

10.

# HALOGEN DERIVATIVE OF ALKANE AND ARENES

Halogen के products

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Date: 31/12/2021

$\Rightarrow$  HALOALKANE AND HALOARENES

T.M. = 4 M

- \* Aromatics = Aromatic hydrocarbon/compound

- \* Derivative = Product

- \* Halogen Derivative = Product with Halogen

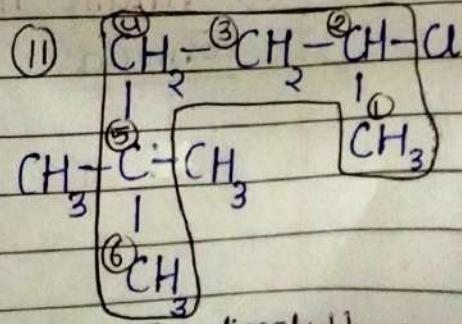
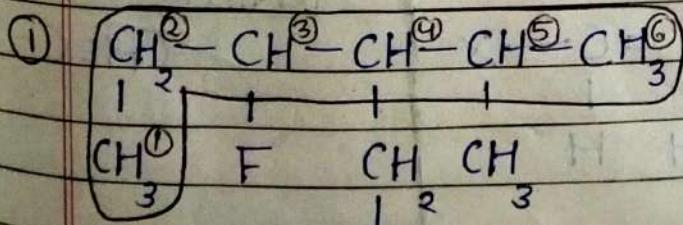
- \* Haloalkane = Halogen derivative of alkanes

= When halogen reacts with alkane (substitution) to produce halo product.

- \* Haloarenes = Halogen derivative of arenes

= When halogen reacts with arenes (substitution) to produce halo product

# IUPAC of Haloalkane :-



(ii) 2-Chloro-5,5-dimethylhexane

Shrikumar (i) 3-Fluoro-4-ethyl-5-methylhexane

## # Classification of halogen derivative of alkane

A) On the basis of number of halogen atom in alkane

Monohalogen      Dihalogen      Trihalogen      Tetrahalogen  
derivative      derivative      derivative      Polyhalogen derivative

\* Classification of monohalogen compounds:

B) On the basis of hybridisation and diff. properties

~~Vinyllic~~ ① Haloalkane / Alkyhalide ( $R-X$ ) → formula

① Allylic halide ( $sp^3$ )

Formula: →



Dif. than others

(iii) Benzylic halide

Formula: →

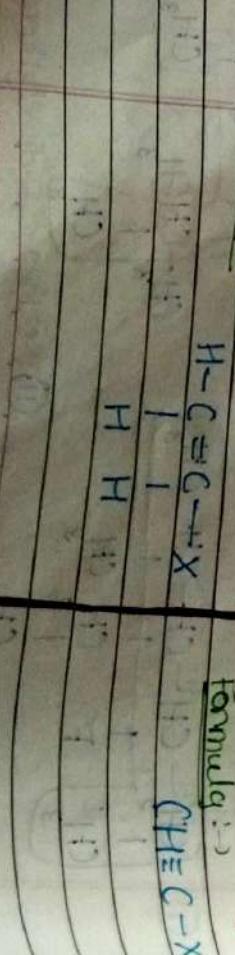


~~double~~ ② Vinyllic halides:

Formula: →

~~ole~~ ③ Haloalkyne

Formula: →



## # Classification of halogen derivatives: →

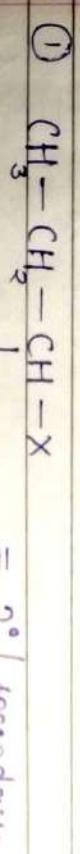
1. Haloalkane or alkyl halide and other functional group containing compound.

2. Show that  $sp^3$  hybridized carbon.

3. This classification is based on functional group containing carbon atom is directly attached to "how many numbers of carbon atoms" as follows.

Primary      Secondary      Tertiary  
alkyl halide      alkyl halide      alkyl halide  
(1°)                  (2°)                  (3°)

\* Examples: →



= 1° / Primary  
= 3° / Tertiary

## Nomenclature

Common Name:

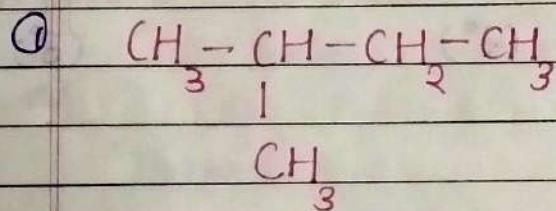
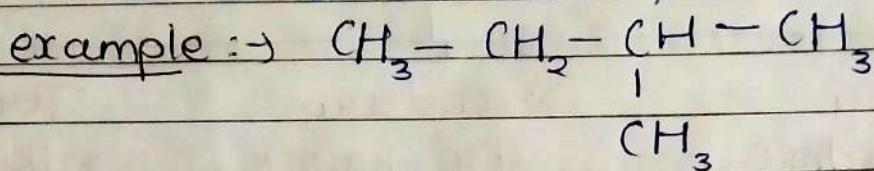
Alkyl halide

IUPAC name

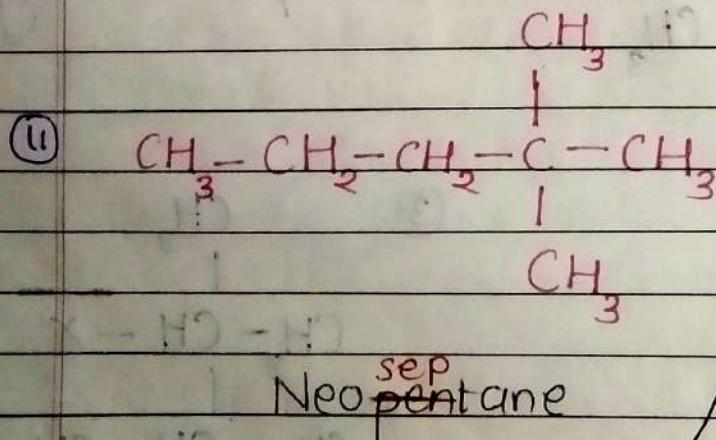
Haloalkane

1) Iso :-

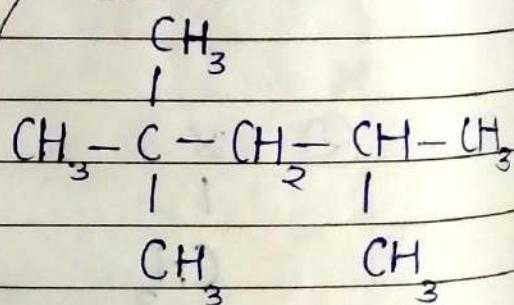
When one methyl branch is attached to 2<sup>nd</sup> no. of carbon atom, is called as 'iso alkyl'.



Isopentane



Example :-



Neooctane

2) Neo :-

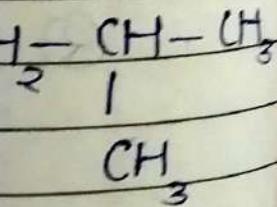
When the two methyl is present at the second no. of carbon atom is called as 'neo'.

name

alkane

linked to  
as "iso alkyl"

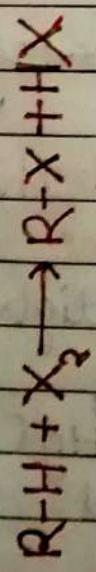
ole :→



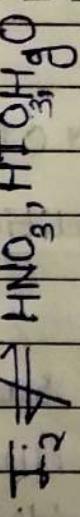
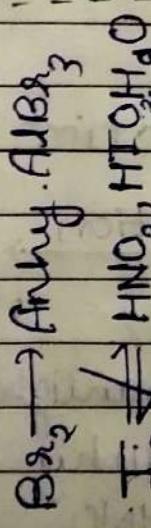
ane

ent at the  
calledPreparation of Halogenoalkane / Alkyl halide

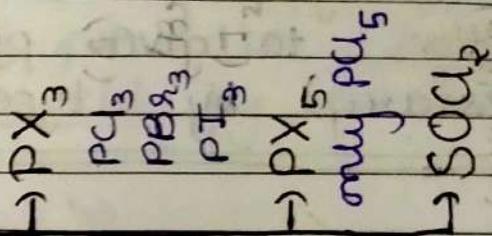
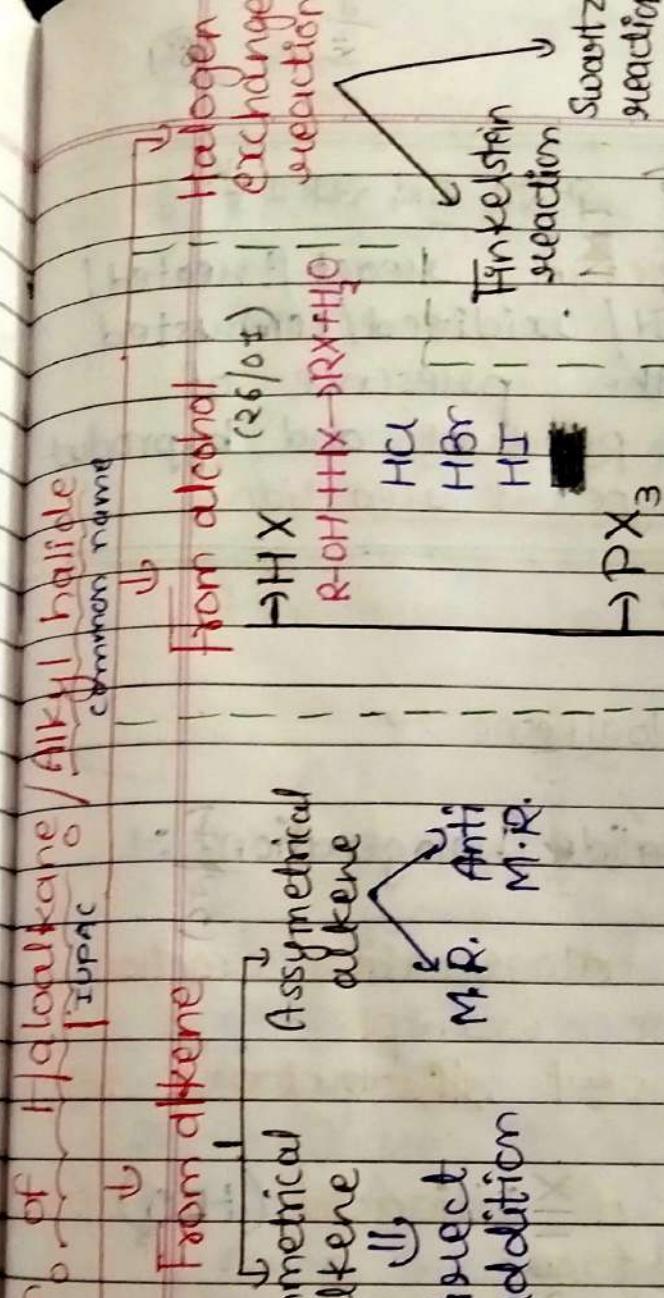
From alkene  
⇒ Halogenation  
Reaction



$\text{Cl}_2 \rightarrow$  Sunlight /  
U.V. light



$\text{F}_2 \rightarrow$  Not proceed



M.R.  
Anti  
M.R.

Direct  
addition

Symmetrical  
alkene

Asymmetrical  
alkene

From alkene

M.R.  
Anti  
M.R.

Hinkelstein  
reaction

Somov's  
reaction

Halogen  
exchange  
reaction

## \* General Statement :-

## ਹਮੇਸ਼ਾ ਧਾਰ ਰਖਨਾ

When reactant react / heated / heated / boiled / reduced / oxidised / combusted with reagent in the presence of condition to give product and byproduct (if necessary) by type of reaction.

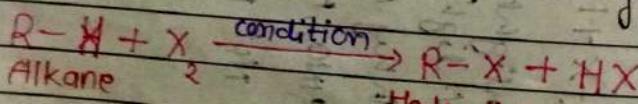
## # Preparation of $\alpha$ -Haloalkane :-

A) From alkane / alkyl halide (halogenation) :-

### QUESTIONS

- 1) Define and explain halogenation reaction with minimum one example.
  - 2) How will you convert ~~2,2-dibromopropane~~ isobutane into butyl bromide?
  - 3) What is the action of iodic acid ( $\text{HIO}_3$ ) on 2,2,3-trimethylpentane?
  - 4) Why chlorination on alkane not proceed?

\* General reaction of halogenation :-



Alkanes

$\text{Br}_3 \rightarrow \text{Anhydride} / \text{U.V. light}$

$$\text{HNO}_3 \neq \text{H}_3\text{NO}_3$$

$$\text{F} \xrightarrow{\text{HNO}_3, \text{HIO}_3, \text{HgCl}_2}$$

$F_2 \rightarrow$  Not proceeded

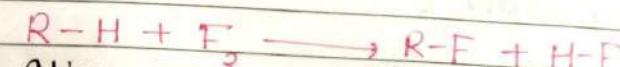
~~or proceed~~

### a) Fluorination :-

General Statement :-

When alkane reacts with fluorine to produce fluoroalkane and hydrofluoric acid by substitution reaction.

General Reaction: →



## Alkane

fluoro <sup>hydrofluoric</sup>  
-octane acid

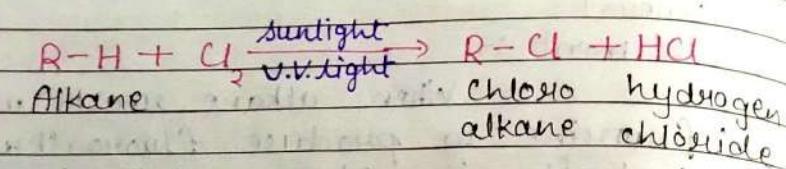
1. In this reaction, reactant and product, both sides are dangerous for living being.
  2. Because, it is poisonous and explosive.
  3. Therefore, it is very risky to every living being as well as for environment.
  4. Therefore, we do not proceed this reaction.

b) Chlorination : →

## General Statement :-

When alkane reacts with chlorine in the presence of sunlight or U.V. light to produce chloroalkane by substitution reaction.

General reaction :-



Example :

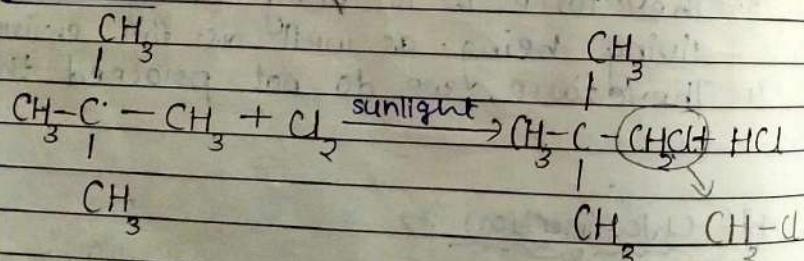
Ques: How the chlorine reacts on neopentane?

*Ans: ->*

### Statement :-

When neopentane / 2,2-dimethyl  
propane reacts with chlorine in the  
presence of sunlight or U.V. light  
to produce 1-chloro-2,2-dimethyl  
propane by simple substitution reaction

## Reaction :-



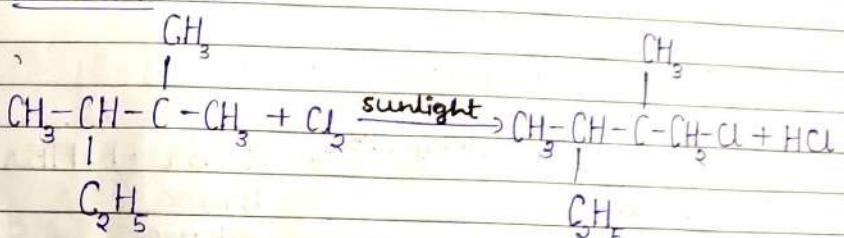
(Neopentane)  
2,2-dimethylpropane

~~2-chloro-2,2-dimethyl~~  
propane

## ① Statement $\rightarrow$

When 2,3-dimethylbutane reacts with chlorine in the presence of sunlight or U.V. light to produce 1-chloro-2,3-dimethylpentane by simple substitution reaction

Reaction :-



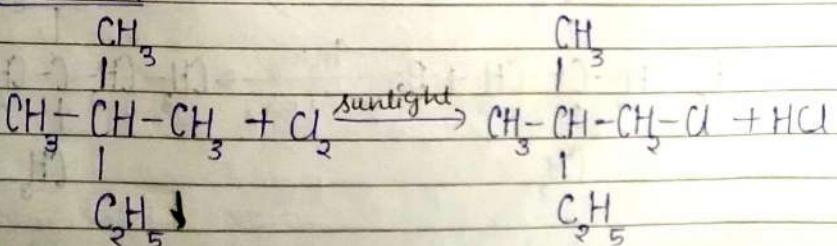
2,3-dimethylpentane

1-chloro-2,3-dimethylpentane

## ⑪ Statement :-

When 2,2-dimethylbutane reacts with chlorine in the presence of sunlight or U.V. light to produce 1-Chloro-2,2-dimethylbutane by simple substitution reaction.

Reaction :-



~~3,3-dimethyl~~  
~~butane~~

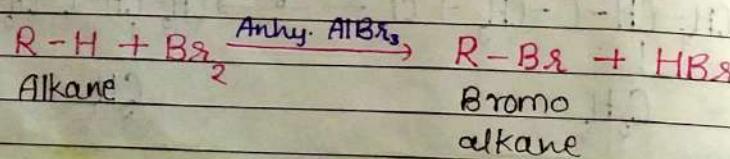
1-chloro-2,2-dimethyl  
butane

c) Bromination :-

General statement :-

When alkane reacts with bromine in the presence of anhydrous aluminium bromide to produce bromoalkane by simple substitution reaction.

General Reaction :-

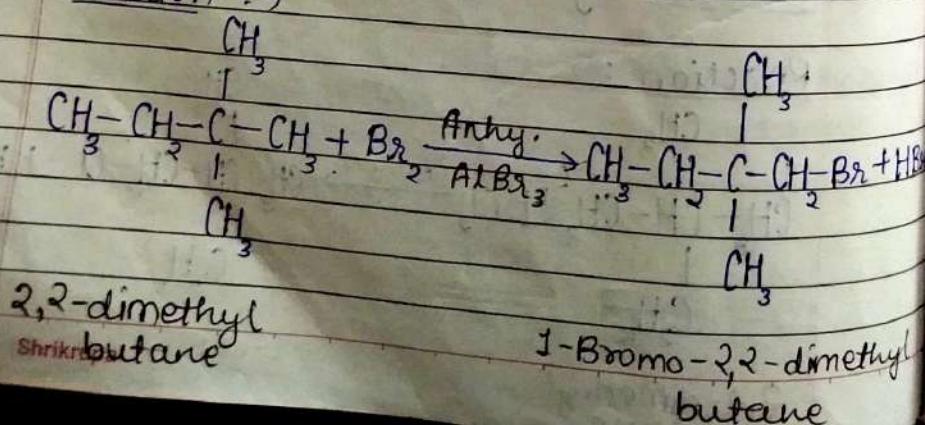


\* Example :-

i) Statement :-

When 2,2-dimethylbutane reacts with bromine in the presence of anhydrous aluminium bromide to produce 1-Bromo-2,2-dimethyl butane by simple substitution reaction.

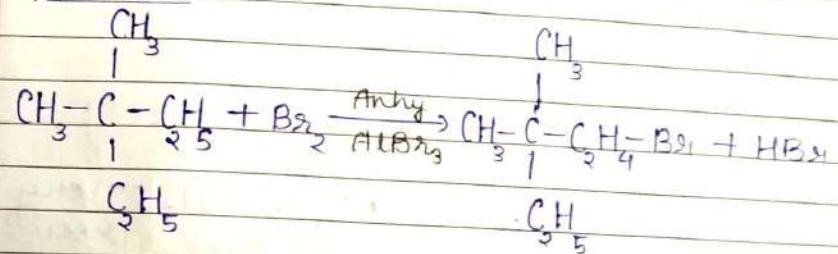
Reaction :-



ii) Statement :-

When 2,2-dimethylpentane reacts with bromine in the presence of anhydrous aluminium bromide to produce 1-Bromo-2,2-dimethyl pentane by simple substitution reaction.

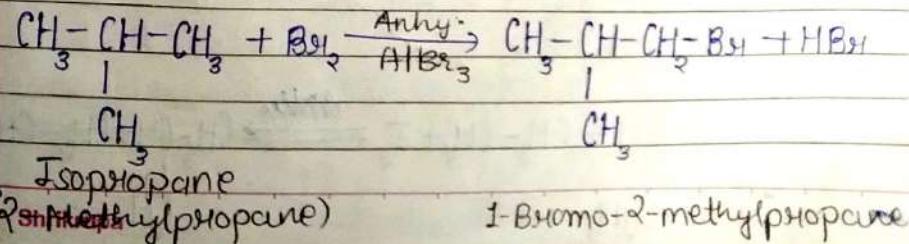
Reaction :-



iii) Statement :-

When isopropane / 2-Methylpropane reacts with bromine to produce in the presence of anhydrous aluminium bromide to produce 1-Bromo-2-methylpropane by simple substitution reaction.

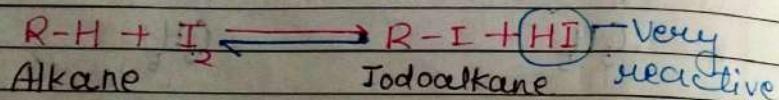
Reaction :-



c) Iodination  $\rightarrow$ General Statement  $\rightarrow$ 

When alkane reacts with iodine to produce iodo-alkane with very active substance HI.

- Due to the presence of reactive HI, reaction goes reverse.

Reaction  $\rightarrow$ 

- In the above reaction produced product is in very less amount, because of equilibrium (reversible).
- To improve the percentage of product use different condition like  $\text{HNO}_3$ ,  $\text{HIO}_3$ ,  $\text{HgO}$  first not produce HI.

Example  $\rightarrow$ Statement  $\rightarrow$ 

When 3-Methylpentane reacts with iodine to produce 1-Iodo-3-methylpentane with very active substance HI.

Reaction  $\rightarrow$ 

Shrikrupa  $\text{C}_2\text{H}_5$  3-methylpentane

$\text{CH}_3 - \underset{3}{\text{CH}} - \text{CH}_2 - \text{CH}_3 - \text{I}$  1-Iodo-3-methylpentane

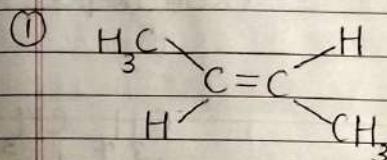
## B) From alkene

Symmetrical  
(direct addition)

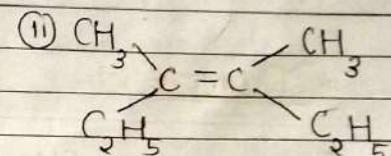
Assymetrical  
M.R.                      Anti M.R.

## a) Symmetrical alkene (direct addition)

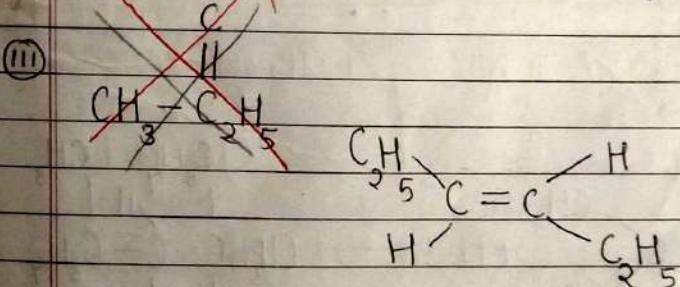
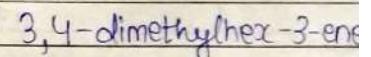
Symmetrical alkene  $\rightleftharpoons$  doubly bonded carbon atom पर एक ग्रृहीत ब्रॉन्चेस (each) होती हैं। असमिक्त अल्कीन ग्रूप होती हैं।

Example  $\rightarrow$ 

But-2-ene



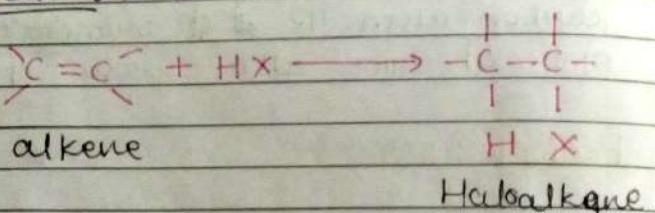
3,3-dimethylhex-3-ene



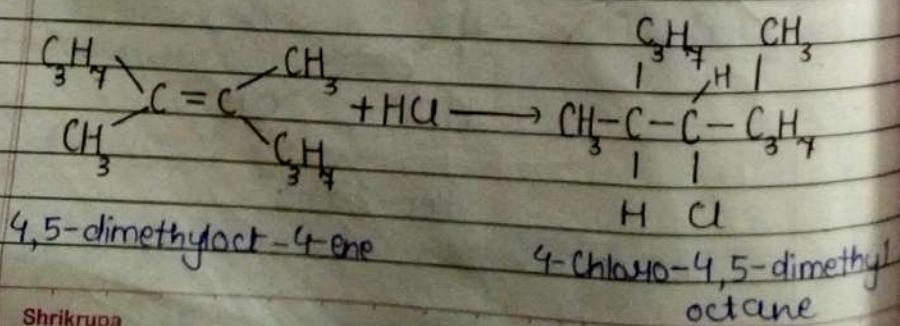
Hex-3-ene

General Reaction :-Statement :-

When symmetrical alkene reacts with hydrohaloic acid (hydrogen halide)  $\{H-X\}$  then get direct addition product as haloalkane.

