by hydroxide ion (-OH)

Haloalkane to alcohol - conversion
Substrate - Alkyl halide (R-X)
Reagent - aqueous NaOH / KOH

$$R-X + (aq.)\ NaOH \longrightarrow R-OH + NaX$$
Alkyl halide → Alcohol

i) Ethyl bromide to ethanol

$$CH_3-CH_2Br + NaOH(aq.) \longrightarrow CH_3-CH_2-OH + NaBr$$

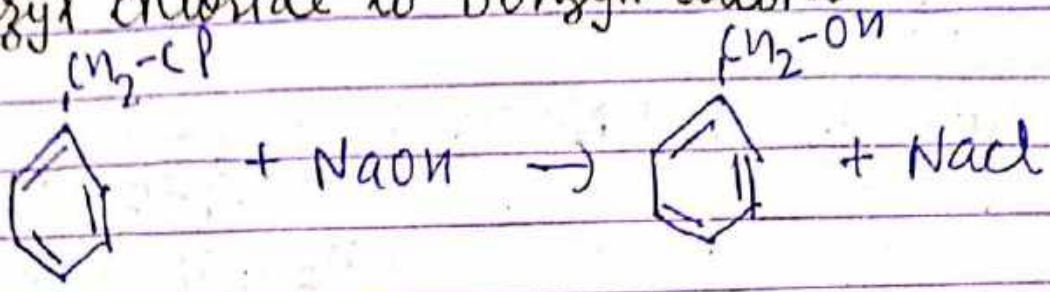
ii) Isopropyl chloride to isopropyl alcohol

$$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3 + NaOH\ (aq.) \longrightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 + NaCl$$

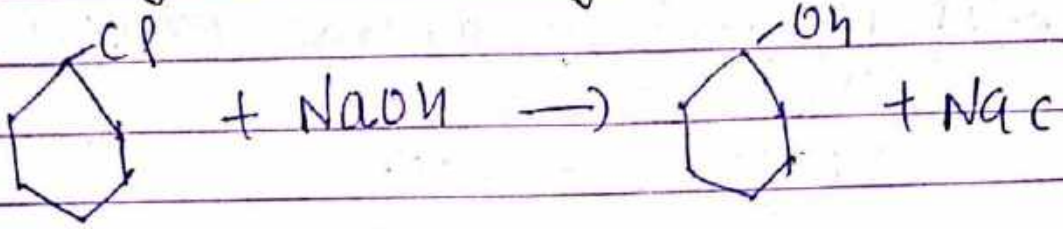
iii) Tert butyl chloride to tert butyl alcohol

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Cl + NaOH \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH + NaCl$$

iv) Benzyl chloride to Benzyl alcohol



v) Cyclohexyl chloride to cyclohexanol



2. Displacement by alkoxide ion

Substrate - R-X

Reagent - sodium Alkaoxide (NaOR)

conversion

Haloalkane to Ethers

$$R-X + NaOR \rightarrow R-O-R + NaX$$

Haloalkane — Ethers

i) Ethyl bromide to methoxy ethane

$$CH_3-CH_2-Br + NaOCH_3 \rightarrow CH_3-CH_2-O-CH_3 + NaBr$$

ii) Isopropyl chloride to 2-methoxy propane

$$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 + NaO-CH_3 \rightarrow CH_3-\underset{\underset{OCH_3}{|}}{CH}-CH_3 + NaCl$$

iii) Ethyl chloride to ethoxy ethane

$$CH_3-CH_2-Cl + NaO-CH_2-CH_3 \rightarrow CH_3-CH_2-O-CH_2-CH_3 + NaCl$$

3. Displacement by cyanide ion (CN^-)

Substrate – R–X

Reagent – KCN

$$R-X + KCN \rightarrow R-CN + KX$$

Alkyl cyanide – CN

Alkane nitrile – IUPAC

Conversion

Haloalkane to Alkyl cyanide / Alkane nitrile

1) Ethyl bromide to propane nitrile

$$CH_3-CH_2Br + KCN \rightarrow CH_3-CH_2-CN + KBr$$

2) Ethanol to propane nitrile

$$CH_3-CH_2-OH + SOCl_2 \rightarrow CH_3-CH_2-Cl + SO_2 + HCl$$

$$CH_3-CH_2-Cl + KCN \rightarrow CH_3-CH_2-CN + KCl$$

3) Propene to butane nitrile

$CH_3-CH=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3-CH_2-CH_2-Br$

$CH_3-CH_2-CH_2Br + KCN \rightarrow CH_3-CH_2-CH_2CN + KBr$

4) Methyl chloride to ethane nitrile

$CH_3Cl + KCN \rightarrow CH_3CN + KCl$

Note Above reaction is used in the ascending of series.