Reaction :-Example :-Statement :-

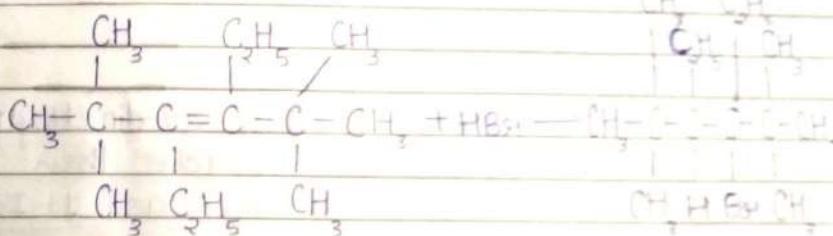
When 4,5-dimethyloct-4-ene reacts with hydrogen chloride then get direct addition product as 4-chloro-4,5-dimethyl octane.

Reaction :-

Ques: What is the action of hydrobromic acid on 3,4-diethyl-2,2,5,5-tetramethylhex-3-ene?

Statement :-

When 3,4-diethyl-2,2,5,5-tetramethylhex-3-ene reacts with hydrobromic acid then get direct addition product as 3-Bromo-3,4-diethyl-2,2,5,5-tetramethylhexane.

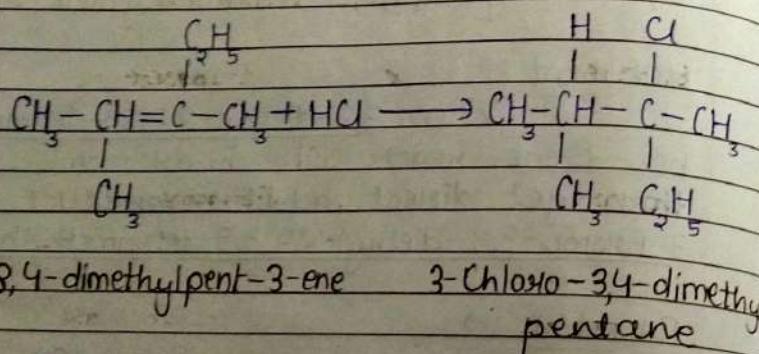
Reaction :-

3,4-diethyl-2,2,5,5-tetramethylhex-3-ene

Statement :-

When 3,4-dimethylpent-2-ene reacts with hydrochloric acid then get direct addition product as 3-Chloro-3,4-dimethylpentane.

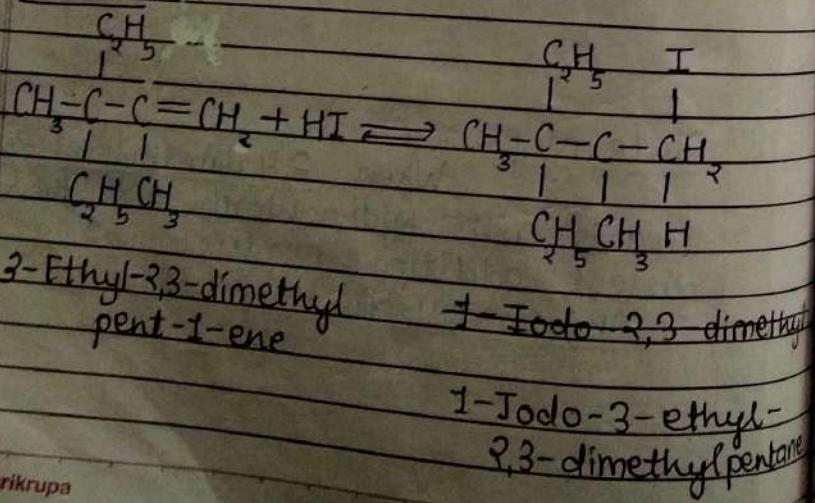
### Reaction :-



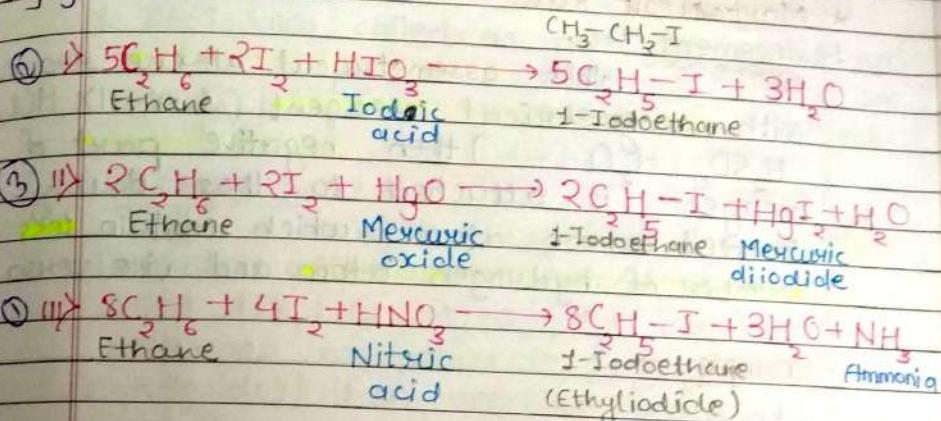
### (iii) Statement :-

When 3-Ethyl-2,3-dimethylpent-1-ene reacts with hydrogen iodide then get direct addition product as 1-Iodo-3-ethyl-2,3-dimethylpentane.

### Reaction :-



### A] d] Iodonation :-



### B] b] Assymetrical alkene :-

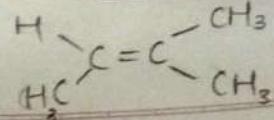
For assymetrical alkene addition of HX give two type of product.  
For the selection of major product use following rules.

#### Rule-1:

Markovnikoff Rule

#### Rule-2:

Anti-Markovnikoff Rule



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### \* Markovnikoff Rule :-

#### 1. Statement :-

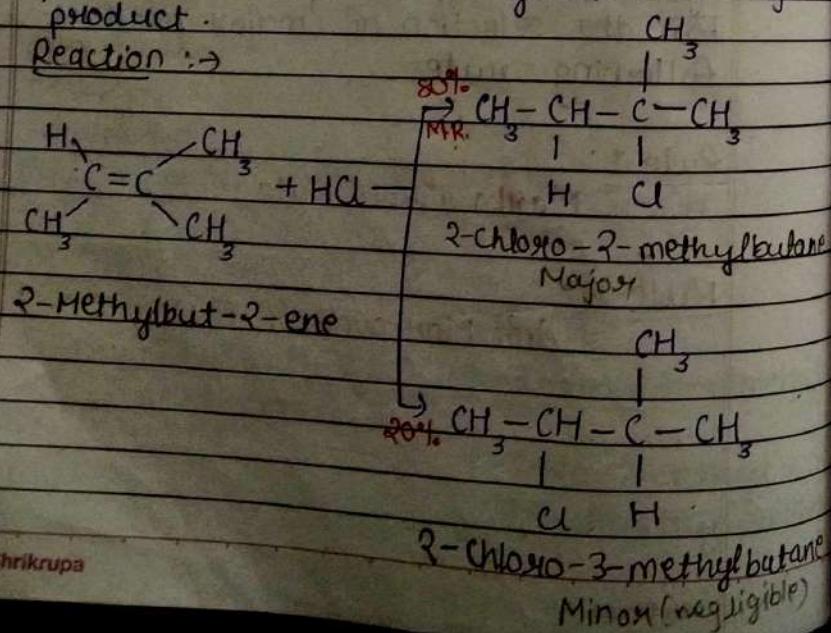
When asymmetrical alkene reacts with asymmetrical reagent (like,  $\text{HX}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}_2$ , etc.) then negative part of reagent is attached to those doubly bonded carbon atom which contain less number of hydrogen atom and vice versa.

#### Example :-

#### Statement :-

When 2-Methylbut-2-ene reacts with hydrogen chloride then chloride (negative part of reagent) is attach to those doubly bonded carbon atom which contain less number of carbon atom and produces 2-chloro-2-methylbutane as major product.

#### Reaction :-



### \* Anti-Markovnikoff Rule :-

1. It is also called as peroxide effect or Kharasch effect or Mayo-Kharasch effect

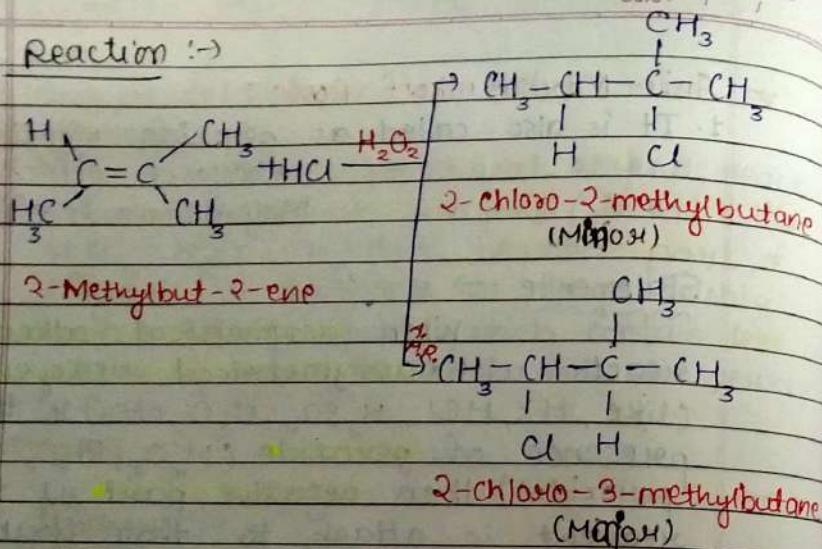
#### Statement :-

When asymmetrical alkene reacts with asymmetrical reagent (like,  $\text{HX}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}_2$ , etc.) in the presence of peroxide ( $\text{H}_2\text{O}_2$ ,  $\text{Ph}_2\text{O}_2$  (diphenyl peroxide)) then negative part of the reagent is attach to those doubly bonded carbon atom which contain MORE number of hydrogen atom and vice versa.

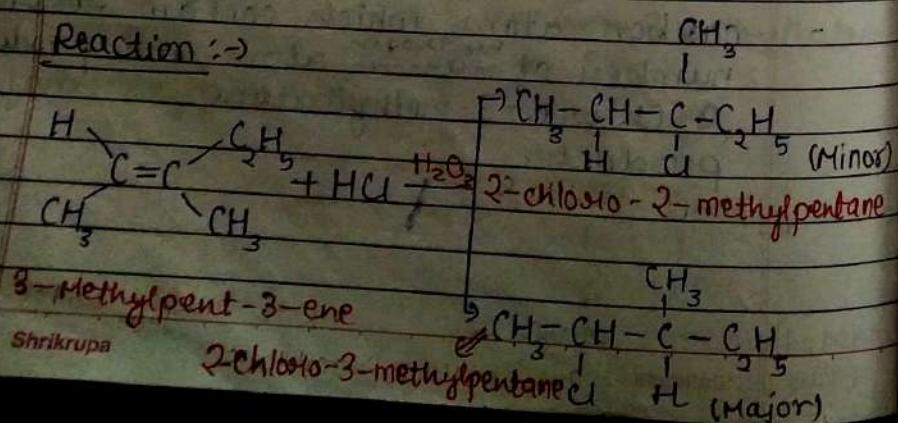
#### Example :-

#### 1. Statement :-

When 2-Methylbut-2-ene reacts with hydrogen chloride in the presence of hydrogen peroxide then chloride is attached to those doubly bonded carbon atom which contain less more number of <sup>hydrogen</sup> carbon atom and produces 2-Chloro-3-methylbutane as major product.

Reaction :-(ii) Statement :-

When 3-Methylpent-3-ene reacts with hydrogen chloride in the presence of hydrogen peroxide the chloride is attached to those doubly bonded carbon atom which contain more number of hydrogen atom and produces 2-chloro-3-methylpentane as major product.

Reaction :-

c) From alcohol :-

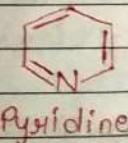
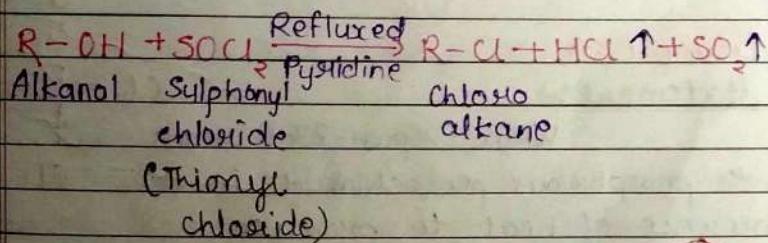
d) Thionyl chloride  $\text{SOCl}_2$  :-

i. This reaction is commonly called as **Darzon's reaction**

General Statement :-

When alcohol is refluxed with thionyl chloride or sulphonyl chloride ( $\text{SOCl}_2$ ) in the presence of pyridine to form 100% haloalkane because byproduct ( $\text{SO}_2$  and  $\text{HX}$ ) is evaporated. This reaction is called as **Darzon reaction**.

ii. Darzon's reaction always produce chloroalkane.

General Reaction :-

## Phosphorous oxychloride

(500 M ⚡)

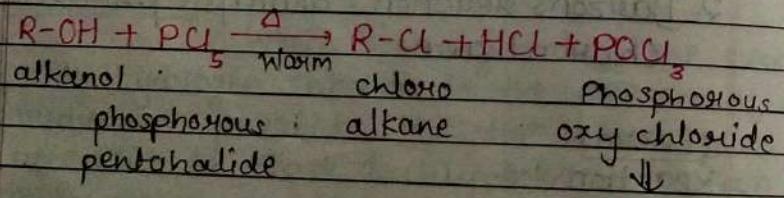
b) By  $\text{PX}_5$  (Phosphorous pentahalide)

1. Only phosphorous pentachloride ( $\text{PCl}_5$ ) is exist other pentahalides ( $\text{PX}_5$ ) are not exist  $\{\text{PB}_5\text{Cl}_5 \text{ and } \text{PI}_5\}$ .

General statement :-

When alkyl reacts with phosphorous penta-chloride in the presence of heat to produce chloroalkane with phosphorous oxychloride and hydrochloric acid.

General Reaction :-

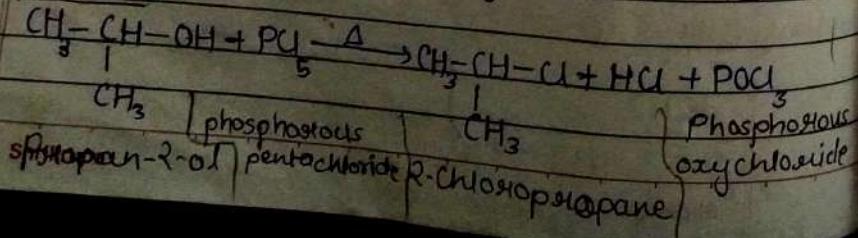


### \* Example :-

### Statement :-

When Propan-2-ol reacts with phosphorous pentachloride in the presence of heat to produce 2-Chloropropane with phosphorus oxychloride and hydrochloric acid.

Reaction :-

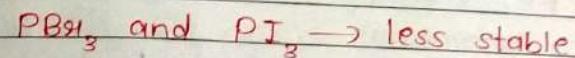
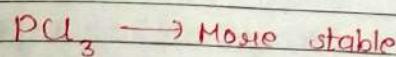


Phosphorous acid = oxyacid of phosphorus

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\*\*\*\* million (500 M \*)

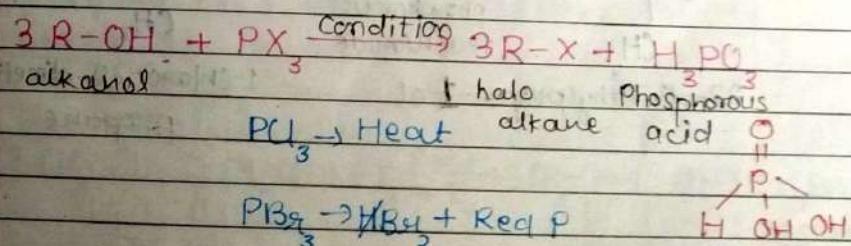
] By  $\text{PX}_3$  (Phosphorous trihalide)



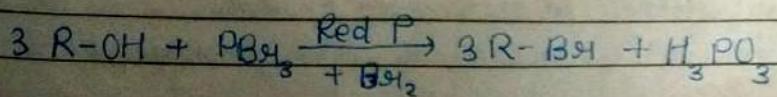
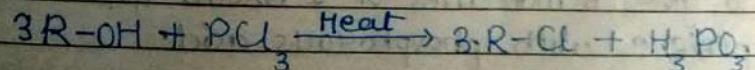
## General Statement :-

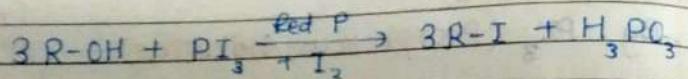
When three molecules of alkanol reacts with phosphorous tri-halide in the presence of particular condition to produce three molecules of haloalkane with phosphorous acid ( $H_3PO_3$ )

General Reaction :-



\* Example :-



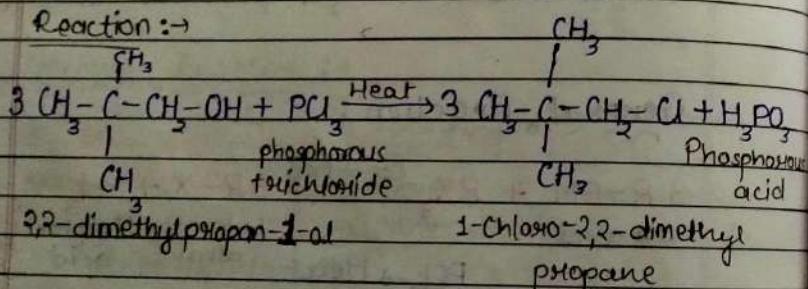


## \* Examples :-

① statement  $\Rightarrow$  3 molecules of

When 2,2-dimethylpropan-1-ol reacts with phosphorous trichloride in the presence of heat to produce 1-Chloro-2,2-dimethylpropane with 3 molecules of phosphorous acid.

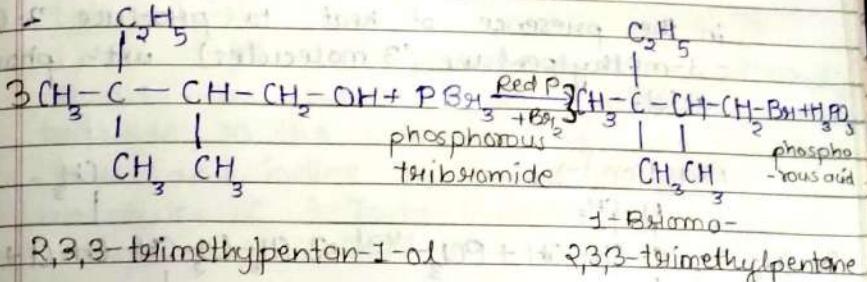
Reaction :-



## (11) Statement :-

When 3 molecules of 2,2,2-trimethyl pentan-1-ol reacts with phosphorous tribromide in the presence of red phosphorous and bromine to give 3 molecules of 1-Bromo-2,2,2-trimethyl pentane with phosphorous acid.

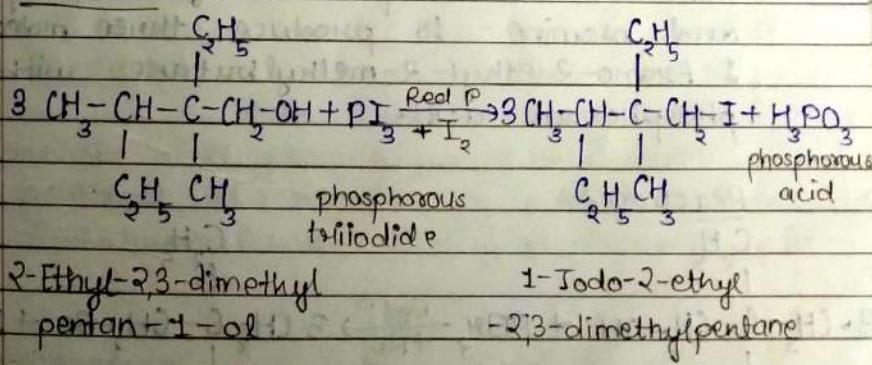
Reaction :-



### III Statement :-

When 3 molecules of 2-Ethyl-2,3-dimethylpentan-1-ol reacts with phosphorous triiodide in the presence of solid phosphorous and iodine to produce 3 molecules of 1-Iodo-2-ethyl-2,3-dimethylpentane with phosphorous acid.

Reaction:-

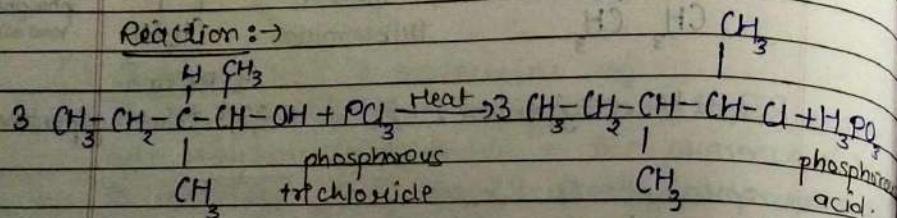


## IV Statement :-

When 3 molecules of 3-Methylpentan-2-ol reacts with phosphorous trichloride

in the presence of heat to produce 3-Chloro-  
-3-methylpentane (3 molecules) with phosphorous  
acid.

Reaction :-



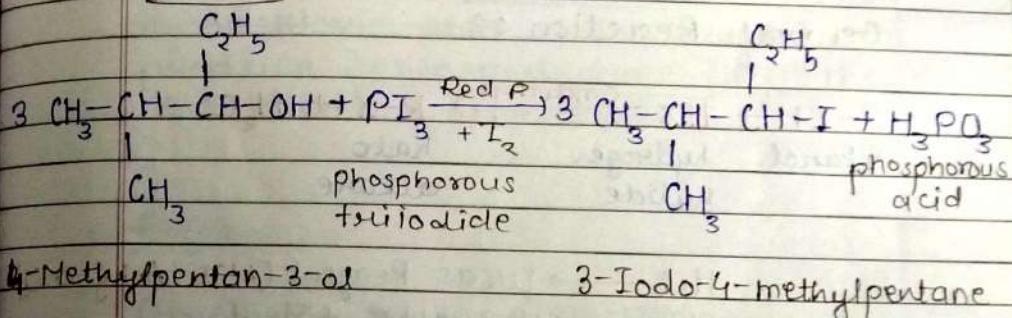
3-Methylpentan-2-ol

2-Chloro-3-methylpentane

(V) Statement :-

When three molecules of 4-Methyl pentan-3-ol reacts with phosphorous triiodide in the presence of red phosphorus and iodine to produce three molecules of 3-Iodo-4-methylpentane with phosphorous acid.

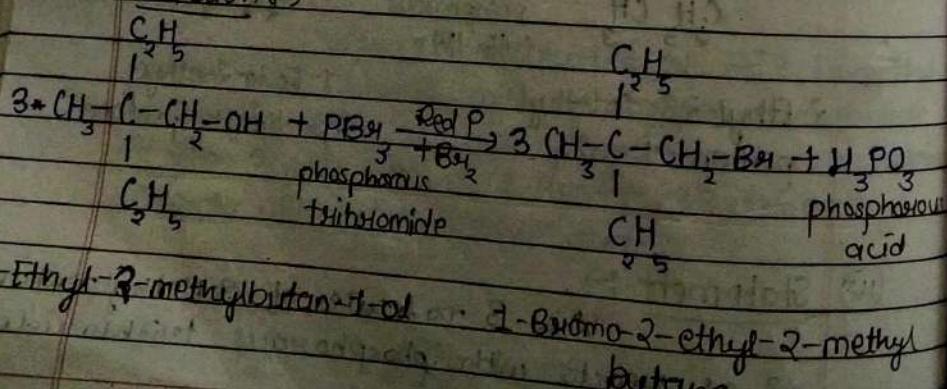
Reaction :-



(VI) Statement :-

When three molecules of 2-Ethyl-2-methylbutan-1-ol reacts with phosphorous tribromide in the presence of red phosphorous and bromine to produce three molecules of 1-Bromo-2-Ethyl-2-methylbutane with phosphorous acid.

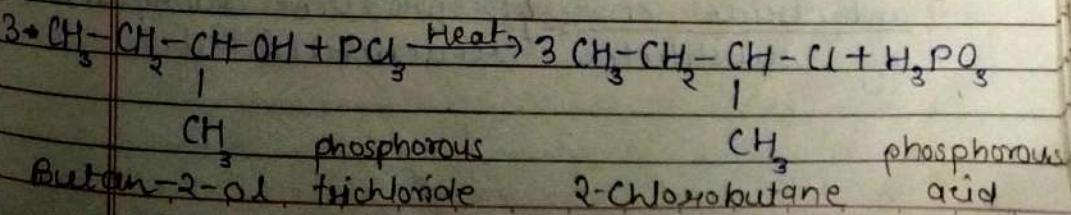
Reaction :-



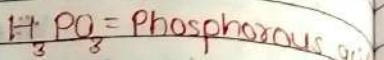
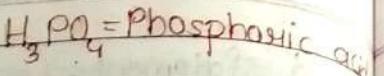
(VII) Statement :-

When 3 molecules of Butan-2-ol reacts with phosphorous trichloride in the presence of heat to produce 3 molecules of 2-Chlorobutane with phosphorous acid.

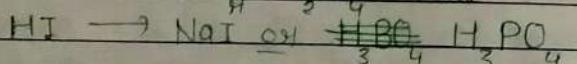
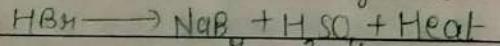
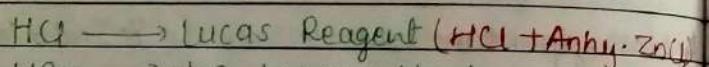
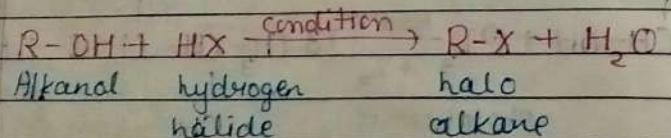
Reaction :-



d) H-X

General statement :-

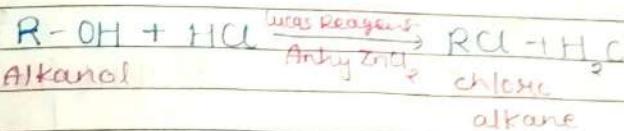
When Alkanol reacts with hydrogen halide in the presence of particular condition to produce haloalkane with water molecule.

General Reaction :-

I.  $\text{HCl}$  = Groove's Process. = Lucas Reagent  
 $= \text{HCl} + \text{Anhy. ZnCl}_2$

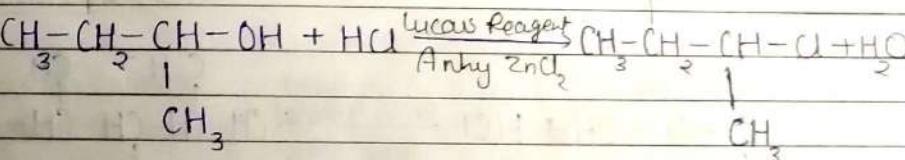
Statement :-

Imp Lucas reagent means mixture of  $\text{HCl}$  and anhydride  $\text{ZnCl}_2$  to produce chloroalkane by substitution reaction.

Reaction :-\* Example :-

(i) Statement :-

When Butan-2-ol reacts with hydrochloric acid Lucas reagent to produce 2-chlorobutane by the substitution reaction.

Reaction :-

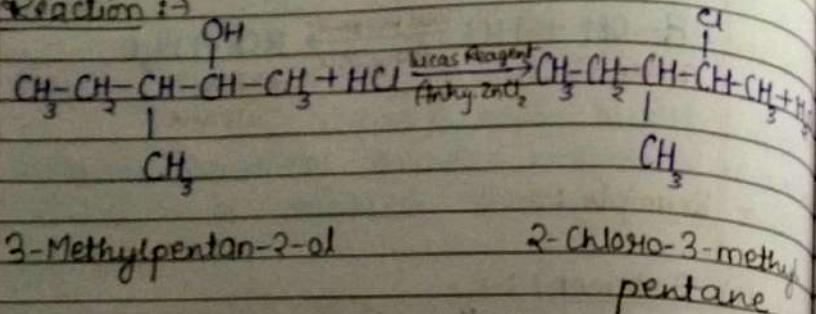
Butan-2-ol

2-Chlorobutane

(ii) Statement :-

When 3-Methylpentan-2-ol reacts with Lucas reagent to produce 2-Chloro-3-methylpentane by the substitution reaction.

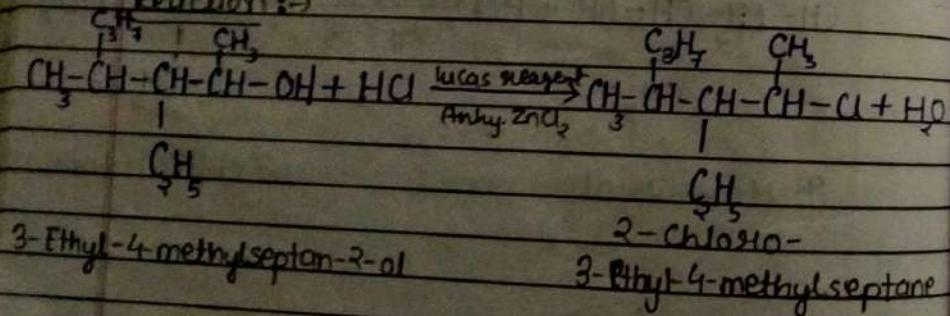
### Reaction :-



### Statement :-

When 3-Ethyl-4-methylheptan-2-ol reacts with Lucas reagent to produce 2-chloro-3-ethyl-4-methylheptane by the substitution reaction.

Reaction :-



## IV Statement :-

When Butanol reacts with Lucas reagent to produce chlorobutane by the substitution reaction:

reaction :-

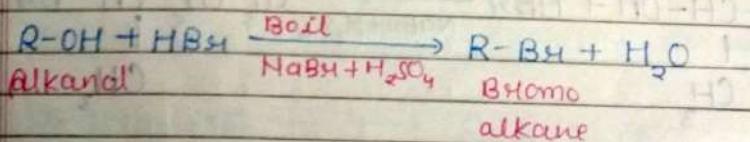


π. НВи

statement :-

When alcohol is boiled with 48% HBr in the presence of NaBr and  $H_2SO_4$  to give Bromoalkane by substitution reaction.

Reaction :-

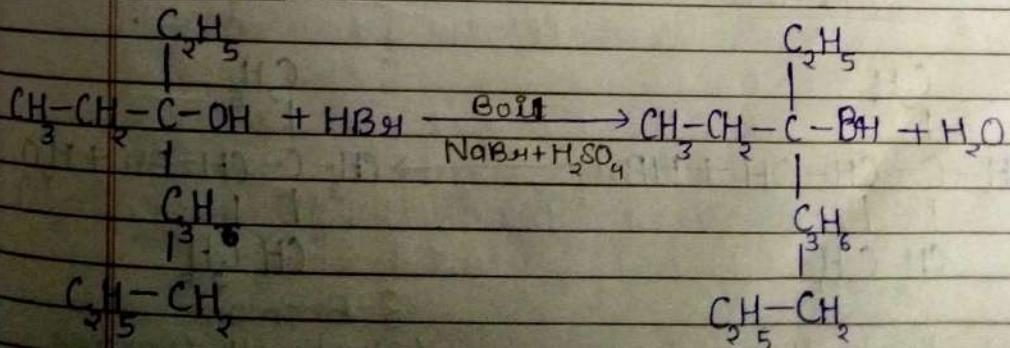


## \* Examples :-

① Statement :-

When 3-Ethynonan-3-ol is boiled with 48% HBr in the presence of NaBr and  $H_2SO_4$  to give 3-Bromo-3-ethyl nonane by substitution reaction.

### Reaction :-



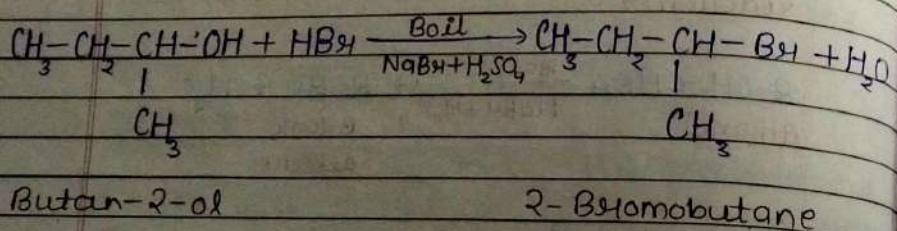
### 3-Ethylnonan-3-ol

### 3-Bromo-3-Phylnonane

(ii) Statement :-

When Butan-2-ol reacts with HBr in the presence of NaBr and  $H_2SO_4$  to produce 2-Bromobutane by the substitution reaction.

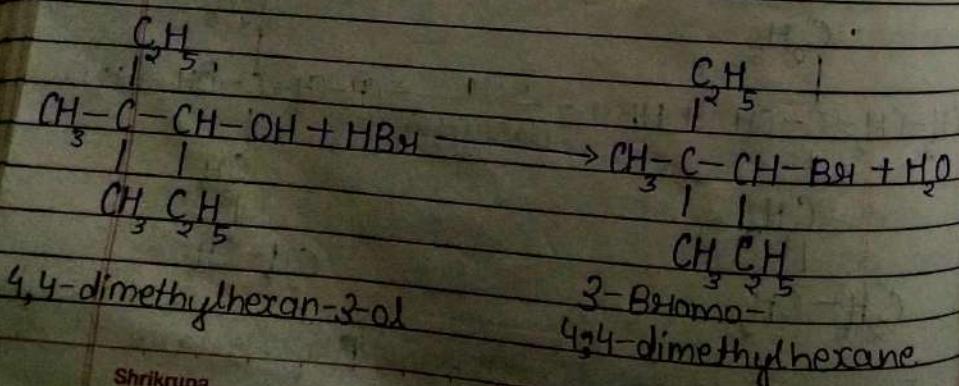
Reaction :-



(iii) Statement :-

When 4,4-dimethylhexan-3-ol reacts with HBr in the presence of NaBr and  $H_2SO_4$  to produce 3-Bromo-4,4-dimethyl hexane by the substitution reaction.

Reaction :-

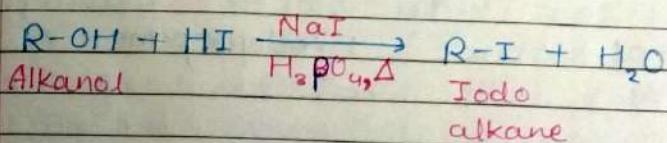


III. HI

Statement :-

When alcohol reacts with HI in the presence of freshly prepared alkali iodide (NaI and/or KI) in 95% phosphoric acid ( $H_3PO_4$ ) to produce very good yield of Iodoalkane by substitution reaction.

Reaction :-

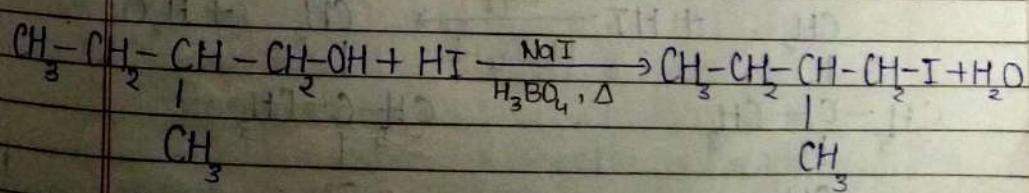


\* Examples :-

(i) Statement :-

When 2-Methylbutan-1-ol is reacts with HI in the presence of freshly prepared NaI in 95% phosphoric acid to produce very good yield of 1-Iodo-2-methyl butane by substitution reaction.

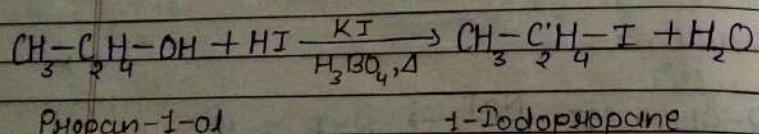
Reaction :-



## ⑪ Statement $\Rightarrow$

Statement :- When Propan-1-ol reacts with HI in the presence of freshly prepared KI in 95% phosphoric acid to produce very good yield of 1-Todopropane by the substitution reaction.

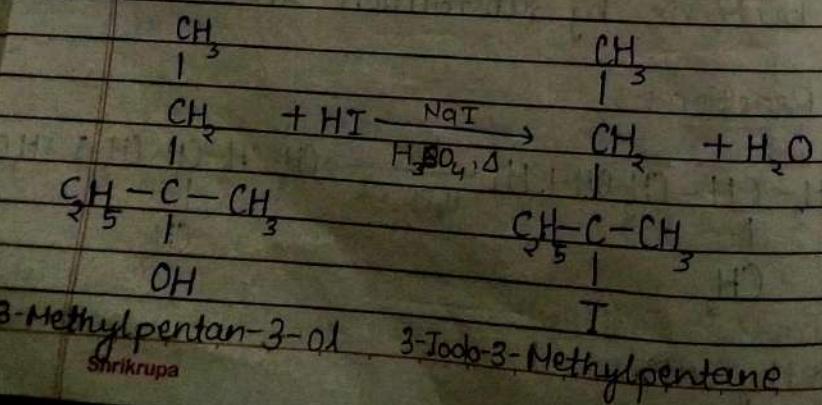
Reaction :-



(iii) Statement :→

When 3-Methylpentan-3-ol reacts with HI in the presence of freshly prepared NaI in 95% phosphoric acid to produce very good yield of 3-Iodo-3-Methylpentane by the substitution reaction.

Reaction :-



D) Halogen exchange method :-

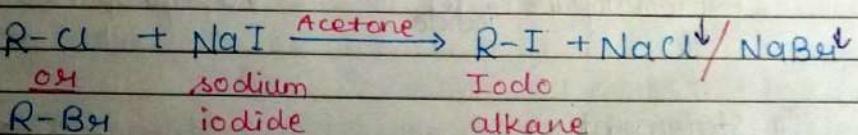
- When chloroalkane or bromoalkane exchange its halide by iodide or fluoride.

a) Finkelstein reaction  $\rightarrow$  ~~old-old~~ example  
(alkane)

Statement :→

When chloroalkane or bromoalkane reacts with sodium iodide ( $\text{NaI}$ ) in the presence of acetone ( $\text{CH}_3\text{COCH}_3$ ) to give iodoalkane plus ppt. of  $\text{NaCl}$  can be separated by simple filtration such a reaction is called as Finkelstein reaction.

## Reaction :-



## \* Examples :-

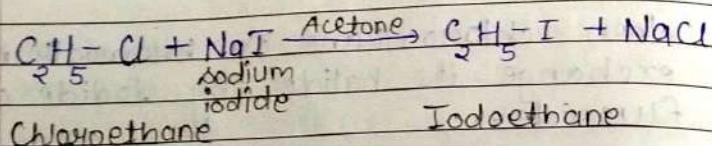
### ① Statement :-

When chloroethane reacts with sodium iodide in the presence of  $\text{CH}_3\text{COCH}_3$  (acetone) to give iodoethane plus ppt. of ~~silver~~ which can be separated by simple filtration. such a reaction is called

## Finkelstein reaction:

### \* Examples :-

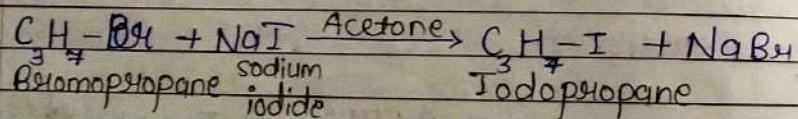
### ① Reaction :-



## ⑪ Statement :-

When Bromopropane reacts with sodium iodide in the presence of acetone to produce Iodopropane plus ppt. of sodium bromide which can be separated by simple filtration; such a reaction is called as Finkelstein reaction.

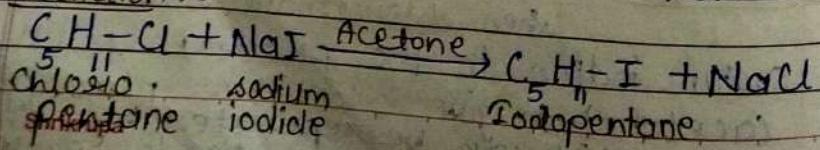
Reaction :-



### III Statement :-

When Chloropentane reacts with sodium iodide in the presence of acetone to produce Iodopentane with ppt. of sodium chloride which can be separated by simple filtration; Such a reaction is called as Finkelstein reaction.

Reaction :-



b) Swarts reaction :-

### Statement :-

When chloroalkane or bromoalkane reacts with metal fluoride ( $\text{AlF}_3$ ,  $\text{Li}_2\text{F}$ ,  $\text{AsF}_3$ ,  $\text{SbF}_3$ ) to produce fluorokane and precipitated metal chloride or metal bromide is called as 'Schwartz reaction'.

## Reaction :-



Chaitanya Bhakti

Bromo

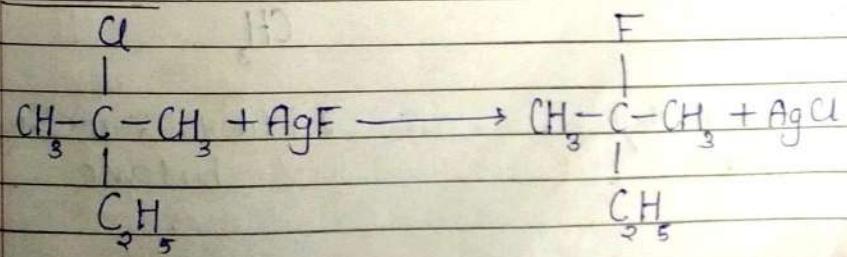
## alkane

**★ Example :-**

Statement :-

When 3-Chloro-3-methylbutane reacts with silver fluoride to produce 3-Fluo-3-methylbutane and precipitated silver chloride is called as 'Sweet's reaction'.

Reaction :-



~~3~~-<sup>3</sup>Schiff base-3-methylbutane

3-Fluoro-3-methyl  
butane

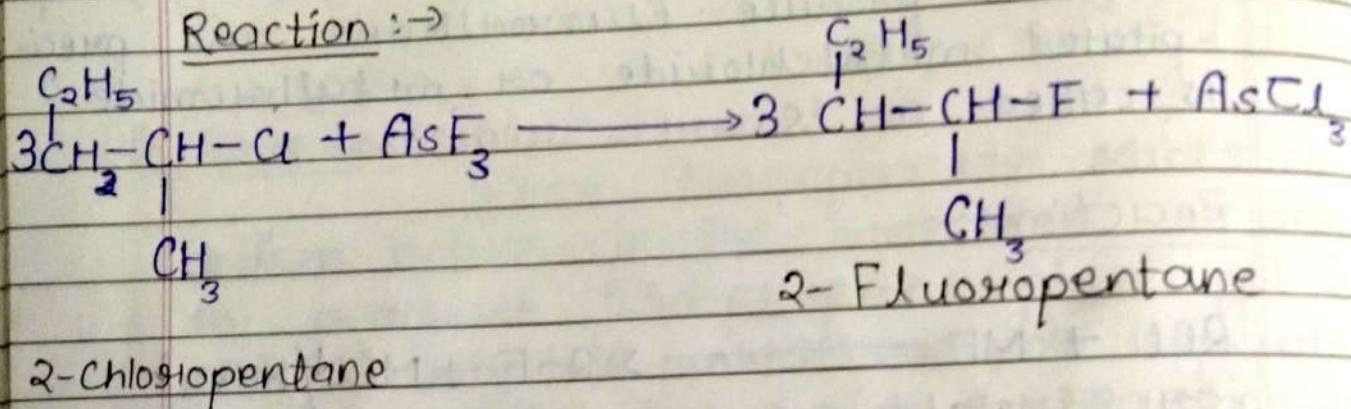
→ three molecules of

\* Examples :-

(i) Statement :-

When 2-chloropentane reacts with arsenic fluoride to produce 2-fluoropentane and precipitated arsenic trichloride is called 'Swartz reaction'.

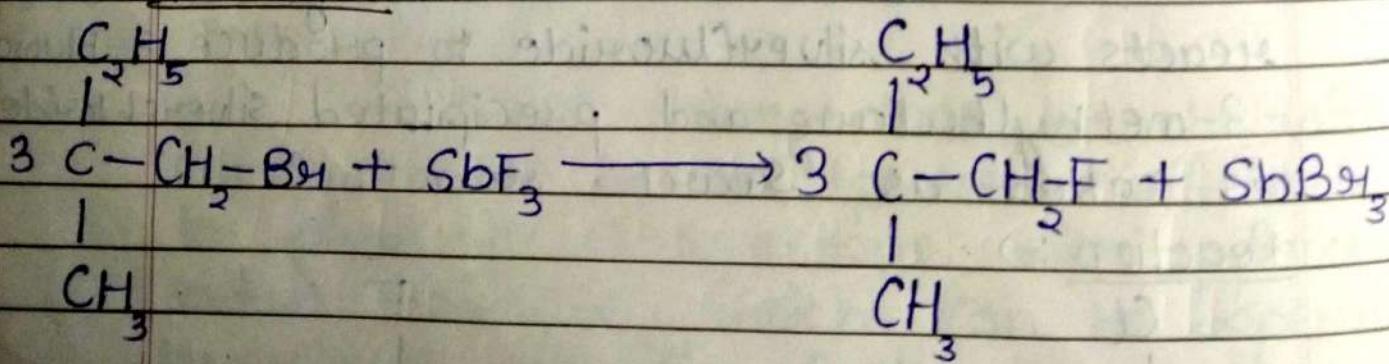
Reaction :-



(ii) Statement :-

When three molecules of 1-Bromo-2-methylbutane reacts with antimony trifluoride to give three molecules of 1-Fluoro-2-methylbutane and precipitated antimony trifluoride is called as 'Swartz reaction'.

Reaction :-



1-Bromo-2-methyl  
butane

1-Fluoro-2-methyl  
butane

## Chemical properties of haloalkane

### Substitution

- Formation of alcohol by NaOH/KOH
- Formation of alcohol by moist  $\text{AgNO}_3$
- Formation of 1° Amine
- Formation of cyanide
- Formation of Isocyanide
- Formation of Ether
- Formation of Ester
- Formation of Nitro
- Formation of Nitride

### Elimination

### $\beta$ -elimination

### Reaction of Metal

Wurtz's

Graignard  
Reagent

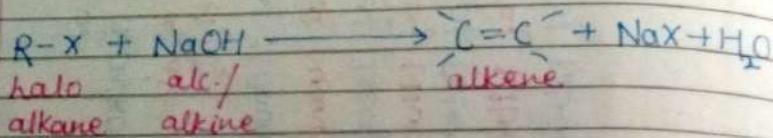
Compare with formation of alcohol by NaOH/  
due to medium change.

## AJ Elimination

### General Statement :-

When haloalkane reacts with alkylhydroxide ( $\text{NaOH}$ ,  $\text{KOH}$ ) in alcoholic medium ( $\text{alc}$  / alk) to produce corresponding alkene by ' $\beta$ -elimination reaction'.

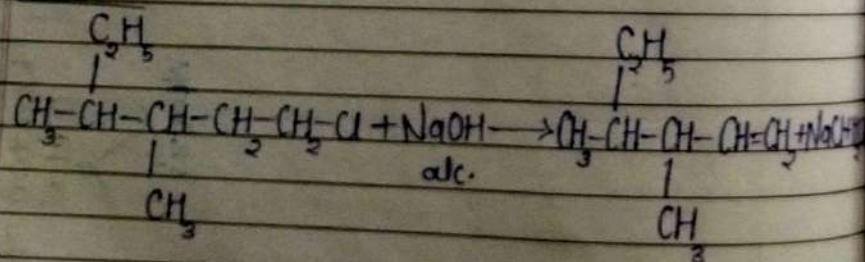
### \* General Reaction :-



\* Example :-

When 1-Chloro-3,4-dimethylhexane reacts with sodium hydroxide in alcoholic medium to produce 3,4-dimethylhex-1-ene with sodium chloride and water by  $\beta$ -elimination reaction.

### Reaction :-



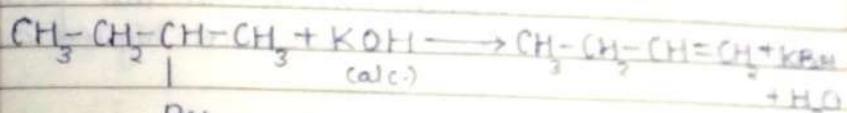
### 1-Chloro-3,4-dimethylhexane

### 3,4-dimethylhex-1-ene

## ⑪ Statement :-

When 2-Bromobutane reacts with potassium hydroxide in alcoholic medium to produce But-1-ene by  $\beta$ -elimination reaction.

Reaction :-



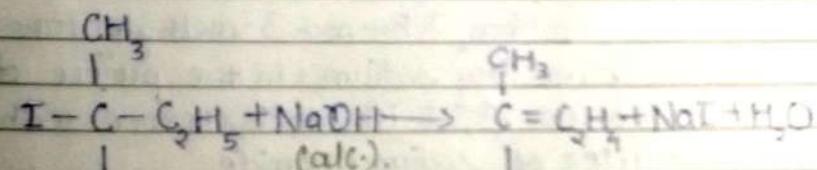
## 2-Bromobutane

But - 1 - e<sub>g</sub> a

### III Statement :-

When 3-Iodo-3,4-dimethylcyclohexene reacts with sodium hydroxide in alcoholic medium to produce 3,4-dimethyl-1,2-ene by  $\beta$ -elimination reaction.

Reaction :-



$$\text{HC}-\text{CH}_3$$

१२६

### 3-methoxy-3,4-dimethylseptane

### 3,4-dimethylpent-2-ene

B elimination :-

Saytzeff rule :- Dehydrohalogenation

What is the Saytzeff rule?