- Alkyl cyanide given different organic compounds like 1) Amine
  ii) Acid amide
  iii) carboxylic acid

1. Alkyl cyanide to amine

It takes place by the reduction reaction addition of hydrogen in the presence of catalyst.

$R-C\equiv N + 2H_2 \xrightarrow{\text{Nitric acid}} R-CH_2-NH_2$

Alkyl cyanide → Amine

i) Ethyl bromide to propanamine

$CH_3CH_2-Br + KCN \rightarrow CH_3-CH_2CN + KBr$

$CH_3-CH_2CN + 2H_2 \xrightarrow{Ni/Pt} CH_3-CH_2CH_2-NH_2$

2) Ethanol to propanamine

$CH_3-CH_2OH + SOCl_2 \rightarrow CH_3-CH_2-Cl + SO_2 + HCl$

$CH_3-CH_2-Cl + KCN \rightarrow CH_3-CH_2CN + KCl$

$CH_3-CH_2CN + 2H_2 \xrightarrow{Ni} CH_3-CH_2CH_2-NH_2$

2. 3) Alkyl cyanide to acid amide ($R-\overset{O}{\overset{\|}{C}}-NH_2$)
It takes place by the partial hydrolysis (addition of H_2O)

$R-C\equiv N + H_2O \xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-NH_2$

Alkyl cyanide — Acid amide

i) Ethyl bromide to propanamide

$CH_3-CH_2Br + KCN \rightarrow CH_3-CH_2CN + KBr$

$CH_3-CH_2CN + H_2O \xrightarrow{H^+} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2$

Conversion

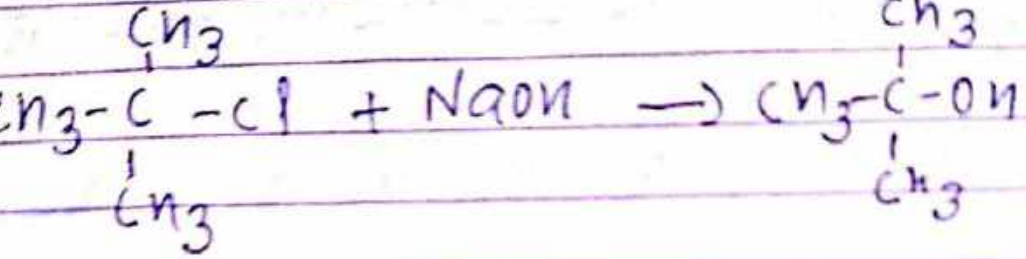
i) Alkyl bromide to ethanol

$CH_3-CH_2Br + NaOH_{(aq)} \rightarrow CH_3-CH_2OH + NaBr$

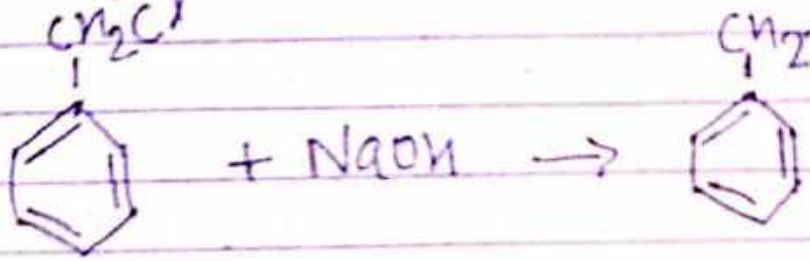
ii) Isopropyl chloride to isopropyl alcohol

$CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3 + NaOH_{(aq)} \rightarrow CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 + NaCl$

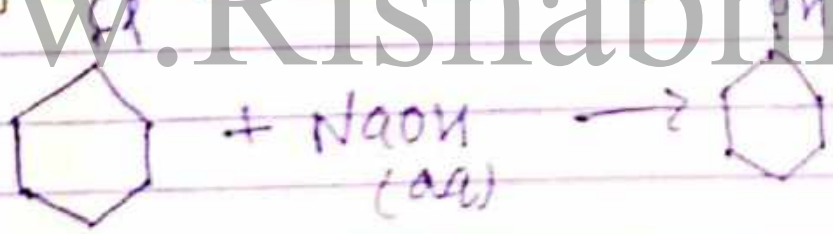
iii) Test butylchloride to test Butyl alcohol