Imp Ques Statement:

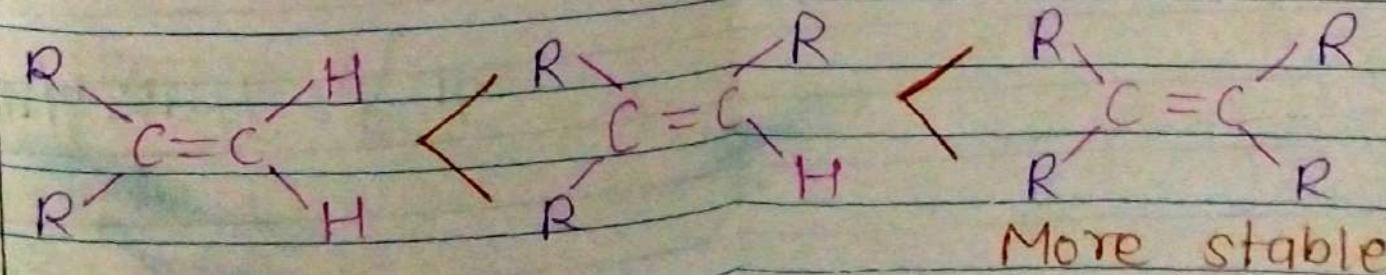
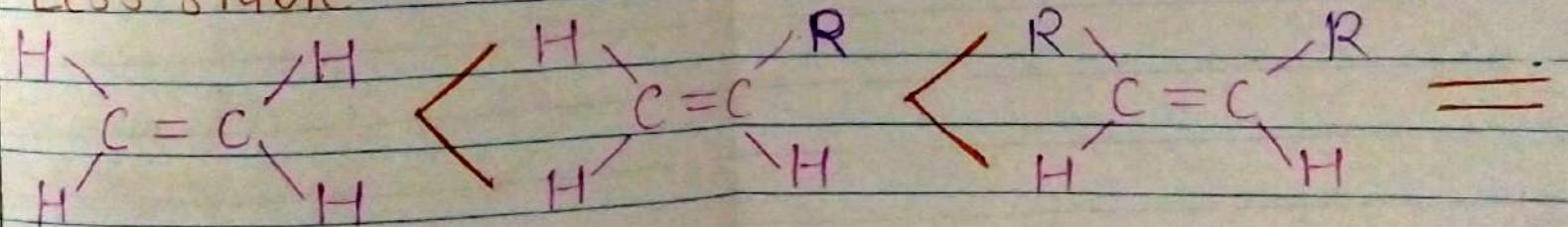
In the  $\beta$ -elimination reaction the preferred product is that alkene which have greater number of alkyl group attached to the doubly bonded carbon atom.

The greater number of alkyl group on doubly bonded carbon atom shows maximum stable product.

Condition

When multiple  $\beta$ -carbon with  $\beta$ -hydrogen undergoes elpmination.

Less stable



$(C_2H_5)_2O \rightarrow$  Dimethyl Ether = Dry Ether

Page No.: 102  
Date:

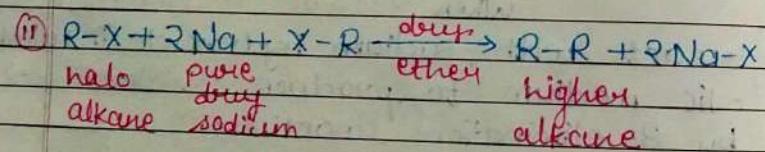
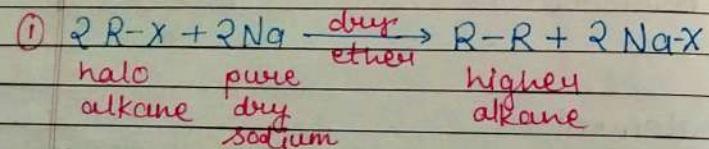
### B) Reaction with metal :-

#### (a) Wurtz's Reaction :-

#### General Statement :-

When the two molecules of that haloalkane (same) reacts with pure dry sodium metal in the presence of dry ether to produce higher alkane.

#### General Reaction :-

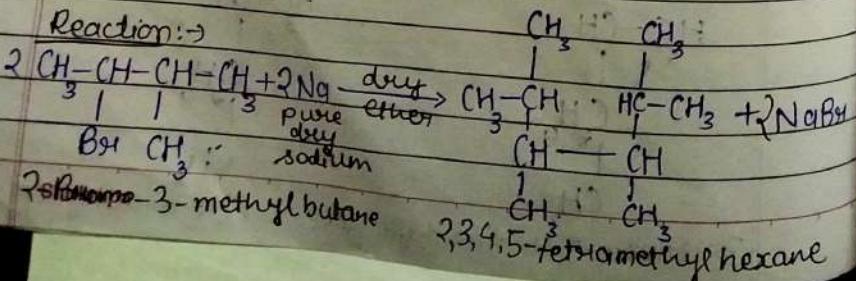


#### \* Example :-

#### ① Statement :- 2 molecules of

When 2-Bromo-3-methylbutane reacts with pure dry sodium in the presence of dry ether to produce 2,3,4,5-tetramethylhexane with two molecules of sodium bromide

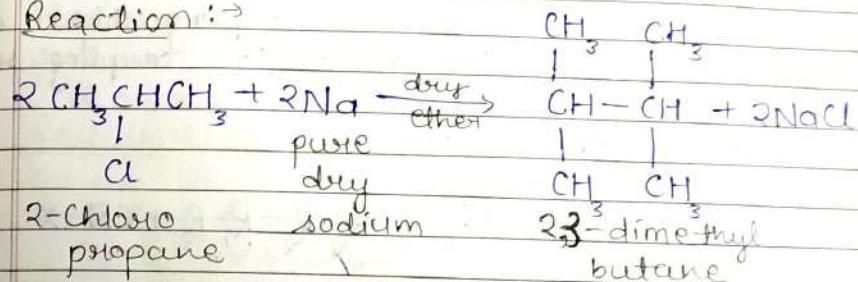
#### Reaction :-



-15

④ Statement :- 2 molecules of when 2-chloropropane reacts with pure dry sodium metal in the presence of dry ether to produce 2,3-dimethylbutane with two molecules of sodium chloride.

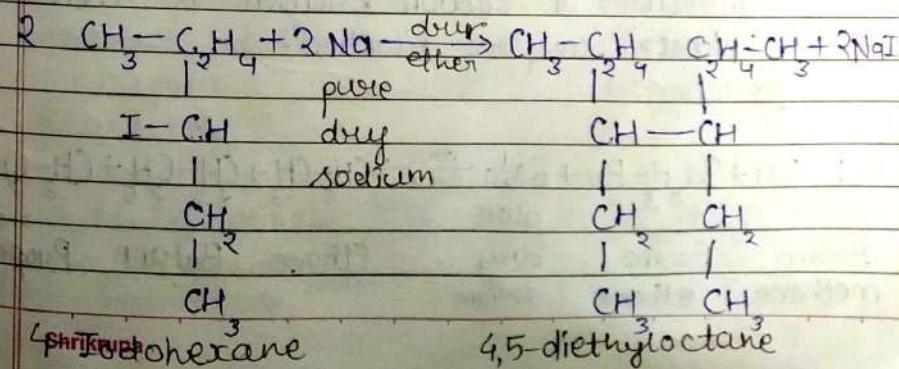
#### Reaction :-



#### ⑤ Statement :-

When 2 molecules of 4-Iodoheptane reacts with pure dry sodium metal in the presence of dry ether to produce 4,5-diethyloctane with two molecules of sodium iodide.

#### Reaction :-



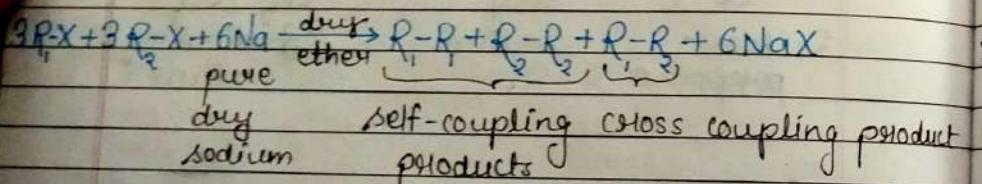
Page No.: 103  
Date:

### \* Wurtz's Coupling reaction (Aliphatic R-X) :-

General statement :-

When the different alkyl but same halide containing alkylhalide reacts with dry pure sodium metal in the presence of dry ether to produce two self coupling product and one cross coupling higher alkane product is called as 'Wurtz's coupling reaction'.

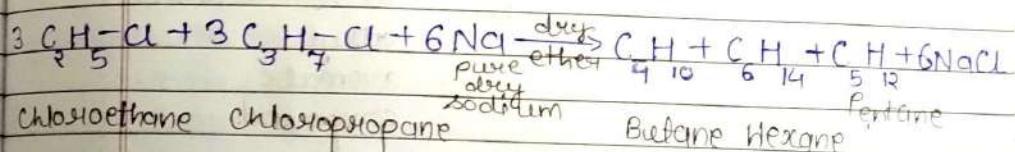
General Reaction :-



### (II) Statement :-

When 3 molecules of Chloroethane and 3 molecules of Chloropropane reacts with pure dry sodium in the presence of dry ether to produce 2 self coupling products as Butane and Hexane and 1 cross coupling product as Pentane is called as 'Wurtz's coupling reaction'.

Reaction :-

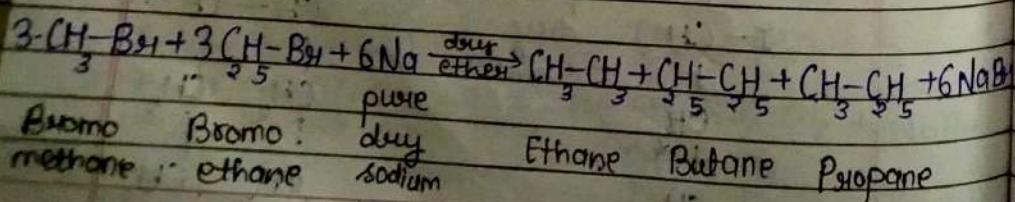


### \* Example :-

#### (I) Statement :-

When 3 molecules of Bromomethane and also of Bromoethane reacts with pure dry sodium in the presence of dry ether to produce two self coupling products as ethane and butane and one cross coupling product as propane with 6 molecules of sodium bromide is called as 'Wurtz's coupling reaction'.

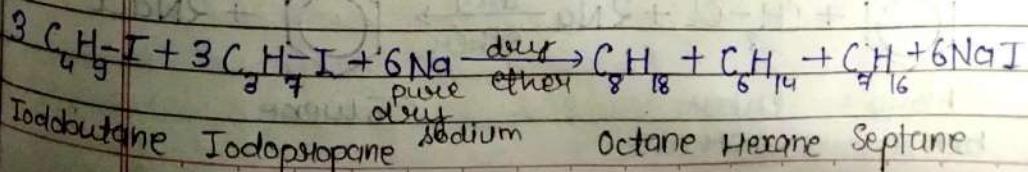
Reaction:-



### (III) Statement :-

When 3 molecules of Iodobutane and 3 molecules of Iodopropane reacts with pure dry sodium metal in the presence of dry ether to produce 2 self coupling products as Octane & Hexane and 1 cross coupling product as Septane with 6 molecules of sodium iodide is called as 'Wurtz's coupling reaction'.

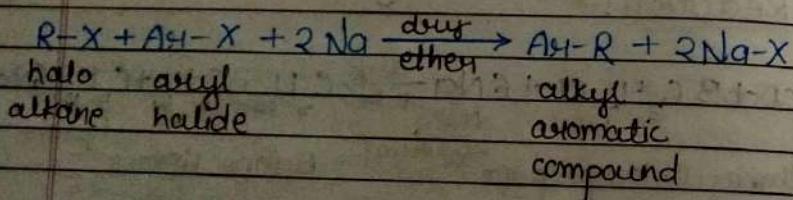
Reaction:-



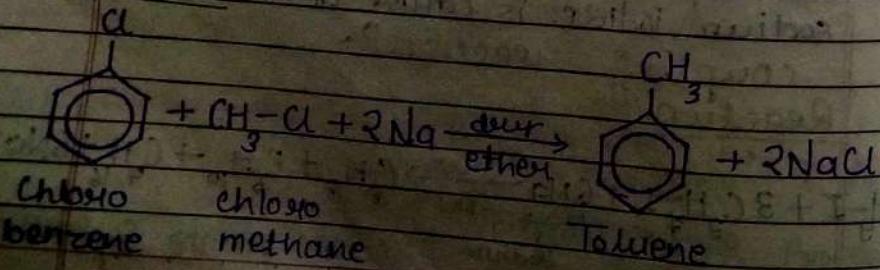
## ★ Wurtz's Fitting Reaction :-

General statement :-

When alkylhalide and arylhalide (both halides are same) reacts with pure dry sodium metal in the presence of dry ether to produce aromatic compound such a reaction is called as 'Wurtz's Fitting Reaction'.

General Reaction :-Example :-Statement :-

When chlorobenzene and chloromethane reacts with dry pure sodium in the presence of dry ether to produce Toluene with two molecules of sodium chloride such a reaction is called as 'Wurtz's Fitting Reaction'.

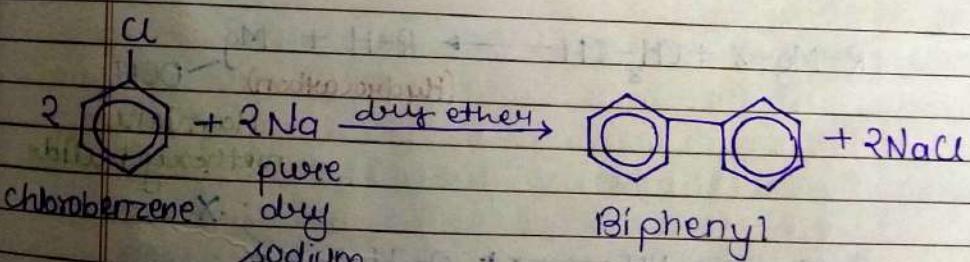
Reaction :-

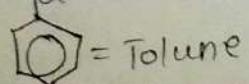
## ★ Fitting Reaction :-

When the two molecules of arylhalide reacts with pure dry sodium metal in the presence of dry ether to produce higher aromatic product, such reaction is called as 'fitting reaction'.

Example :-Statement :-

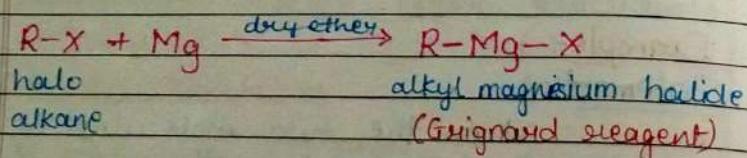
When the two molecules of chlorobenzene reacts with pure dry sodium metal in the presence of dry ether to produce biphenyl, such a reaction is known as 'fitting reaction'.

Reaction :-

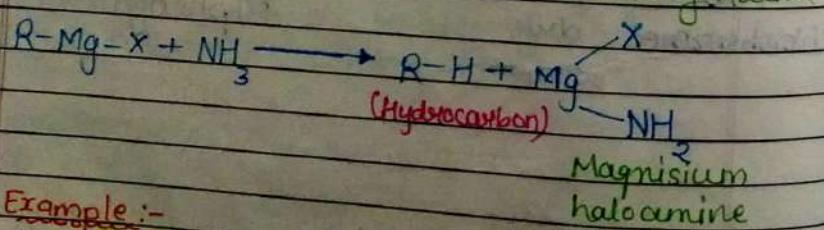
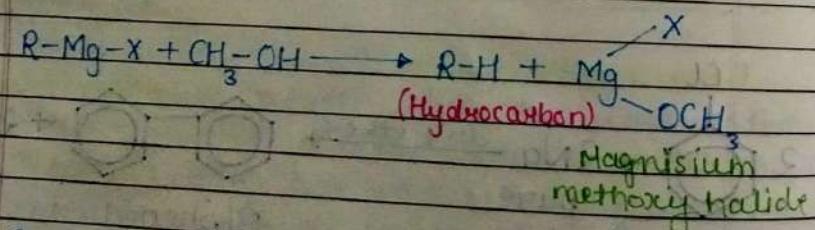


(b) Reaction with Magnesium (formation of Grignard reagent)  $\{R-Mg-X\}$

When alkyl halide is treated with magnesium in dry ether as solvent, it gives alkyl magnesium halide. It is known as Gilman's reagent.

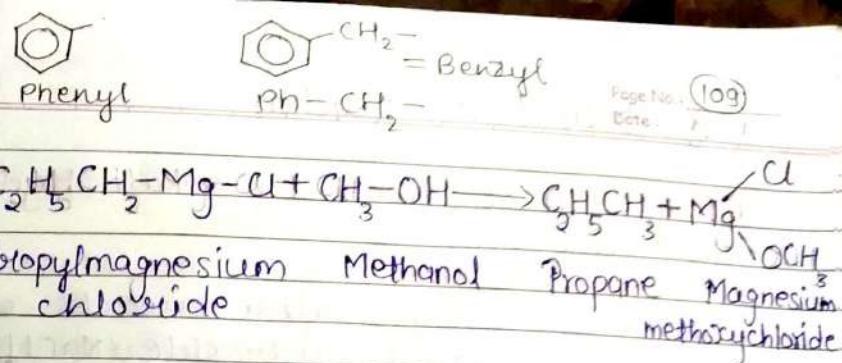


- Grignard reagent are very reactive compounds.
  - They react with water or compounds containing hydrogen attached to electronegative element.

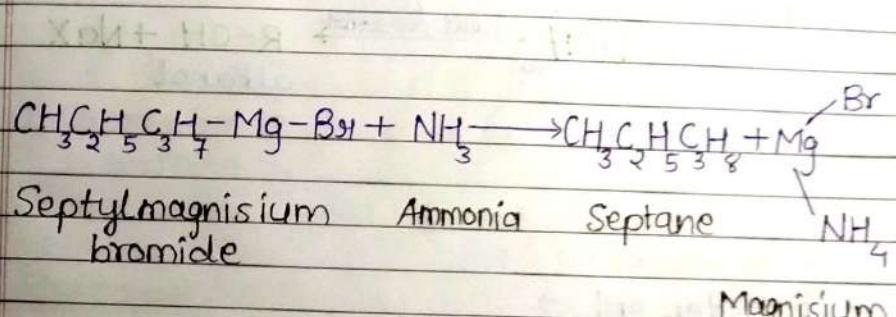


### \* Example :-

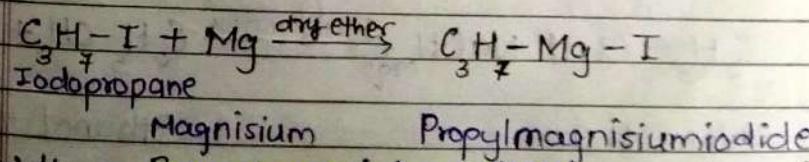
① When Propylmagnesium chloride reacts with Methanol to produce propane and Magnesium methoxy chloride.



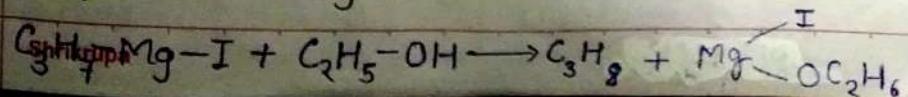
(ii) When **Septylmagnesiumbromide** reacts with Ammonia to produce **Septane** and **Magnesiumbromocamine**.



(iii) When Iodopropane is treated with magnesium in dry ether as solvent, it gives Propyl magnesium iodide; which is a Grignard reagent.



→ When **Potassiummagnesiumiodide** reacts with ethanol to produce Propane and **Magnesiumethoxy iodide**.



## B] Substitution Reaction

Page No.: 110  
Date: / /

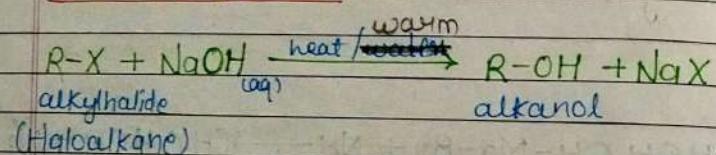
(a) Formation of alcohol by alkali hydroxide

(NaOH, KOH)

\* General statement :-

When the alkyl halide reacts with aqueous alkali hydroxide (NaOH, KOH) under heating/warming to produce corresponding alcohol by substitution reaction.

\* General Reaction :-

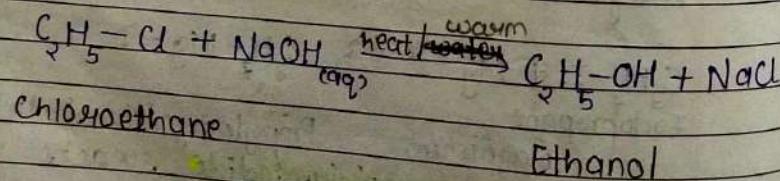


\* Examples :-

(i) Statement :-

When the chloroethane reacts with aqueous sodium hydroxide under heating/warming to produce ethanol by substitution reaction.

Reaction :-

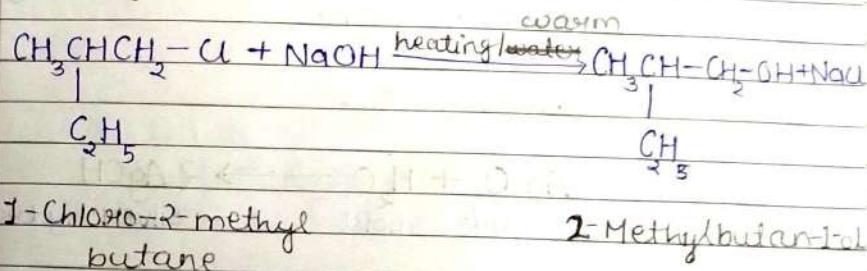


Shrikrupa

(ii) Statement :-

When the 1-Chloro-2-methylbutane reacts with aqueous sodium hydroxide under heating/warming to produce 2-Methylbutan-1-ol by substitution reaction.

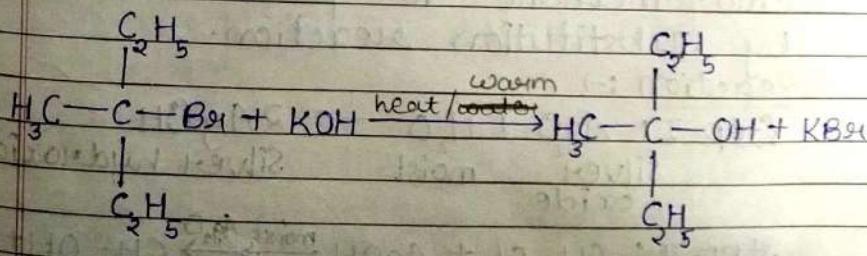
Reaction :-



(iii) Statement :-

When the 3-Bromo-3-methylpentane reacts with potassium hydroxide under heating/warming to produce 3-Methylpentan-3-ol by substitution reaction.

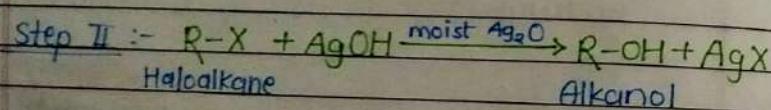
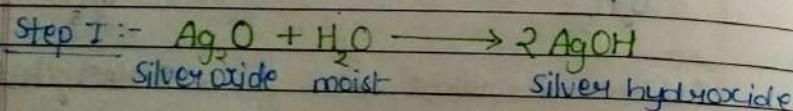
Reaction :-



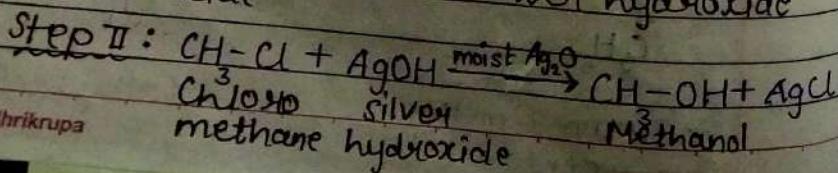
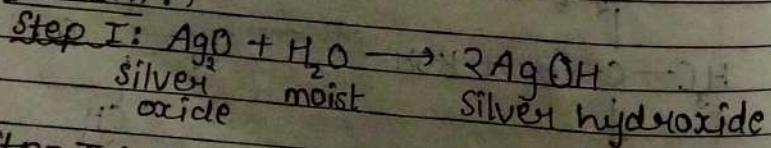
Shrikrupa

(b) Formation of alcohol by moist silver oxide ( $\text{Ag}_2\text{O}$ )**\* General statement :-**

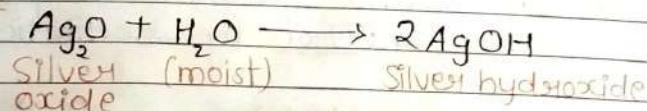
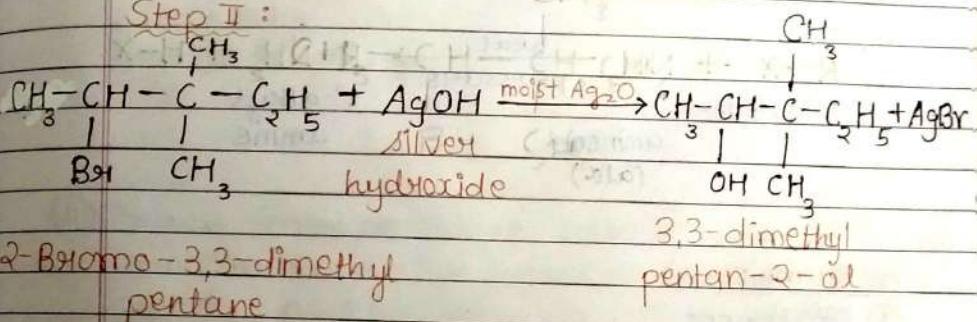
When silver oxide reacts with moist ( $\text{H}_2\text{O}$ ) to produce silver hydroxide, this silver hydroxide mainly reacts with haloalkane to produce alkanol by substitution reaction.

**\* General reaction :-****\* Examples :-****① Statement :-**

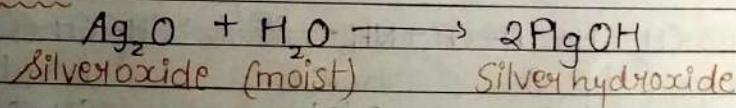
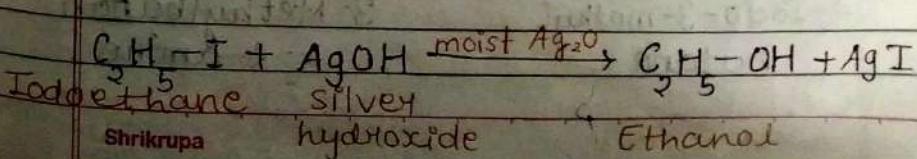
When silver oxide reacts with moist ( $\text{H}_2\text{O}$ ) to produce silver hydroxide, this silver hydroxide mainly reacts with chloromethane to produce methanol by substitution reaction.

**Reaction :-**

(ii) When silver oxide reacts with moist ( $\text{H}_2\text{O}$ ) to produce silver hydroxide, this silver hydroxide when reacts with 2-Bromo-3,3-dimethylpentane to produce 3,3-dimethylpentan-2-ol by substitution reaction.

**Step I:****Step II:**

(iii) When silver oxide reacts with moist ( $\text{H}_2\text{O}$ ) to produce Silverhydroxide, this Silverhydroxide when reacts with Iodoethane to produce Ethanol by substitution reaction.

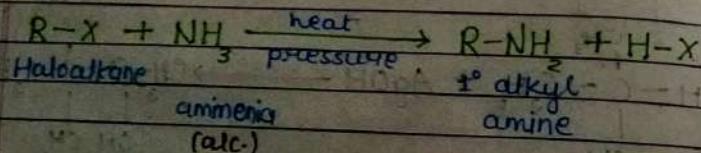
**Step I:****Step II:**

(c) Formation of primary amine :-

\* General statement :-

When alkyl halide reacts with alcoholic ammonia in the presence of heat and pressure to produce primary amine by substitution reaction.

\* General Reaction :-

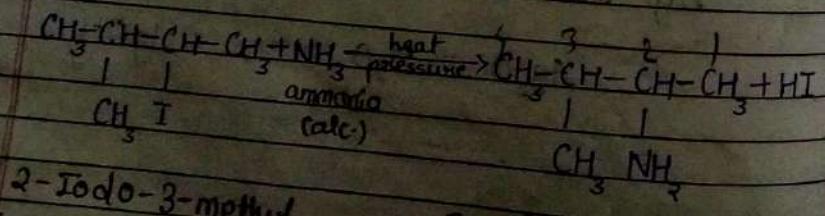


\* Examples :-

① Statement :-

When 2-Iodo-3-methylbutane reacts with ammonia in the presence of heat and pressure to produce 3-Methylbutan-2-amine by substitution reaction.

Reaction :-



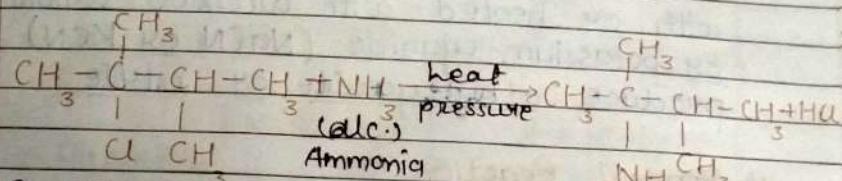
2-Iodo-3-methylbutane

3-Methylbutan-2-amine

3-Methylbutan-2-amine

Shrikrupa

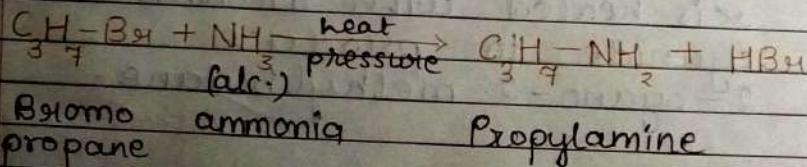
(ii) When 2-Chloro-2,3-dimethylbutane reacts with alcoholic ammonia in the presence of heat and pressure to produce 2,3-dimethylbutan-2-amine by substitution reaction.



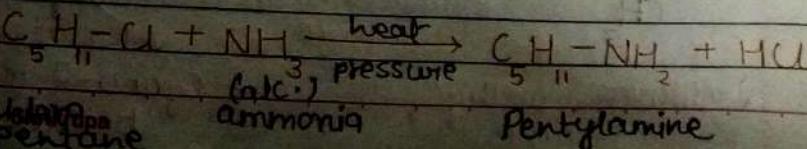
2-Chloro-2,3-dimethylbutane

2,3-dimethylbutan-2-amine

(iii) When Bromopropane reacts with alcoholic ammonia in the presence of heat and pressure to produce Propylamine by substitution reaction.



(iv) When Chloropentane reacts with alcoholic ammonia in the presence of heat and pressure to produce Pentylamine by substitution reaction.

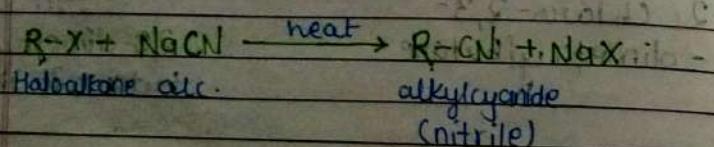


### (a) Formation of cyanide :→

## \* General statement :-

When alkyl halide reacts with  $\text{O}_2$  heated with alcoholic sodium cyanide or potassium cyanide ( $\text{NaCN}$  or  $\text{KCN}$ ) to produce alkyl cyanide or nitrile.

## \* General Reaction :-

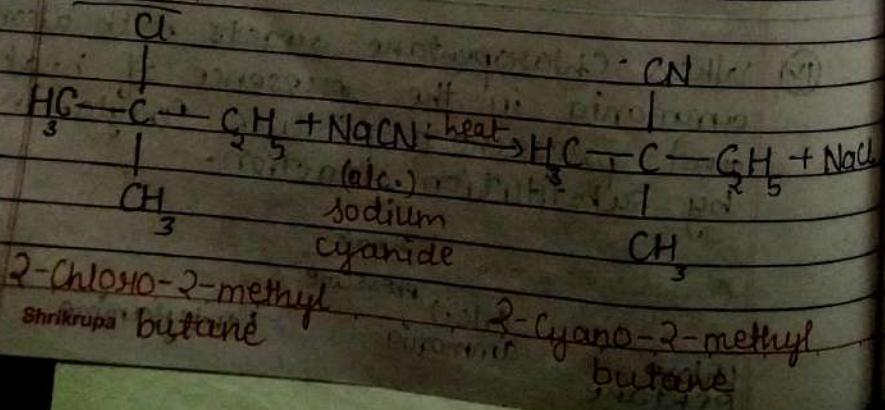


### \* Examples :-

## ① Statement:

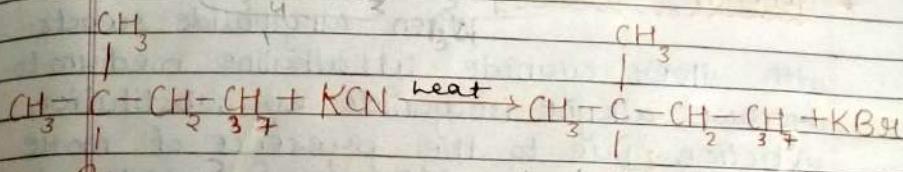
When 2-chloro-2-methylbutane is heated with alcoholic sodium cyanide to produce 2-cyano-2-methylbutane.

## Reaction:



2-Cyano-2-methyl butane is also called as  
2,2-dimethyl butannitrile Page No.: (117)

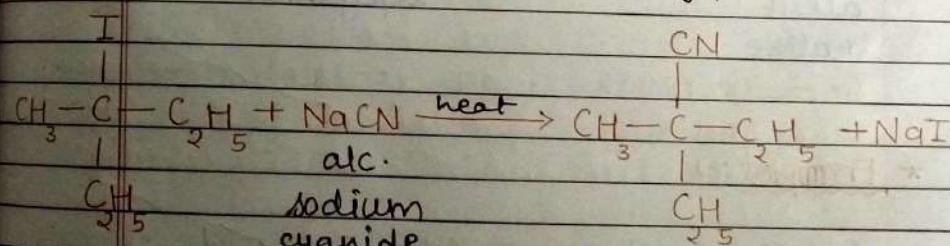
(11) When 2-Bromo-2-methylhexane is heated with alcoholic potassium cyanide to produce 2-Cyano-2-methylhexane.



~~2-Bromo-2-methyl  
hexane~~

2-Cyano-2-methylhexane

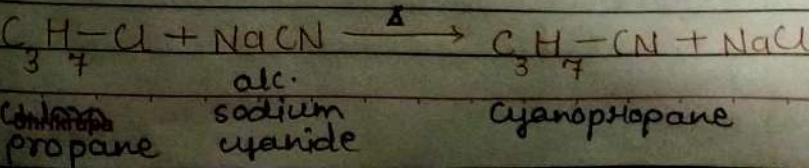
(iv) When 3-Todo-3-methylpentane is heated with alcoholic sodium cyanide to give 3-cyano-3-methylpentane.



3-Iodo-3-methylpentane

3-Cyano-3-methyl pentane

When Chloroform is heated with potassium cyanide to give Cyanoform.

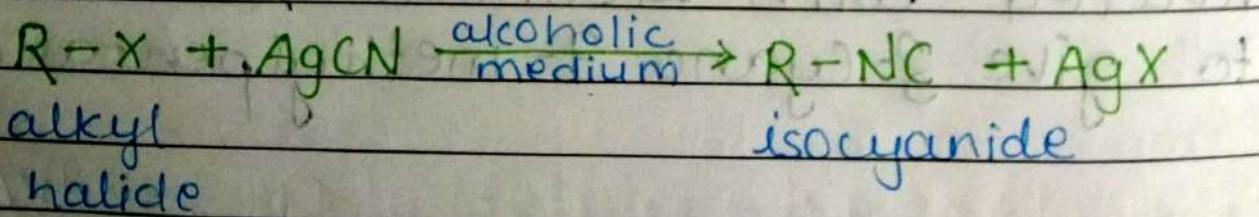


(e) Formation of isocyanide :-

\* General statement :-

When alkylhalide reacts with silver cyanide in alkaline medium to produce alkyne isocyanide by substitution reaction. {Due to the presence of more basic medium cyanide shows ambidentated nature and nitrogen have a tendency to form bond not carbon involve such type of bond called isocyanide bond or F.G.}

\* General Reaction :-

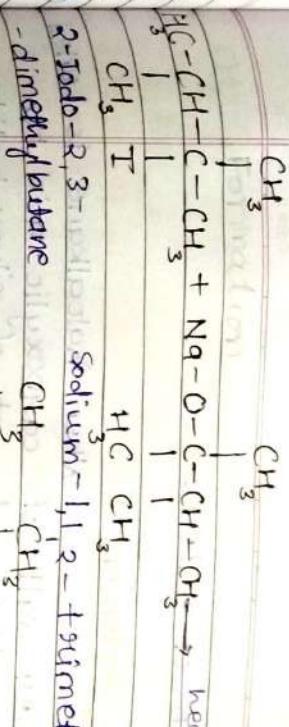


\* Examples :-

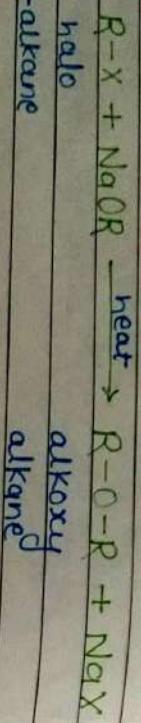
(f) Formation of ether :-



When haloalkane reacts with sodium alkoxide in the presence of heating to produce ether by substitution reaction



\* General Reaction :-



\* Examples :-)

When chloroethane reacts with sodiummethoxide in the presence of heat to produce methoxyethane by substitution reaction

(11) When pentyl bromide reacts with

Sodium methoxide in the presence of heat to produce ethoxypentane by substitution reaction.

$$\text{C}_5\text{H}_{11}\text{-Br} + \text{NaOC}_2\text{H}_5 \xrightarrow{\Delta} \text{C}_5\text{H}_{11}\text{-O-C}_2\text{H}_5 + \text{NaBr}$$

Pentyl bromide      Sodium ethoxide      Ethoxypentane

⑩ When 3-Chloropentane reacts with

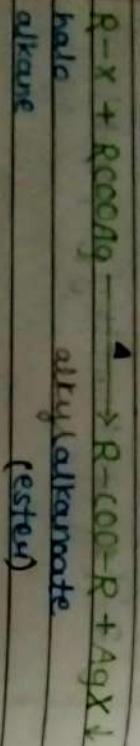
When 2- $\alpha$ -odo-2,3-dimethylbutano reacts with sodium-1,1,2,6-tinemethyl propanoate in the presence of  $\text{Pb}(\text{OAc})_4$  give 2- $\alpha$ - $\alpha$ -iodo-2,3-dimethylbutano.

(q) Formation of ester: →

\* General statement: →

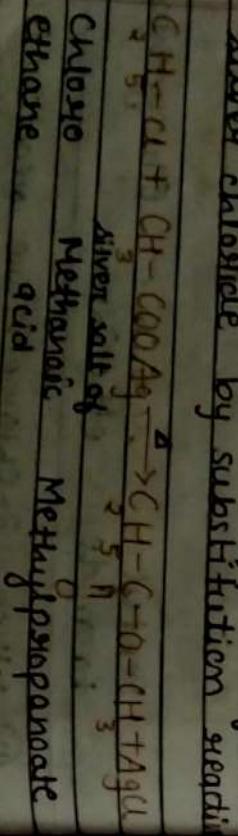
When alkane is heated with silver salt of carboxylic acid to produce ester and ppt. of silver halide by substitution reaction.

\* General reaction: →



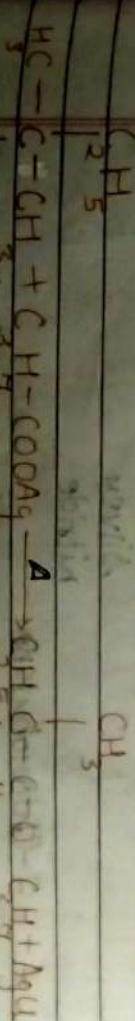
\* Examples:

① When chloroethane heated with silver salt of methanoic acid to produce methyl propanoate and ppt. of silver chloride by substitution reaction.



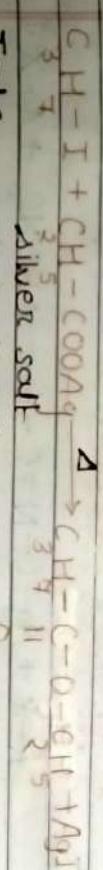
Chloroethane      Methanoic acid      Methyl propanoate

⑦ When 2-Bromopropane is heated with silver salt of methanoic acid to give chloroform and ppt. of silver chloride by substitution reaction.



2-Chloropropane      Methanoic acid      Chloroform

(ii) When 2-chloro-2-methylbutane is heated with silver salt of propanoic acid to produce Propyl(2,2-dimethyl) septanoate and ppt. of silver chloride by substitution reaction.



Bu<sup>1</sup>

of methanoic acid

Methylbutanoate

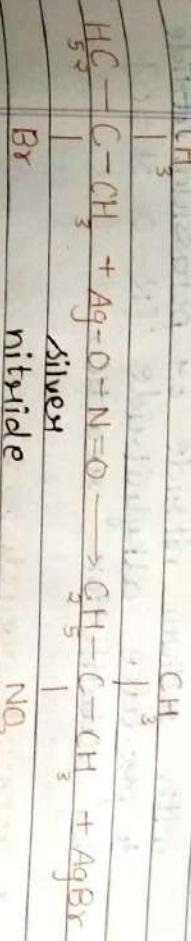
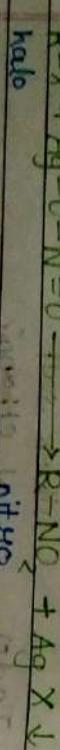
### (b) Formation of Nitro

\* General statement :→

When halokane reacts with silver nitride ( $\text{Ag}-\text{O}-\text{N}=\text{O}$ ) to produce nitroalkane by substitution reaction.

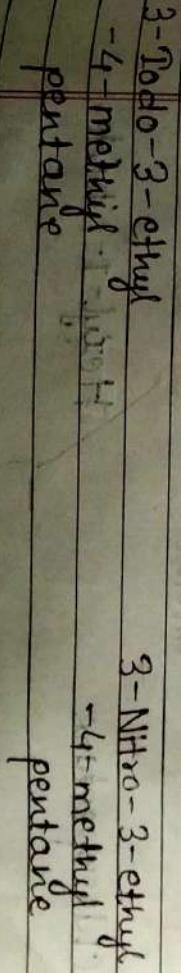
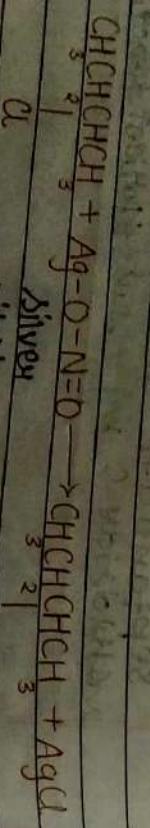
→ Due to the presence of silver, nitrogen have tendency to form a bond with alkyl.

\* General reaction :→



(ii) When 2-Bromo-2-methylbutane reacts with silver nitride ( $\text{AgNO}_2$ ) to give 2-Nitro-2-methylbutane by substitution reaction.

① When 2-Chlorobutane reacts with silver nitride ( $\text{AgNO}_2$ ) to produce 2-Nitrobutane by substitution reaction.



(i) Formation of Nitride : →

\* General statement : →

When haloalkane reacts with sodium nitride or potassium nitride to produce alkynitride [R - O - N = O] by substitution reaction.

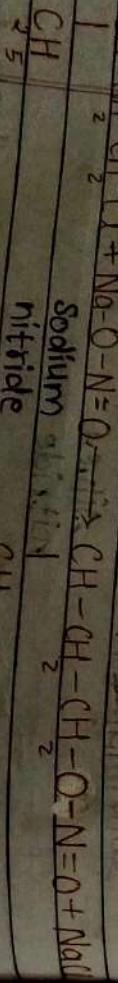
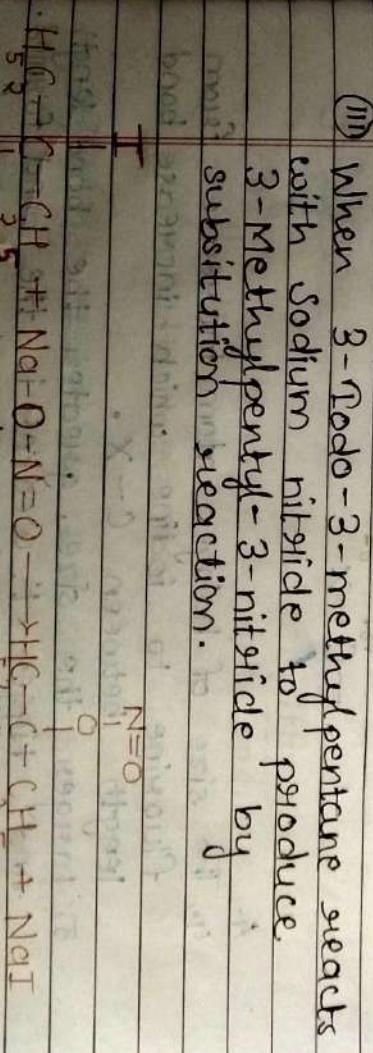
\* General reaction : →



Example : → When chloroethane reacts with

- ① When 1-Chloropentane reacts with sodium

nitride to produce Pentyl-1-nitride by substitution reaction.

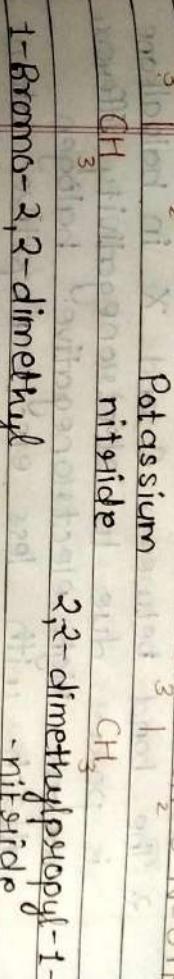
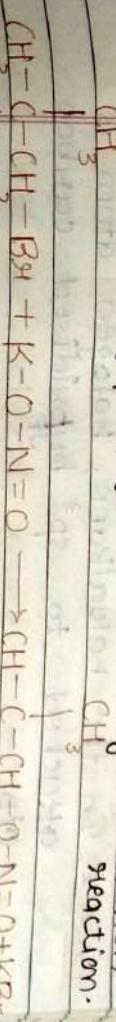


1-Chloropentane

Pentyl-1-nitride

(ii) When 1-Bromo-2,2-dimethylpropane reacts

with Potassium nitride to produce 2,2-dimethylpropyl-1-nitride by substitution reaction.



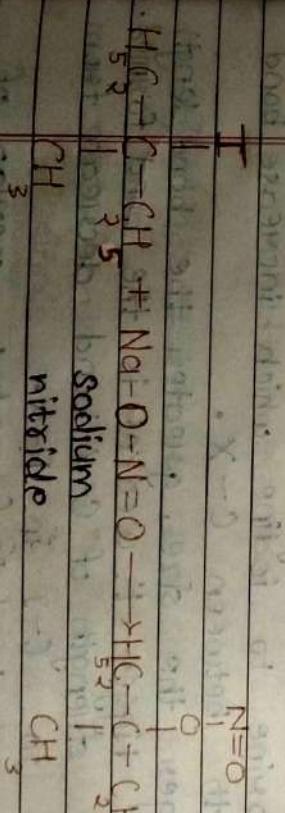
1-Bromo-2,2-dimethylpropane

potassium nitride

2,2-dimethylpropyl-1-nitride

potassium bromide

- With sodium nitride reacts with 3-Methylpentyl-3-nitride by substitution reaction.



Sodium

nitride

CH<sub>3</sub>

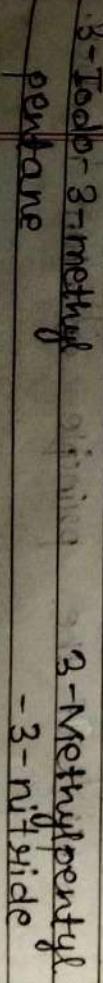
nitride

CH<sub>3</sub>

nitride

CH<sub>3</sub>

nitride



3-Methylpentyl

3-nitride

CH<sub>3</sub>

nitride

CH<sub>3</sub>

nitride

CH<sub>3</sub>

nitride

1-Chloropentane

Pentyl-1-nitride

Ques → Explain the nature of C-X bond in alkyl halide?

1. In the halalkane, halogen atom is attached to  $sp^3$  hybridised carbon atom.
2. The bond between C and X in halalkane is polar due to electronegativity difference means high electronegative halogen attach with less electronegative atom.
3. The carbon atom exhibit partial positive charge and halogen show partial negative charge.

### ③ # Nucleophilic substitution mechanism :-

#### A) d-d configuration :-

#### b) Ordinary light :-

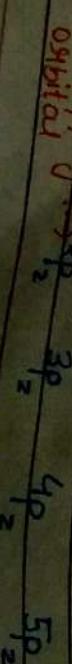
Ray of different wavelength vibrating in all possible planes, perpendicular to the direction of propagation of light.

#### b) Mono-chromatic light :-

Mono-chromatic light consist of ray of single wavelength (light of single colour) vibrating in different planes perpendicular to the direction of propagation of light.

e.g. laser light.

Overlapping



(13)

Date:

Page No.:

Optical activity depends upon chirality of solution

Plane of plane polarised light (PPL) towards right (clockwise) is called as "optical activity".

The organic substance which have a tendency to rotate plane polarised light towards plane of plane polarised light called as "optically active substance".

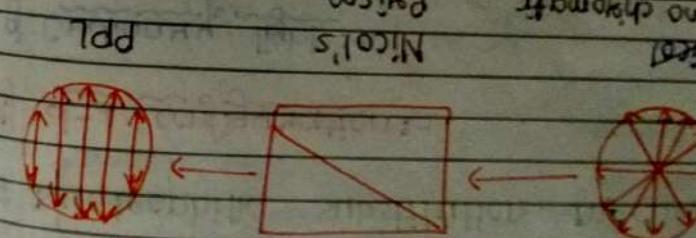
\* Optical activity :-

(c) Plane Polarised Light :- When the ordinary plane polarised light is passed through Nicol's prism it emerges out of it clockwise, since always vibration in the plane of wave consists of the light passing through Nicol's prism.