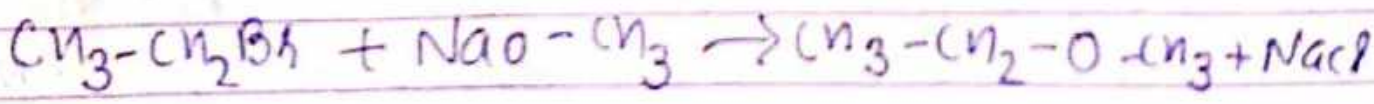
iv) Benzyl chloride to Benzyl alcohol



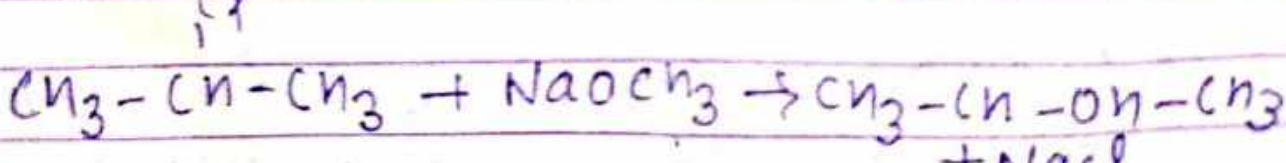
v) cyclohexyl chloride to cyclohexanol



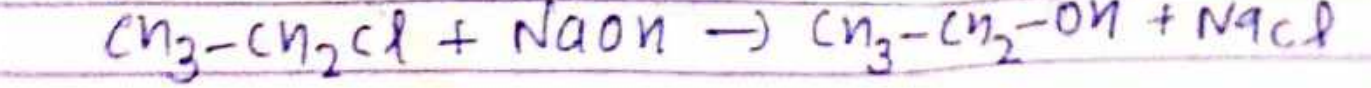
vi) Ethyl bromide to methoxy ethane



vii) Isopropyl chloride to 2-methoxy propane



viii) Ethyl chloride to ethoxy ethane



ix) Ethyl bromide to propane nitrile

$CH_3-CH_2Br + KCN \rightarrow CH_3-CH_2CN + KBr$

x) Ethanol to propane nitrile

$CH_3CH_2OH + SOCl_2 \rightarrow CH_3-CH_2Cl + SO_2 + HCl$

$CH_3-CH_2Cl + KCN \rightarrow CH_3-CH_2CN + KCl$

xi) propene to butane nitrile

$CH_3-CH=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3-CH_2-CH_2-Br$

$CH_3-CH_2-CH_2-Br + KCN \rightarrow CH_3-CH_2-CH_2CN + KBr$

xii) Methyl chloride to ethane nitrile

$CH_3Cl + KCN \rightarrow CH_3CN + HCl$

xiii) Ethyl bromide to propanamine

$CH_3-CH_2Br + KCN \rightarrow CH_3-CH_2CN + KBr$

$CH_3-CH_2CN + 2H_2 \xrightarrow{Ni/Pt} CH_3-CH_2-CH_2-NH_2$

xiv) Ethanol to propanamine

$CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$

$CH_3CH_2Cl + KCN \rightarrow CH_3CH_2CN + KCl$

$CH_3CH_2CN + 2H_2 \xrightarrow{Ni/Pt} CH_3-CH_2-CH_2-NH_2$

xv) Ethyl bromide to propanamide

$CH_3CH_2Br + KCN \rightarrow CH_3CH_2CN + KBr$

$CH_3CH_2CN + H_2O \xrightarrow{H^+} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2$

3. Alkyl cyanide to carboxylic acid

– By the complete hydrolysis of alkyl cyanide carboxylic acid is formed.