Nicol's prism is made up of calcite (CaCO<sub>3</sub>) which is a combination of two minerals fused to base by Canada balsam.

→ It is actually a combination of two minerals fused to base by Canada balsam.

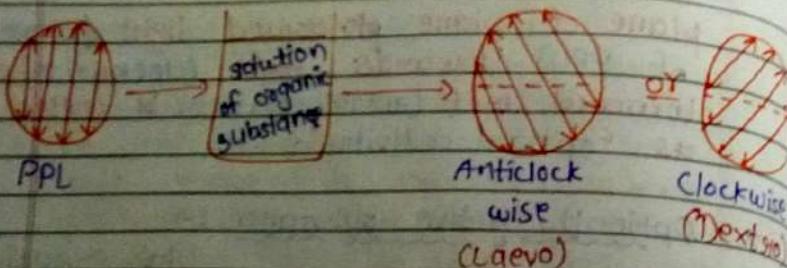
→ Optical activity :-



(d) Plane Polarised Light :- When the ordinary plane polarised light is passed through a crystal of zinc blende = ZnS = zinc sulphide, it is reflected from the surface of gold foil as shown in the figure.

Zinc blende = ZnS = zinc sulphide  
When the ordinary plane polarised light is reflected from the surface of gold foil as shown in the figure.

Me - Methyl =  $\text{CH}_3$   
Et - Ethyl =  $\text{C}_2\text{H}_5$   
(en) - diethylene

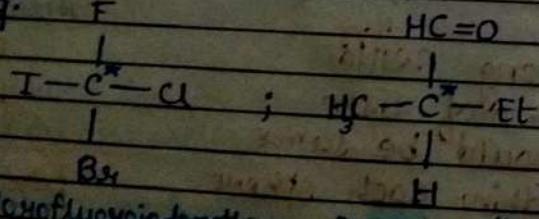


- \* Example of optically active substance :-  
1) Glucose 2) lactic acid 3) Chiral carbon atom containing compound

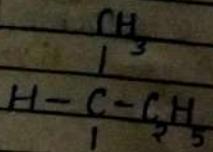
### ③ \* Chiral :-

When the carbon atom (only one) is attached to four different atoms or group of atoms such a carbon is called as 'chiral carbon atom'.

Eg. F



Bromo chloro fluoro iodomethane 2-Methylpropanal



2-Chlorobutane

Shrikrupa

\* represents chiral carbon atom

### ④ Dextro rotatory molecule :-

Molecule which can rotate the plane of plane polarised light to the right hand side (R.H.S.) are known as 'Dextro rotatory molecule'.  
Dextro = right = clockwise

→ It is denoted by (+) or 'd' sign  
eg. (+)-lactic acid,  
d-Glucose

### ⑤ Laevo rotatory molecule :-

The molecule which can rotate the plane of plane polarised light to the left hand side (L.H.S.) are known as 'Laevo rotatory molecule'.  
Laevo = left = anticlockwise

→ It is denoted by (-) or 'l' sign.

eg. (-)-lactic acid  
l-Glucose

### ⑥ Optical inactivity :-

When plane polarised light is passed through a solution of certain organic compound then the plane polarised light does not get rotated through a certain angle. This property / phenomenon of a certain organic substance not to rotate the plane of plane polarised light towards right or left is called as 'optical inactivity'.

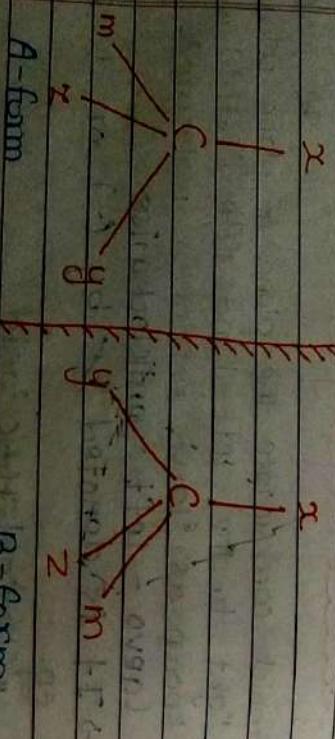
dextro = clockwise  
laevo = anticlockwise

Optical inactivity shown by **achiral** carbon atom containing a **symmetrical** compound.

\* Ans

(1) \* Enantiomers :-

The stereoisomers which are non-superimposable mirror images of each other and rotate the plane of plane polarised light through the same angle in opposite directions are known as 'enantiomers' or enantiomorphs'



A-form

Enantiomers

B-form

(2) \* Racemic mixture / Racemates :-

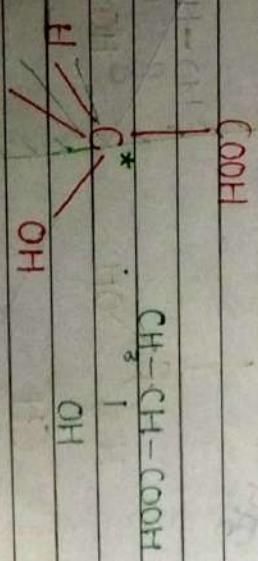
The equimolar amount of dextro and laevo isomers are mixed and the resulting mixture is found to be optically inactive due to external compensation such optically inactive case known as 'racemic mixture' or 'stereoisomer'. This is depicted by diagram

Shrikru

Ques: Explain the optical activity of lactic acid.

Ans: 1. Optical activity :-

When the plane polarised light passed through the solution of lactic acid which contain one chiral carbon atom therefore plane of plane polarised light get rotate left hand side and right hand side with same angle, such property shown by lactic acid which is called as 'optical activity of lactic acid'.  
2. Structure of lactic acid with chiral carbon atom :-



COOH

$\text{CH}_3-\text{CH}-\text{COOH}$

H

OH

Lactic acid  
(2-Hydroxypropanoic acid)

Second carbon is chiral carbon atom.

Eq.  $(\pm)$  Lactic acid  $\text{C}_3\text{H}_6\text{O}_3$

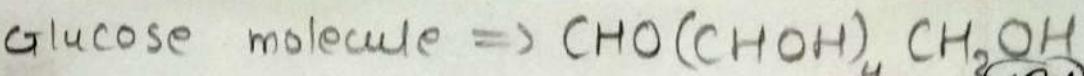
~~impossible~~  $\Rightarrow$  impossible

Page No.:  
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## Enantiomers :-

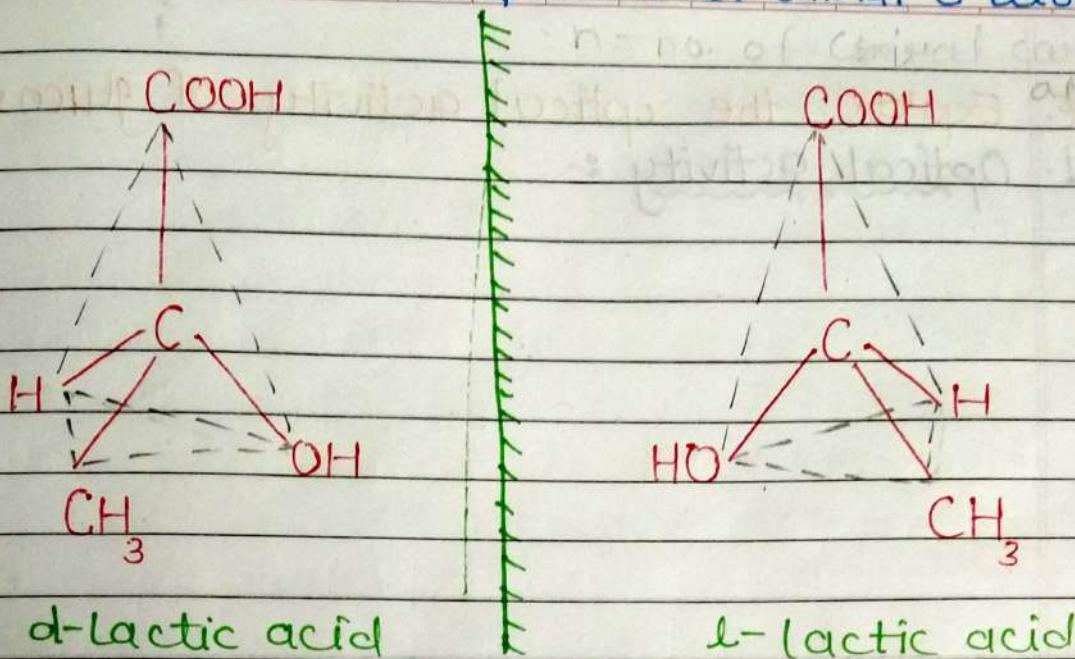
In the lactic acid second carbon show chirality means  $-CH_3$ ,  $-COOH$ ,  $-OH$  and  $-H$  groups attach on carbon atom, lactic acid show non-superimposable mirror image means 'enantiomers'.



$2^n$  = No. of Enantiomers;  $n$  = no. of Chiral C-atom

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### Enantiomers of lactic acid

4. Racemate / Raemic mixture :-

The equimolar

amount of dextro and laeo isomers of lactic acid are mixed and the resulting mixture is found to be optically inactive due to external compensation such optically inactive lactic acid is known as racemic mixture. It is denoted as / written as, 'dl-lactic acid'.

chiral = chiral

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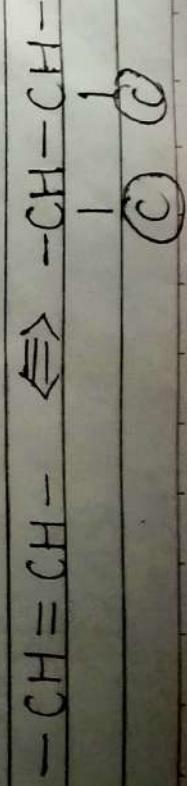
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### B) R-S configuration :-

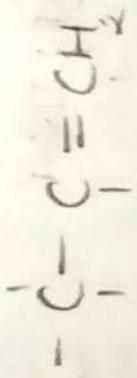
1. R-S convention or 'Cahn-Ingold-Prelog system' is based on the priority of groups attached to chiral carbon atom.
2. The priority first assigned on the basis of atomic number of the atom that is directly attached to chiral carbon atom.
3. The atom with lowest atomic number is given the lowest <sup>last</sup> priority.
4. The atom with next higher atomic number is given the next priority and so on.
5. When a priority can not be assigned on the basis of atomic number of atom that is directly attached to the chiral centre.
6. Then the next set of atom in the unassigned group is examined. This process is continue till decision is made.
7. When a multiple bond is present both the atoms attached to the double or triple bond are considered to be duplication or triplication.

Example



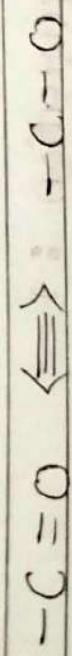
2-Phantom C-atom

Shrikrupa



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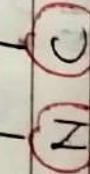
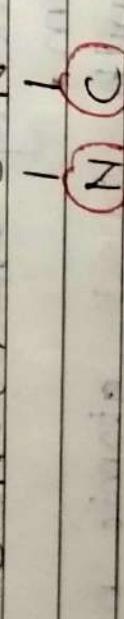
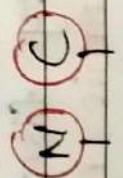
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Phantom O-atom

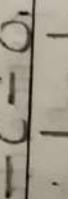
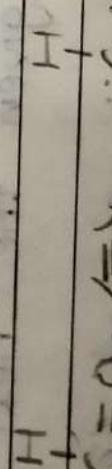
Phantom C-atom

\*  
~~trap~~



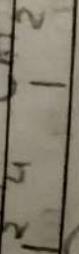
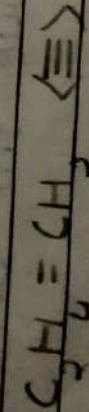
2- Phantom N-atom

2- Phantom C-atom

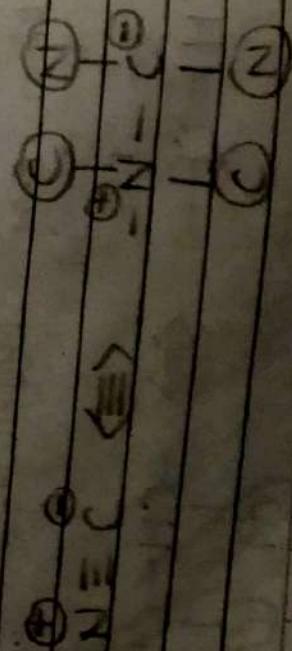


Phantom O-atom

Phantom C-atom



2- Phantom C-atom



$-C^{\bullet}-OR =$  Ether

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8. The priority sequence is determined by consideration of duplicated or triblicated structures in which there are phantom atoms.

\*★ 9. The order of priority is,

$I > Br > Cl > SO_3^- > NH_3^+ > COOCH_3 > OH^-$   
 $> NO_2 > CHO_3^+ > COOCH_3 > COOH > CONH_2$   
 $> COCH_3 > CH_3CHO > CH_3^2OH > CN^- > CH_3^-$   
 $> C_2H_5 > CH_3 > D > A > H$ .

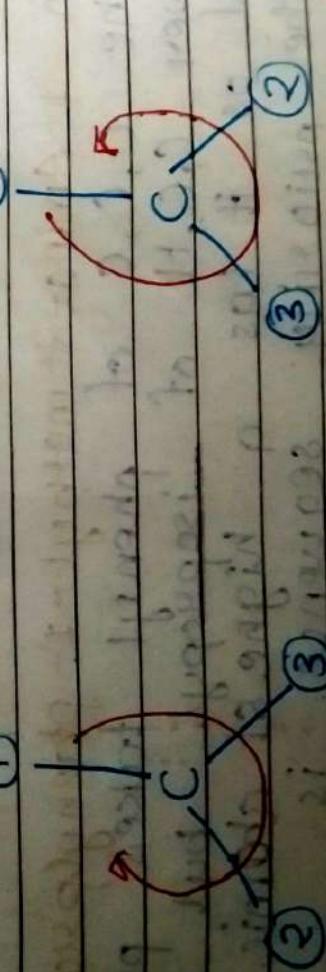
10. The R-S convention is based on the actual three dimensional or tetrahedral structure of molecule.

11. The molecule is viewed with the group of lowest priority behind chiral carbon atom.

12. If the clockwise arrangement of order three groups is in descending priority. The (R) and (S) are from the latin word, 'rectus' meaning right and 'sinister', meaning left.

13. If the group of lowest priority is on the front side of chiral carbon atom the actual configuration will be opposite to the observed configuration.

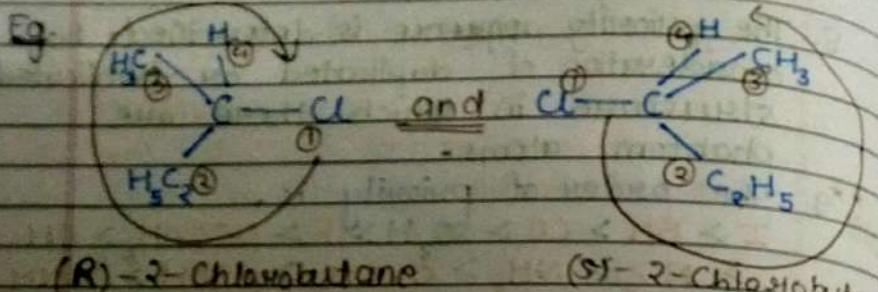
①



S-configuration  
R-configuration

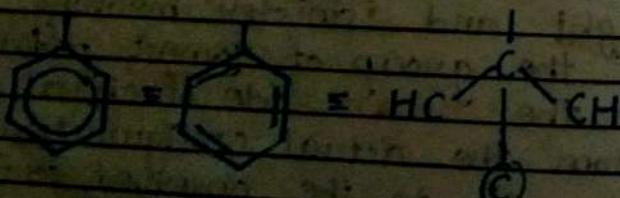
Kekulé & six carbon ring structures  
वेन्यु ३८

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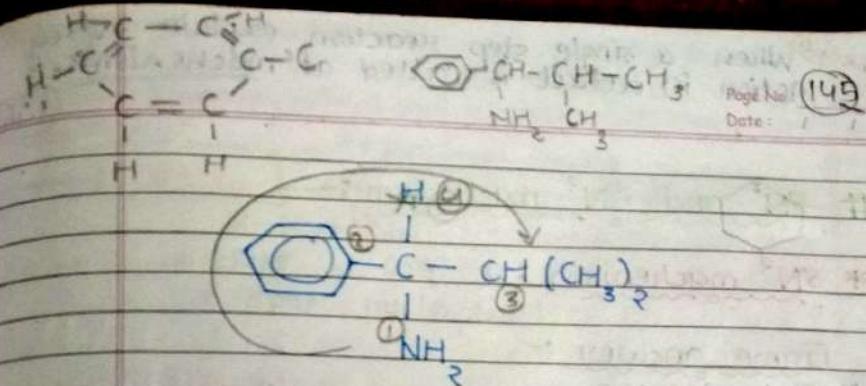


Q4 Aldehyde ( $-CHO$ ) group is given higher priority than  $-CH_2OH$  group. This is because of carbon atom in aldehyde group is attached to the one hydrogen atom, one oxygen atom and one phantom oxygen atom ( $H, O, O$ ) and the carbon atom in  $-CH_2OH$  group is attached to <sup>two</sup> hydrogen atoms and one oxygen atom ( $H, H, O$ )

Q5 To phenyl group is considered as one of the Kekulé structures

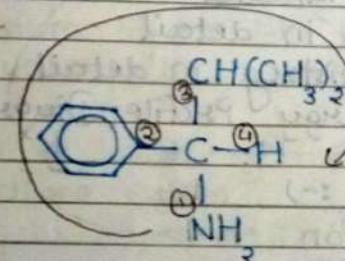


Q6 To 1-Amino-2-methyl-1-phenylpropane, the C.C.C. of phenyl takes priority over C.C.H. of imidaryl but not over N or F i.e. not higher atomic no., the priority of higher atomic no. is  $NH_2 > CH_3 > F$



1-Amino-2-methyl-1-phenylpropane

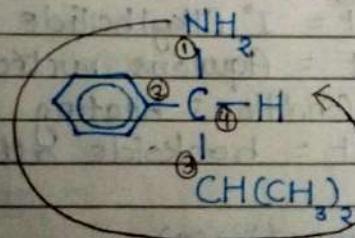
Rectus form:-



Clockwise

(R)-1-Amino-2-methyl-1-phenylpropane

Sinister form:-



Anticlockwise

(S)-1-Amino-2-methyl-1-phenylpropane

Mechanism When a single step reaction explain every action in detail is called as 'mechanism'.

## # $SN^2$ and $SN^3$ mechanism :-

### \* $SN^2$ mechanism :-

Frame answer :-

- (i) Introduction.
- (ii) Chemical reaction
- (iii) Chemical kinetics
- (iv) Mechanism in detail
- (v) Stereochemistry in detail
- (vi) EPD - Energy Profile Diagram

### (i) Introduction :-

S - Substitution

N - Nucleophile

2 - Bimolecular

means Bimolecular nucleophilic substitution reaction that concept is symbolized by  $SN^2$

### 2. Conditions :-

(a) Reactant = 1° Alkyl halide (ions) ( $R-X$ )

(b) Reagent = Aqueous nucleophile ( $OH^-$ )

(c) Reaction Condition = Heating

(d) Product = backside attack (100%)

(inversion)

### (ii) Chemical reaction :-

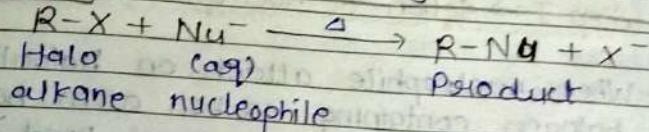
#### General reaction :-

When haloalkane reacts with aqueous nucleophile to produce corresponding substituted product by heating.

Lewis base Nucleophile = -ve charge = Electron rich species  
↓ donors Nucleus loving

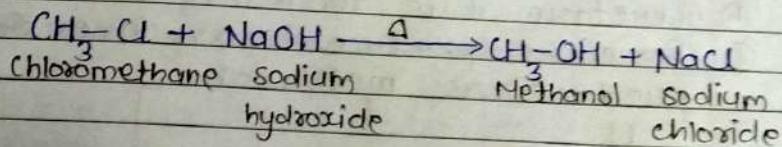
Lewis acid = Electrophile = +ve charge = Electron deficient species  
↓ acceptors Electron loving

### (b) Example

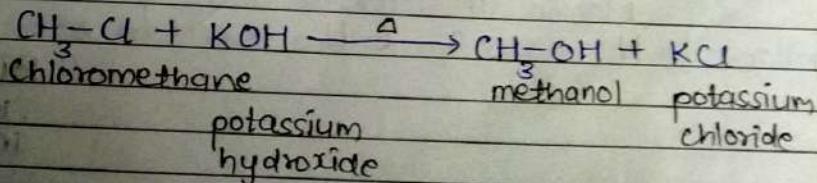


### (b) Example :-

When chloromethane is heated with aqueous sodium hydroxide / potassium hydroxide to give methanol by nucleophilic substitution reaction.



or

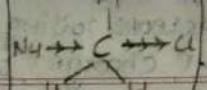


### (iii) Mechanism :-

The mechanism of  $SN^2$  reaction is single step.

Therefore it is rate determining step (RDS).

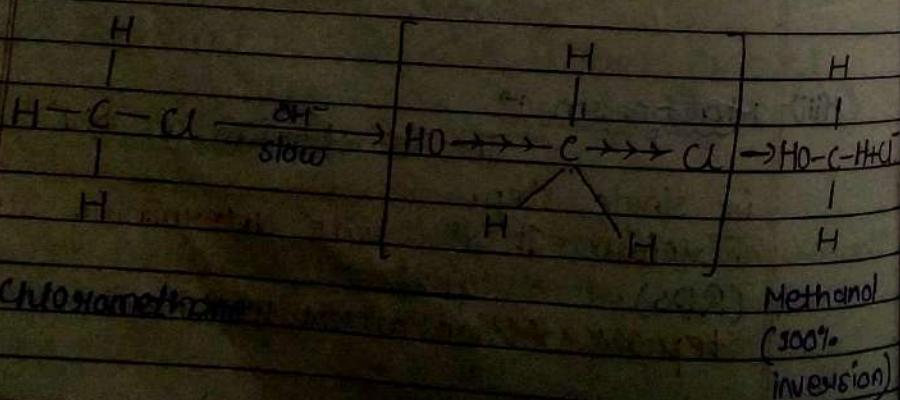
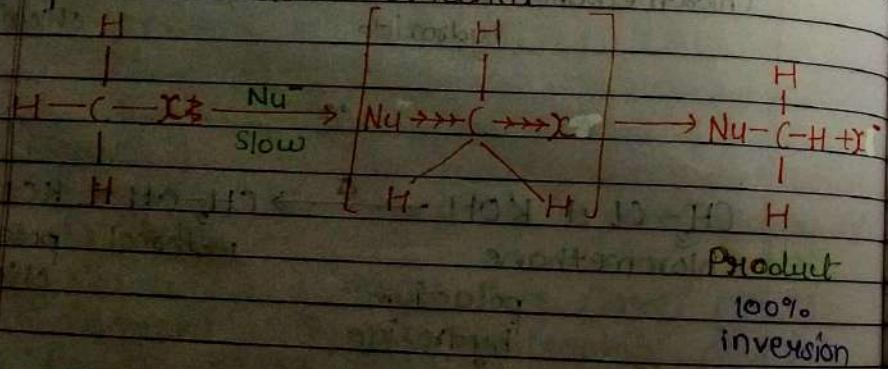
Step 1  $\nrightarrow$  Action of nucleophile



Unsaturated sphere

### Step I : Action of nucleophile :-

1. When nucleophile attack on haloalkane means halogen containing carbon atom by 100% backside of carbon-halogen bond ( $\text{C}-\text{X}$  bond).
  2. Therefore, it is 100% inversion reaction.
  3. Therefore produce 100% inversion product.
- (a) When  $\text{OH}^-$  attack on chloromethane means by 100% backside of carbon-chlorine bond ( $\text{C}-\text{Cl}$  bond).
- (b) Therefore it is 100% inversion reaction.
- (c) Therefore produce 100% inversion product i.e. methanol.



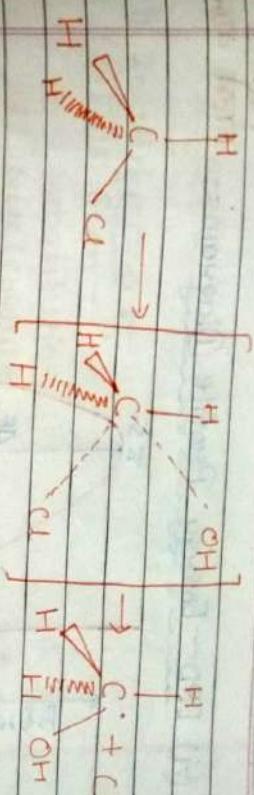
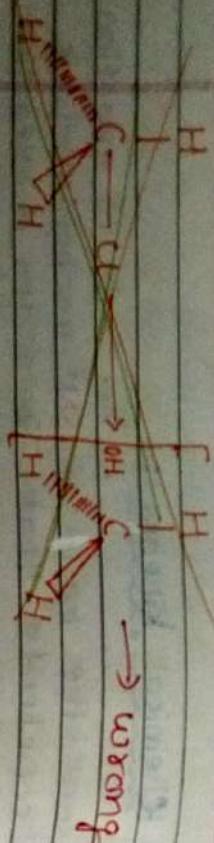
Chloromethane

### (iv) Chemical kinetics :-

1. The rate of reaction on the basis of  $\text{SN}^2$  mechanism we conclude that single step of reaction is slow step reaction which is called as rate determining step used for calculation of rate of reaction.
2. The rate of reaction is directly proportional to product of concentration of reactants present in the RDS means slow step.
3. According to above mechanism, rate  $R \propto [\text{CH}_3\text{Cl}] [\text{OH}^-]$
4. Therefore, this reaction is bimolecular because the order of above rate reaction is 2.