$R-C\equiv N + 2H_2O \xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-OH + NH_3$

Alkyl cyanide — carboxylic acid

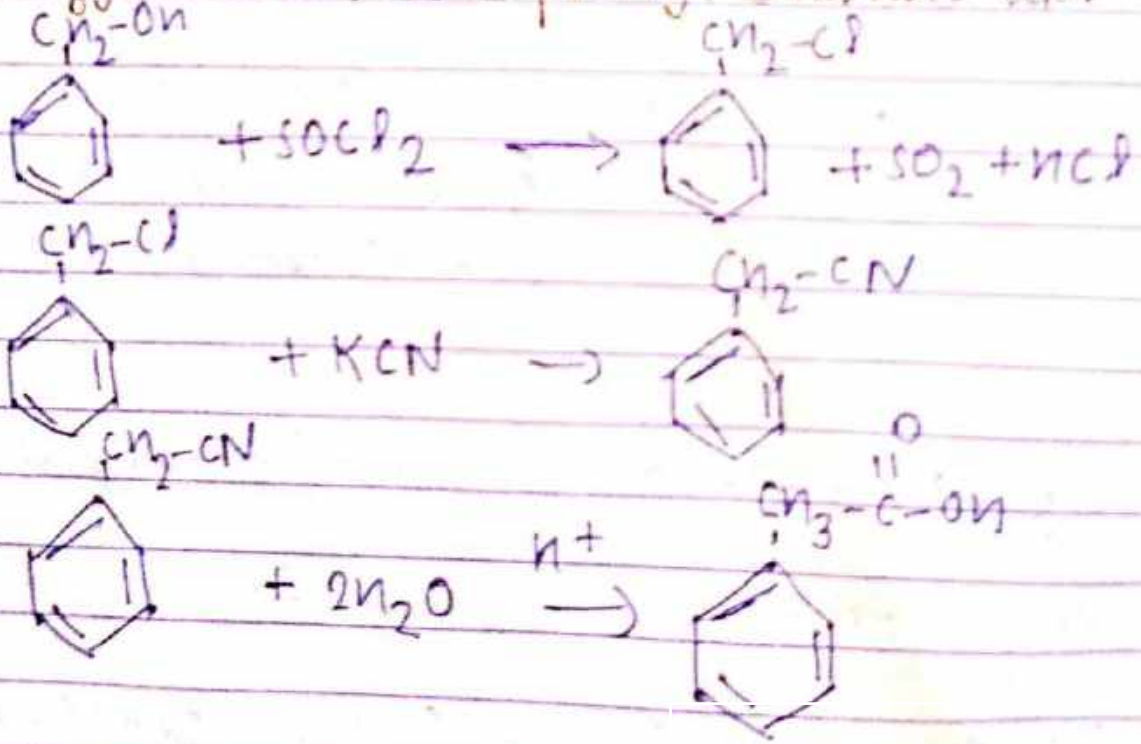
conversion

i) Ethyl bromide to propanoic acid

$CH_3CH_2Br + KCN \rightarrow CH_3CH_2CN + KBr$

$CH_3CH_2CN + 2H_2O \xrightarrow{H^+} CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH + NH_3$

ii) Benzyl alcohol to 2-phenyl ethanoic acid



iii) Ethanol to propanoic acid

$CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$

$CH_3CH_2Cl + KCN \rightarrow CH_3CH_2CN + KCl$

$CH_3CH_2CN + 2H_2O \xrightarrow{H^+} CH_3CH_2-\underset{\underset{O}{\|}}{C}-OH + NH_3$

☆ Displacement by isocyanide conversion

Alkyl halide to Alkyl isocyanide

Substrate → R–X

Reagent → Ag–CN – silver cyanide

In Ag–CN, Ag–CN bond is covalent in nature so that it does not ionise, therefore lone pair electron present on nitrogen atom act as donor site and forms isocyanide

$R-X + Ag-C\equiv N \longrightarrow R-NC + AgX$

Alkyl isocyamide or Alkanisocyanitrile

i) Ethyl bromide to ethyl isocyanide

$CH_3CH_2Br + Ag-CN \rightarrow CH_3-CH_2NC + AgBr$

ii) Propanol to propyl isocyanide

$CH_3CH_2CH_2OH + SOCl_2 \rightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$

$CH_3CH_2CH_2Cl + Ag-C\equiv N \rightarrow CH_3CH_2CH_2NC + AgCl$

* Displacement by nitrile ion (NO_2^-)

Conversion - Haloalkane to alkane nitrite

Substrate $\rightarrow R-X$

Reagent - KNO_2 - potassium nitrile

$K^+ - \bar{O} - N=O$

$R-X + K^+ - \bar{O} - N=O \rightarrow R-O-N=O + KX$

Haloalkane — Alkanenitrite