### (v) Stereochemistry :-

1. Stereochemistry is totally depend on mechanism of reaction, to explain its structural representation or geometry.
2. The ~~be~~ nucleophile ( $\text{OH}^-$ ) attack on the carbon atom from backside of carbon-halide bond ( $\text{C}-\text{Xl}$  bond).
3. Because it is least hindrance and there is electrostatic force of attraction between nucleophile and positively charged particle.



三

In this case  $\text{CH}_3\text{-OH}$  formed from backside attack<sup>3</sup> ~~out~~ by frontside attack is one and the same.

\* Even if the ~~same~~ is the same.

Ever since the attack has taken place from some other side than the same

$\text{CH}_3\text{-OH}$  bond would be formed.

\* heretofore, it is not possible to know from which side <sup>the</sup> micrometeorites

4. Due to the backside attack the tetrahedral arrangement about carbon atom in the product has become opposite to the reactant, this is known as inversion of configuration.

inversion of configuration -

Frontside attack take place :-  
In case of frontside attack the occupier takes position with occupied by C. In the meantime

the position of the  $H_2$  and  $H_3$  also sterically  
the carbon atoms. The  $H_2$  and  $H_3$  also sterically  
2. Therefore, the coordination of carbon  
is retained. This is shown in ~~below~~.

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(vi) E.P.D - Energy Profile Diagram :- दिति अंतर्गत विषय

\*  $S_N^1$  mechanism :-

(i) Introduction :-

(i) Full form :-

S = Substitution

N = Nucleophile

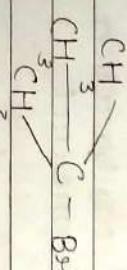
1 = Unimolecular

means Unimolecular nucleophilic substitution reaction that concept is symbolized by  $S_N^1$ .

(ii) Condition :-

(a)

Reactant =  $3^\circ$  alkyl halide ( $R_3C-X$ )



where,  
 $R$  = Reactant = Chloromethane  $\rightarrow CH_3Cl$

P.T. Product = Methanol  $\rightarrow CH_3OH$   
 T.S. = Transition State =

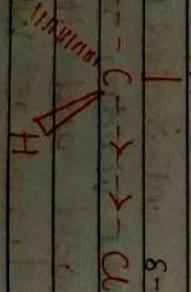
$= \left[ \begin{array}{c} H \\ | \\ O- \\ | \\ C- \\ | \\ Cl \end{array} \right]$

(b) Reagent = Strong nucleophile ( $OH^-$ )

(c) Reaction condition = heating (Δ)

(d) Product = 50% frontside attack product

+ 50% backside attack product



T.S.

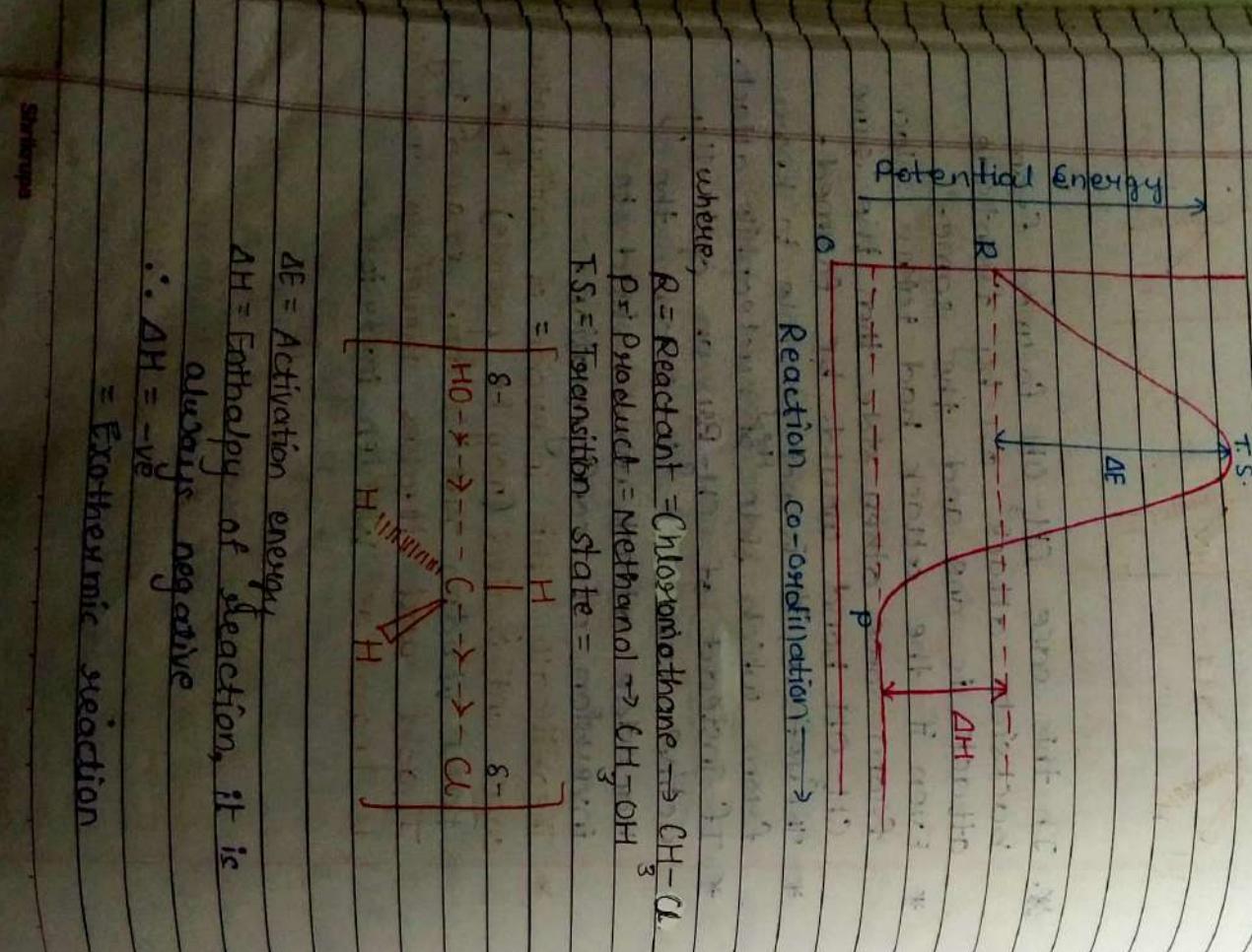
Reaction co-ordination  $\rightarrow$

Statement :-

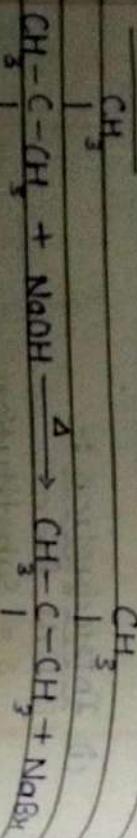
$\Delta E$  = Activation energy  
 $\Delta H$  = Enthalpy of reaction, it is

always negative

$\therefore \Delta H = -ve$   
 = Exothermic reaction



Reaction :-



Bu

OH

2-Bromo-3-methyl  
propane      2-Naethyl  
propan-2-ol

(ii) Mechanism :-

The 2nd reaction mechanism

is proceed out in two steps.

A) Formation of carbocation

B) Formation of product

Step-A] → Formation of carbocation

i. When alkylhalide (2-Bromo-3-methylpropane) is heated then carbon bromide bond (C-Br bond) slowly breakdown and form tertiary butyl carbocation.

2. This carbocation had planar geometry. This step is very slow, therefore, it is RDS (rate determining step).

3. The reaction is in equilibrium.

4. Therefore, this step involve in calculation

of rate of reaction (rate law).

5. The reaction is in equilibrium.

6. This tertiary butyl carbocation is

planar geometry and highly un-

stable.

7. This tertiary butyl carbocation is

planar geometry and highly un-

stable.

8. Due to this planar geometry

central positive carbon atom

easily attack with nucleophile.

9. The tertiary butyl carbocation,

positive carbon atom have multiple

option on position for nucleophilic attack

on positive carbon atom.

10. That means positively charge carbon

atom on tertiary butyl carbocation

have frontside as well as backside attack.

Formation of product

OR

Action of carbocation on nucleophile

OR

1. Tertiary butyl carbocation have

planar geometry.

2. Due to this planar geometry

central positive carbon atom

easily attack with nucleophile.

3. The tertiary butyl carbocation,

positive carbon atom have multiple

option on position for nucleophilic attack

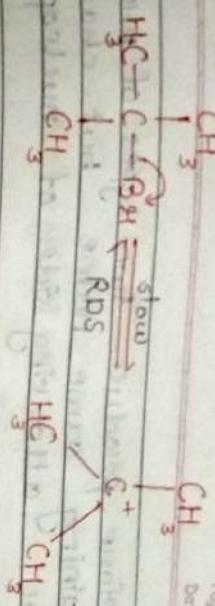
on positive carbon atom.

4. That means positively charge carbon

atom on tertiary butyl carbocation

have frontside as well as backside attack.

Reaction :-



2-Bromo-3-methyl

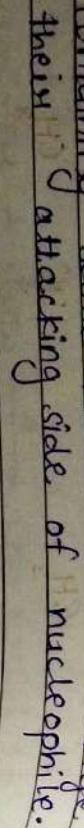
propane

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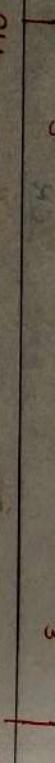
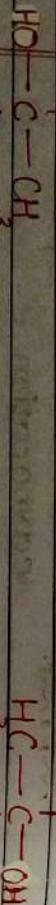
5. Therefore, produce two types of product containing same name but change their attacking side of nucleophile.

R & [Reaction]



$\text{HC}-\text{CH}_3$        $\text{CH}_3$        $3^\circ$  Butylcarbocation

Backside attack      Frontside attack



50% Eversion

50% Retention

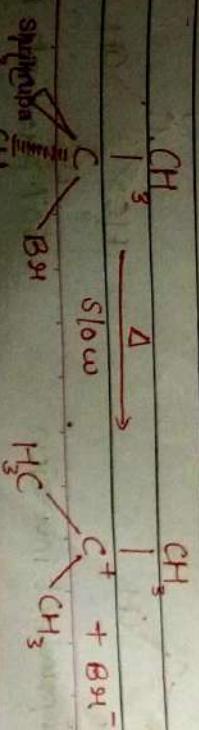
(iv) Steriochemistry :-

On the basis of mechanism  $\text{SN}^+$  mechanism proceed two steps.

#### A) Formation of carbocation:

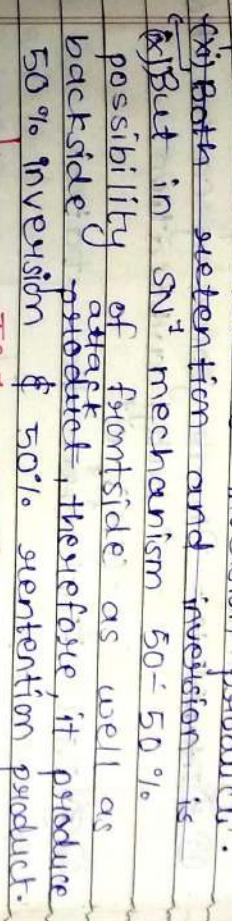
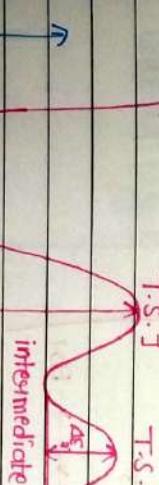
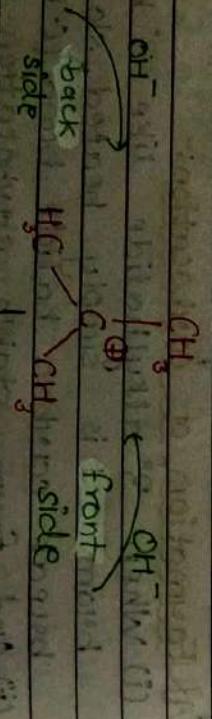
- When  $3^\circ$  alkylhalide like  $3^\circ$  butyl bromide is simply heated, slowly break carbon halide bond ( $\text{C}-\text{Br}$  bond).
- And form stable carbocation like  $3^\circ$  butylcarbocation.
- This structure in  $3^\circ$  butylcarbocation show planar geometry.

- Because of RDS step means 1st step of mechanism is slowest step indicate state determining step (RDS).
- According to note now on first step of mechanism we conclude that halide of substrate is in starting with



### b) Action of nucleophile $\rightarrow$

- Due to the presence of planar geometry of carbocation they do not have fix point of reaction.
- Therefore, nucleophile is very confuse how to attack.
- Because, nucleophile have major two options for attack on  $3^\circ$  butyl carbocation either backside or frontside may be different angle.
- This is observed ~~because~~ phenomenon due to planar geometry of carbocation.
- Such planar carbocation give two options for attacking of strong nucleophile either frontside or backside of both (racely).
- And produce 50% inversion and 50% retention (racemic mixture).



When the nucleophile attack on carbocation from front side such action called as 'retention', therefore, produce product called as 'retention product'. When the nucleophile is attack on carbocation by backside such action called as 'inversion', that's why produce product called as 'inversion product'.



Whereas

① R = Reactant =  $3^\circ$  butyl bromide ( $\text{CH}_3)_3\text{C}-\text{OH}$

②  $P = P_{\text{product}} = 3^\circ$  butyl alcohol ( $\text{CH}_3)_3\text{C}-\text{OH}$

③  $\Delta E_1 = \text{First activation energy for reactant}$

means first mechanism step.

④  $\Delta E_2 = \text{Second activation energy for carbocation}$

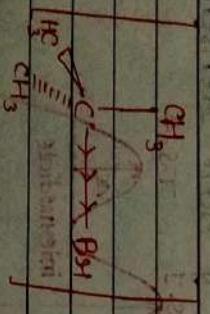
that means second step mechanism energy

⑤ ⑥ Intermediate := Planar geometry carbocation

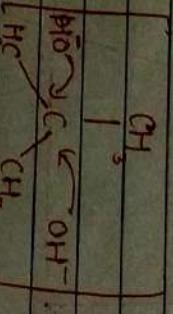
=  $3^\circ$  butyl carbocation

$= (\text{CH}_3)_3\text{C}^+$

⑦ ⑧ TS: I = First transition state



⑨ TS: II = Second transition state



\* Difference b/w  $\text{SN}^+$  and  $\text{SN}^2$  mechanism.

Factor  $\text{SN}^2$   $\text{SN}^+$

A) Kinetics 2<sup>nd</sup> order 1<sup>st</sup> order

B) Molecularity Bimolecular Unimolecular

C) Number of One step Two steps

D) Bond making Simultaneous first the bond in and bond breaking the reactant breaks and then a new bond in product is formed.

E) Transition state One step, one transition state. Two steps, two transition states.

F) Direction of Only backside Backside attack and attack of frontside attack nucleophile

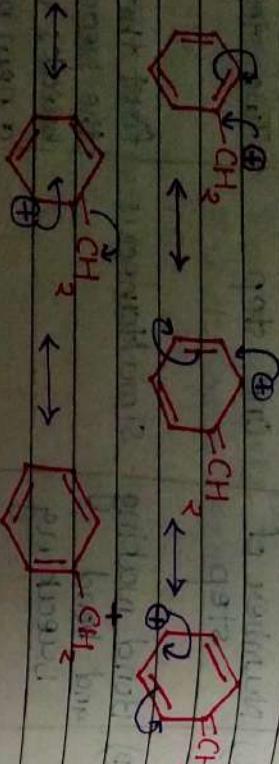
G) Stereochemistry Inversion of configuration Racemisation -ation (If substrate (or substrate is optically active) optically active)

H) Type of substrate Mainly 1<sup>o</sup> substrate Mainly 3<sup>o</sup> substrate

I) Polarity of Non polar solvent Polar solvent shrinkage favourable favourable

## \* Benzylic halide and Allylic halide :-

1. Benzylic halide and Allylic halide undergoes  $S_N^2$  mechanism.
2. The carbocation formed undergoes stabilisation through the resonance.
3. The resonating structures are



$R-X$	$CH_3-Br$	$CH_3-CH_2-Br$	$CH_2CH_2Br-CH_3$	$(CH_3)_3C-Br$
a) Types of halide	$1^\circ$ halide	$1^\circ$ halide	$2^\circ$ halide	$3^\circ$ halide
b) relative rate of $S_N^2$	$3^4$	1.00	0.02	0.0008

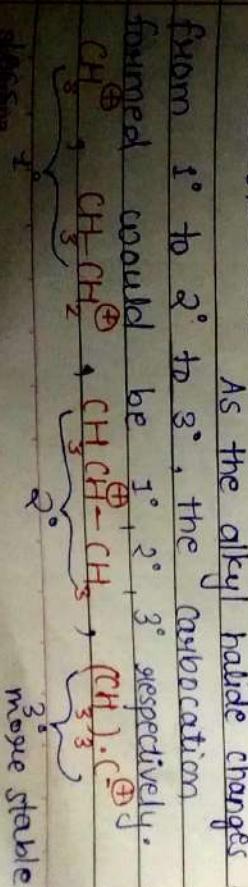
## 2. $S_N^2$ mechanism :-

On the basis of above table we conclude that grounding at  $\alpha$ -carbon - atom ( $\alpha$ -C-atom) increase then,  $S_N^2$  mechanism decrease, i.e.,  $1^\circ$  halides gives  $S_N^2$  mechanism if the ground increase on  $\alpha$ -C-atom (alkyl branch) to form secondary and then tertiary alkyl halide then possibility of  $S_N^2$  mechanism is decreases.

Hence  $S_N^2$  reaction  $1^\circ > 2^\circ > 3^\circ R-X$ .

## 3. $S_N^2$ mechanism :-

As the alkyl halide changes from  $1^\circ$  to  $2^\circ$  to  $3^\circ$ , the carbocation formed would be  $1^\circ$ ,  $2^\circ$ ,  $3^\circ$  respectively.



Topic  
O =  $\rightarrow S_1 - \rightarrow$

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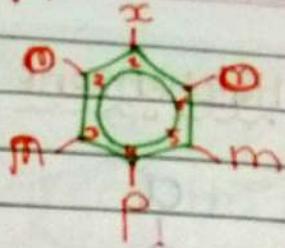
4. The stability order for carbocation is  $3^\circ > 2^\circ > 1^\circ$ .
5. Therefore,  $3^\circ$  substrate preferred  $S_N^2$  mechanism whereas, primary ( $1^\circ$ ) substrate does not prefer  $S_N^2$  mechanism, they mainly show  $S_N^2$  mechanism.
6.  $2^\circ$  alkyl halide show mixed mechanism ( $S_N^2$  as well as  $S_N^2$  mechanism).

ortho = adjacent  
meta = alternate  
para = opposite

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## ④ # Haloarenes

### \* Classification :-



Mono  
Halo  
arenes

Dihalo  
arene

Trihalo  
arene

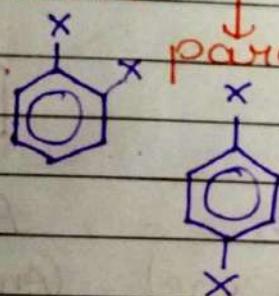
Polyhalo  
arenes

max - same  
mini - diff.

→ Tetra  
→ Peta  
→ Hexa

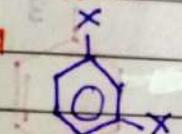


ortho

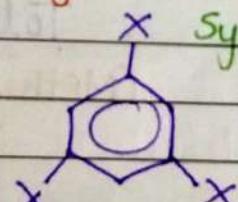


para

meta

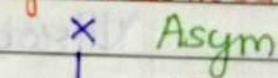


symmetrical



Sym

Asymmetrical



Asym

### \* Nomenclature :-

Common name of

IUPAC name of

Most Imp. names with structures:-

Aniline

Benzoic acid

Anisole

Salicylic acid

Halobenzene

Salicinaldehyde

Phenol

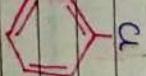
Toluene

Benzaldehyde

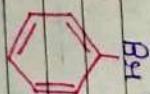
Nitrobenzene

Cumene

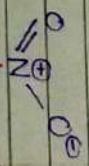
\* Halobenzenes :-



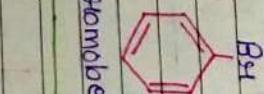
Chlorobenzene



Bromobenzene



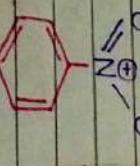
Iodobenzene



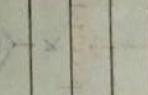
Acyclic acid



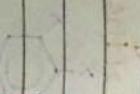
Salicylaldehyde  
(2-hydroxybenzaldehyde)



Aniline



Benzyl alcohol  
(Phenylmethanol)

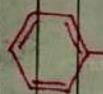


Acetophenone  
(1-Phenylethanone)

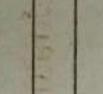
OH

O - CH<sub>3</sub>

C - H



Phenol  
(Hydroxybenzene) Anisole



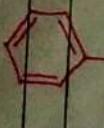
Benzaldehyde  
(Methoxybenzene)

H

C - OH

HC

CH<sub>3</sub>

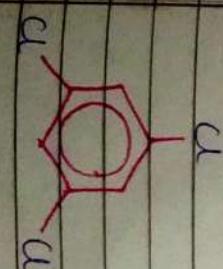


Benzoic acid



Cumene  
(Isopropylbenzene)

(2-phenylpropane)  
(2-methylpropene)

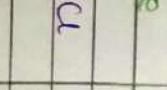


Structure

Common Name

TUPAC Name

Cl



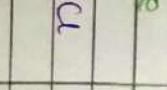
1,2,4 - tri  
chlorobenzene



1,3,5 - tri  
chlorobenzene



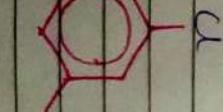
Cl



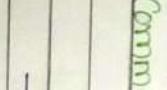
1,3 - di  
chlorobenzene



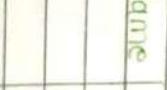
1,4 - di  
chlorobenzene



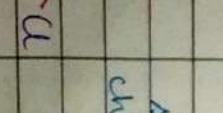
Cl



1,2,4,5 - tetra  
chlorobenzene



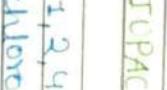
1,2,4,6 - tetra  
chlorobenzene



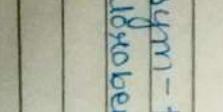
Cl



1,2,3,6 - tetra  
chlorobenzene



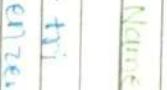
1,2,4,7 - tetra  
chlorobenzene



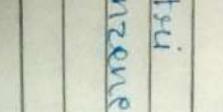
Cl



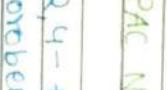
1,2,3,4,5 - penta  
chlorobenzene



1,2,3,4,6 - penta  
chlorobenzene



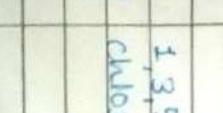
Cl



1,2,3,4,8 - penta  
chlorobenzene



1,2,3,4,9 - penta  
chlorobenzene



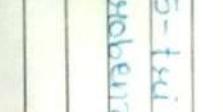
Cl



1,2,3,4,5,7 - hexa  
chlorobenzene



1,2,3,4,5,8 - hexa  
chlorobenzene



Cl



1,2,3,4,5,10 - hexa  
chlorobenzene



1,2,3,4,5,11 - hexa  
chlorobenzene

## Nomenclature of halogenes :-

### Structure

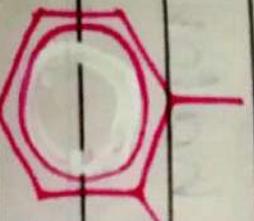
### Common Names

### TUPAC Name

BH

0-dibromo

1,2-dibromo



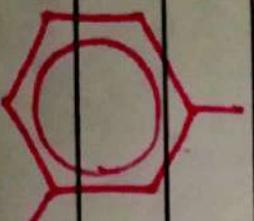
benzene

benzene

BH

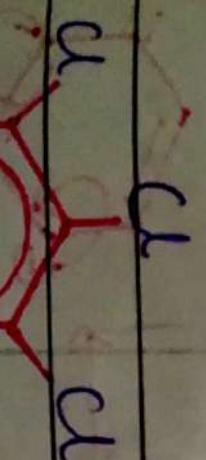
m-dibromo

1,3-dibromo



benzene

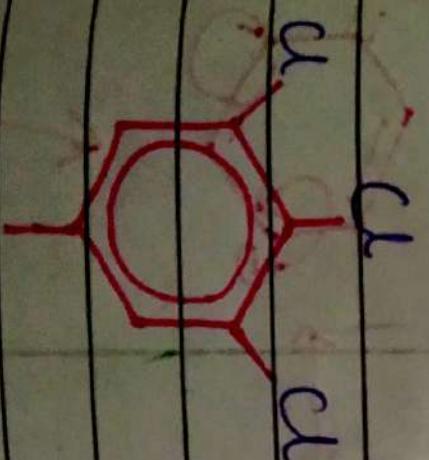
benzene



—

1,2,3,5-tetra  
chlorobenzene

Cl



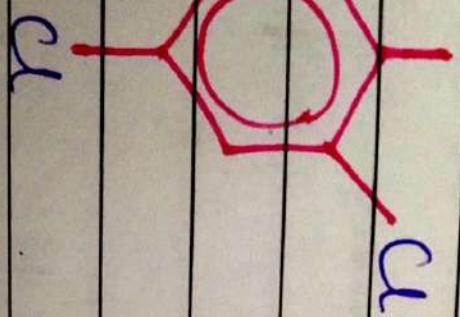
—

### Structure

Common Name      IUPAC Name

yde

(4)



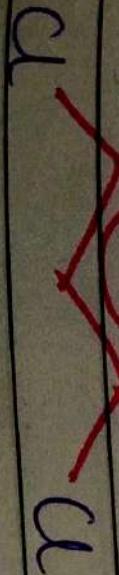
-

1,3,4-tri  
chlorobenzene

cl

cl

(5)



sym-tri

1,3,5-tri

chlorobenzene

chlorobenzene

**Ques:** Explain the nature of C-X bond in halocenes.

**Ans:** 1. In halocene halogen atom is attached to  $\text{sp}^2$  hybridised carbon atom which is present in benzene ring.

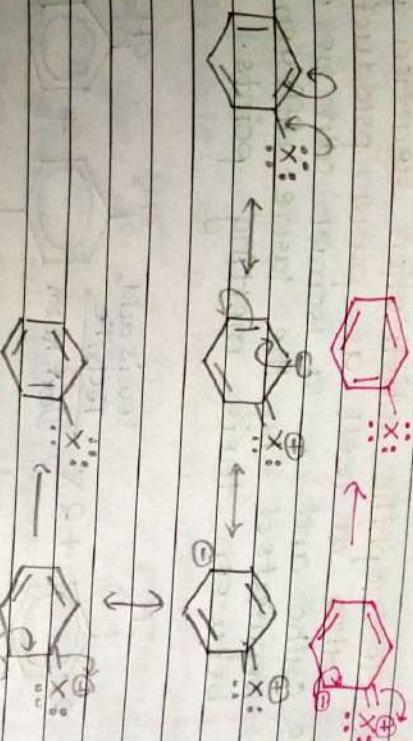
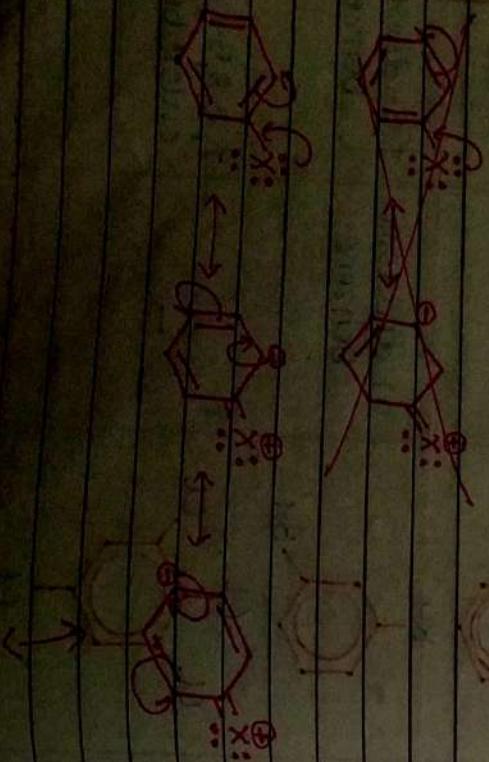
2.  $\text{sp}^2$  hybridised carbon atom forms three sigma ( $\sigma$ ) bond and one pi ( $\pi$ ) bond.

3. The halogen atom contains p orbital with lone pair of electron which increase with p ( $\pi$ ) orbitals of ring to form extended or conjugated system of pi ( $\pi$ ) orbital.

4. The two electrons from the lone pair of halogen atom and six electrons from the six carbons of ring are now associated to all the seven atoms.

5. The delocalisation of these electrons gives double bond character to C-X bond (resonance).

6. Resonance structure of halobenzene are,



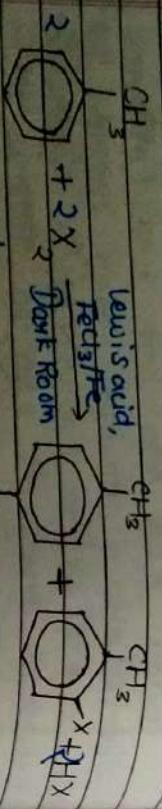
### \* Preparation of halocene :-

① By electrophilic substitution reaction :-

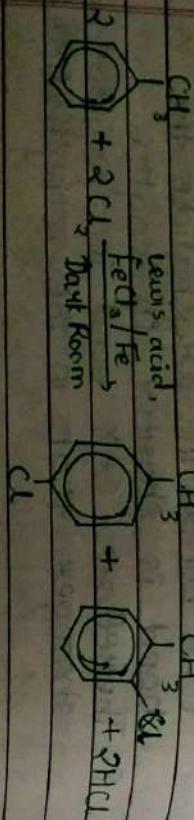
i. Statement:

When arenes (benzene or its derivative) treated with chlorine or bromine molecule in the presence of Lewis acid as a catalyst like  $\text{FeCl}_3$ ,  $\text{FeCl}_3$ , etc. to produce chloroarenes or bromoarenes by electrophilic substitution reaction.

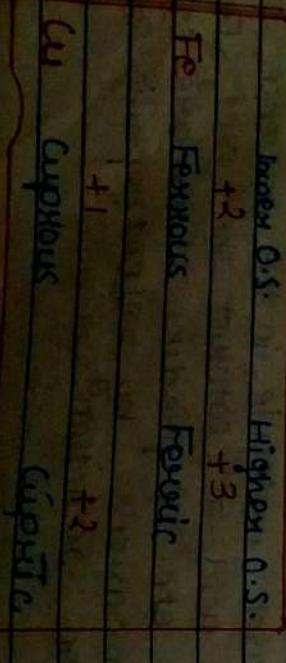
2. Electrophilic substitution reaction product formed as well as para product can be easily separated by the large difference between their melting points.



Toluene  $\xrightarrow{\text{Cu/Bz}_2}$  (p-Halotoluene)

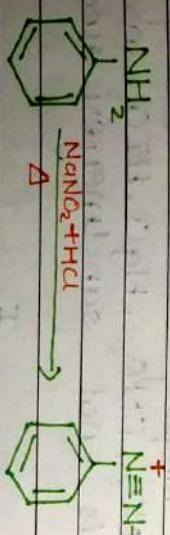


4. The reaction with iodine give reversible hence to prepare iodo product, oxidizing agents are used ( $\text{HIO}_3, \text{HNO}_3, \text{HgO}$ , etc.)
5. Fluorobenzenes can not be prepared by this method as fluorine is highly reactive.

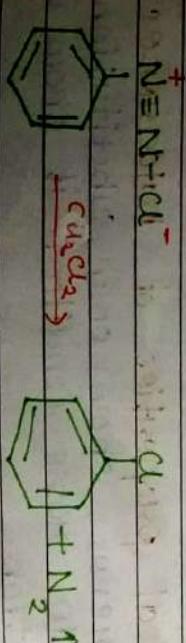


- \* Sandmeyer's reaction →
- Displacement of diazonium group ( $\text{N}\equiv\text{N}^+$ ) by chloride or bromide by using cuprous ( $\text{Cu}^+$ ) salt (+I) is called as Sandmeyer reaction.
  - Example: When primary amines reacts with nitroso acid ( $\text{NaNO}+\text{HCl}$ ) to give diazonium cation ( $\text{R}-\text{N}^+=\text{N}^-$ ) to form benzene diazonium chloride.
  - The diazonium salt treated with cuprous chloride or cuprous bromide to give chlorobenzene or cuprous bromobenzene.

#### Step-I:



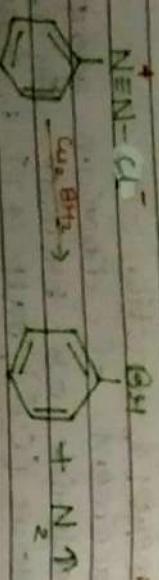
#### Step-II: Sandmeyer



Carbon at 3rd -ve charge, there is a 'lone pair' present.

(172)

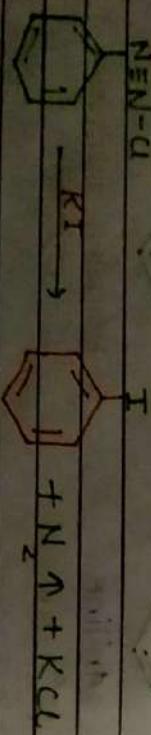
Indirect - lateral head to head overlap  
in carbon compounds  $\rightarrow \pi$  bond  $\Rightarrow$  triple / double bond  
single bond = direct overlap  $\rightarrow$   $\sigma$  bond  
 $\pi$  bond is a weak bond



diazonium chlorides

4. Benzene diazonium salt do not involve formation of iodo benzene by Sandmeyer reaction.

5. To de-benzene is prepared, when benzene diazonium salt (salt means chlorid or bromide) simply reacts with potassium iodide ( $\text{HNO}_3, \text{KNO}_3, \text{HgO}, \text{HIO}_3$  may be used) it is not Sandmeyer reaction.



Ques: Aromatic compound show electrophilic substitution as well as nucleophilic substitution reaction, why?

Ans: 1. Nucleophilic substitution reaction:

2. Under ordinary / normal condition aryl halide do not undergoes nucleophilic substitution reaction.

Ques: Why are less reactive toward the substitution reaction by nucleophilic due to the following reasons:

Reason (i) -

In case of alkyl halide the carbon of  $\text{C-X}$  bond is  $sp^3$  hybridized having less character and greater bond length of 177 pm which requires less energy.

Ques:

Why aromatic compounds show only substitution reaction?

-ve charge = high electron density

Page No. 174

175

energy to break the C-X bond, while in oxyhalide carbon of C-X bond is sp<sup>2</sup> hybridized, having more s character and shorter the bond length of 169 pm; the bond length stronger is bond, and greater is the energy required to break the bond. To break C-X bond in oxyhalide greater energy is required hence oxyhalide is less reactive.

Reason (ii)- The lone pair of electrons of halogen atom in oxyhalide is in conjugation with pi(π) electrons of ring.

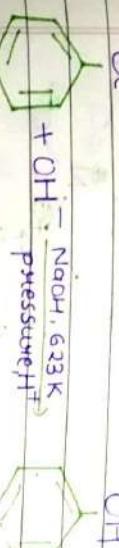
Reason (iii)- Due to the resonance the C-X bond in oxyhalide possesses double bond character.

Reason (iv)- The phenyl cation produced due to self ionisation of haloarene will not be stabilise by resonance which rules out the possibility of SN<sup>1</sup> mechanism. The backside attack of nucleophile is blocked by pi(π) electrons of aromatic ring which rules out SN<sup>2</sup> mechanism.

3. Example of simple nucleophilic substitution reaction:-

The -X bond can be replaced by -OH, -Cl or -NH<sub>2</sub> at higher temperature and under pressure.

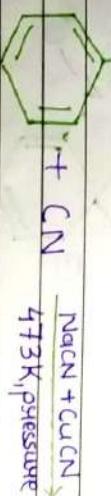
Ex. ①



Chloro  
benzene

Phenol

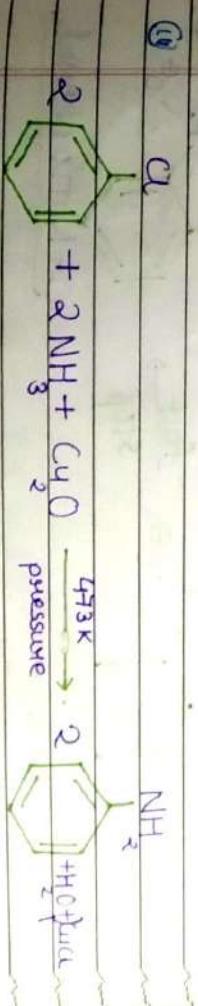
② Cl



Chloro  
benzene

Cyanide  
benzene

ON bond is broken



Chloro  
benzene

Aniline

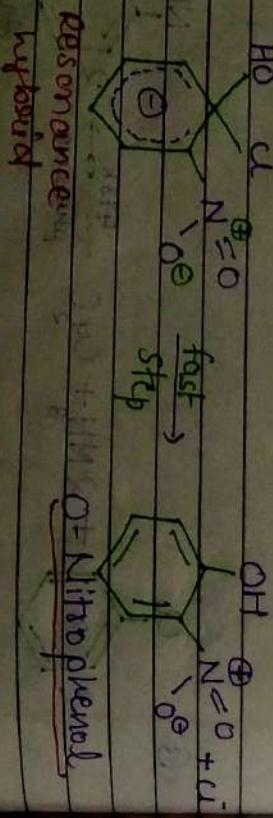
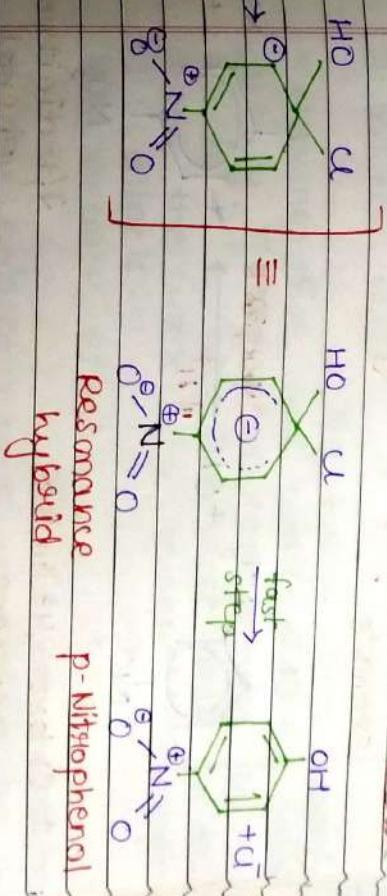
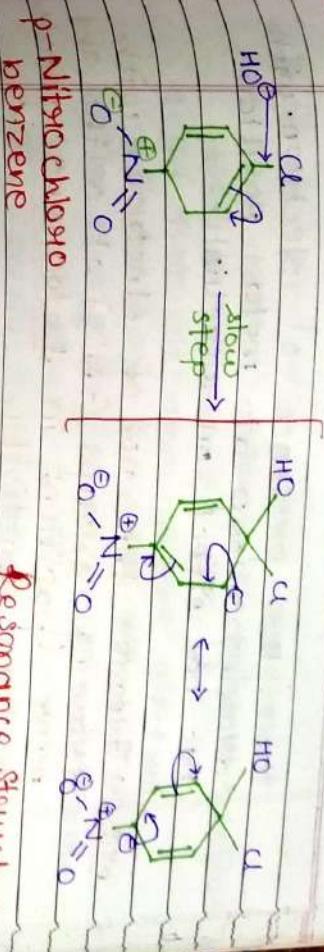
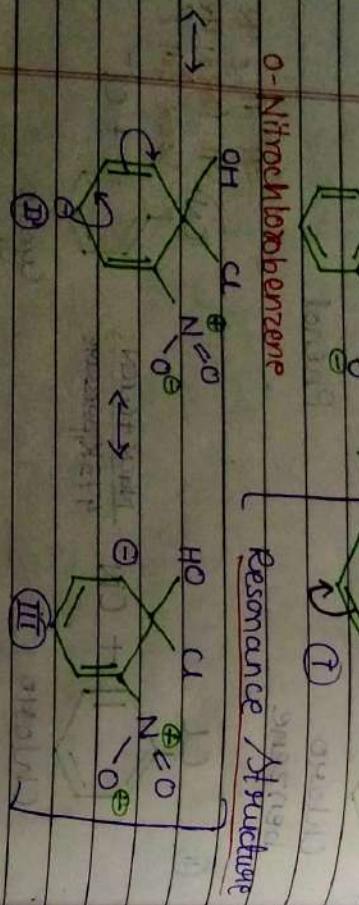
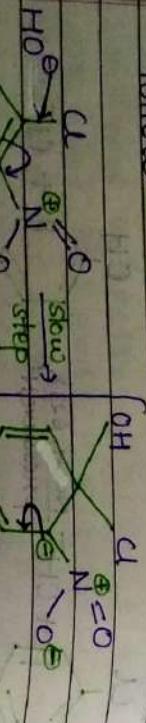
4. A oxyhalide undergoes nucleophilic substitution reaction readily if a strong electron withdrawing group

$\pi$  bond = weak bond = lateral overlap.

like  $-NO_2$  is present at ortho and para position.

(i)  $-NO_2$  group at ortho position with respect to halogen atom :-

The mechanism of reaction is as follow



resonance hybrid

(ii) Then  $-NO_2$  group withdraws at para position with respect to halogen atom:

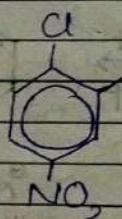
The mechanism is as follows

(iii) In both the above cases the carbanion formed by the attack of nucleophile  $\text{OH}^-$  gets stabilized at ortho and para positions due to stronger electron withdrawing tend.  $-NO_2$  group. Resonating structure do not have negative charge at meta position

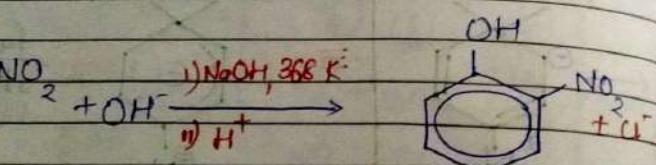
Hence, the presence of electron-withdrawing group at meta position has no effect on reactivity.

Q. (iv) Greater the no. of electron-withdrawing groups ( $-NO_2$ ) at ortho and para position in halobenzenes greater is the reactivity.

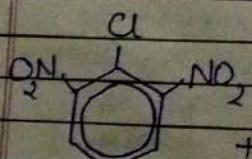
Example :-



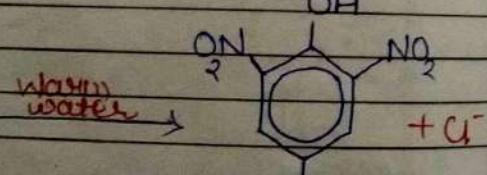
1-Chloro-2,4-dinitrobenzene



2,4-dinitrophenol  
(55% yield)



1-Chloro-2,4,6-trinitrobenzene



2,4,6-trinitrophenol  
(75% yield)

## 2. Electrophile substitution reaction:-

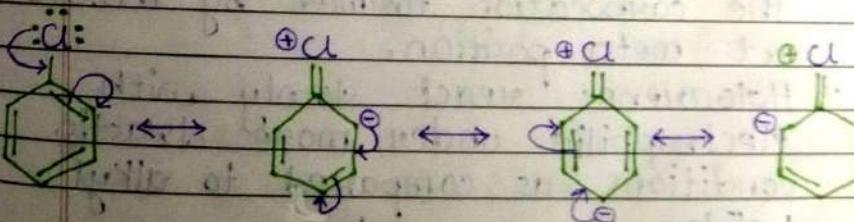
1. Aryl halides undergo electrophilic substitution reactions slowly.
2. The halogen atom shows electron withdrawing inductive effect.
3. It is o,p directing and deactivates benzene ring.
4. This condition is explain as follows:

### (a) Inductive effect :-

The halogen atom is strongly electronegative and withdraws the electron density from the carbon atom to which it is attached, hence aryl halides show the reactivity towards electrophilic attack.

### (b) Resonance effect :-

The resonance structures of e.g. chlorobenzene show increase in electron density at ortho and para position, hence it is o,p directing.



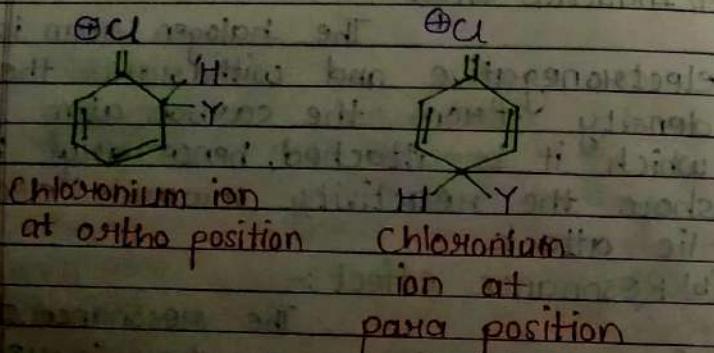
5. The inductive effect and resonance effect compete each other.

6. However, the inductive effect is stronger than resonance effect.

acyl group =  $R-C(=O)Cl$ 

7. Hence, in aryl halides the reactivity is controlled by strongest inductive effect and the  $\sigma,p$  orientation is controlled by weaker resonating effect.

8. The carbocation formed by the attack of electrophile ( $Y^+$ ) on halogenes at ortho and para positions are more stable due to formation of chloronium ion.



9. The chlorinium ion formed is comparatively more stable than either hybrid structures of carbonium ion and also the carbocation formed by attack at meta position.

10. Halogenides react slowly with electrophile under milder drastic conditions as compared to alkyl halides.

### 3. Chemical properties of halogenes

Halogenation

Sulphonation

Friedel-Crafts acylation

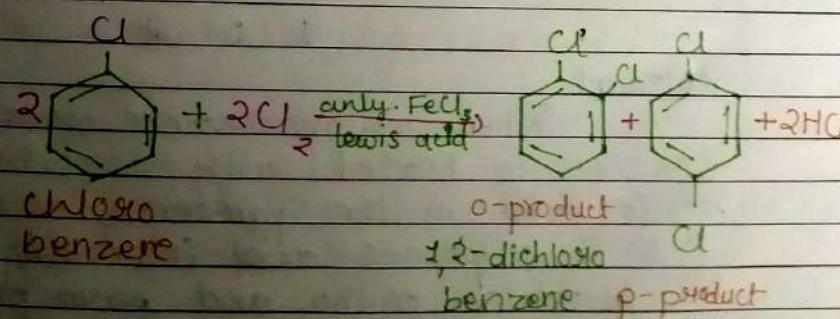
Nitration

Friedel-Crafts alkylation

Benzene derivative form ortho and para product.

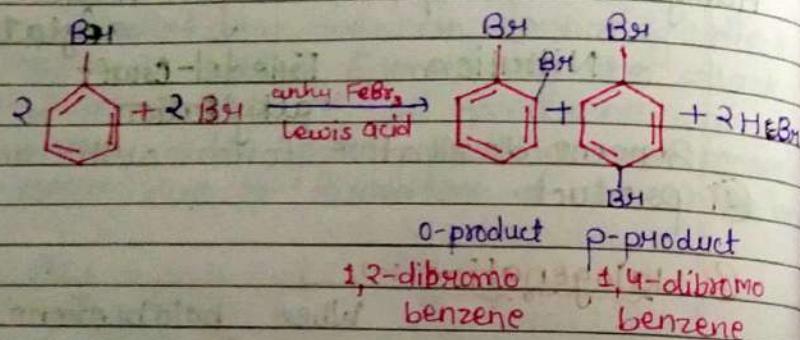
#### ① Halogenation :-

When halobenzene is reacts with chlorine or bromine in the presence of anhydrous ferrous trichloride (Anhy.  $FeCl_3$ ) or ferric bromide ( $FeBr_3$ ) to produce 1,2-dihalobenzene (minor) and 1,4-dihalobenzene (major) by electrophilic substitution reaction.



② When bromobenzene is reacts with bromine in the presence of ferroanhydrous ferrous tribromide ( $FeBr_3$ ) to produce 1,2-dibromo benzene (minor) and 1,4-dibromobenzene (major).

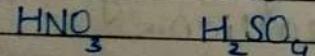
major) by electrophilic substitution reaction



### ② Nitration :-

In aromatic compound nitration is occur by using nitrating mixture.

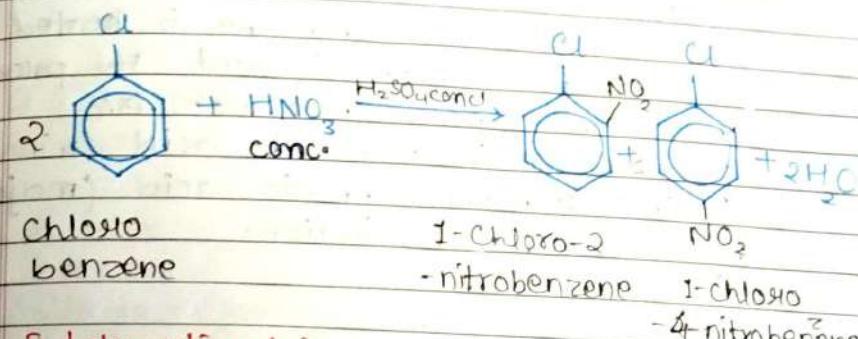
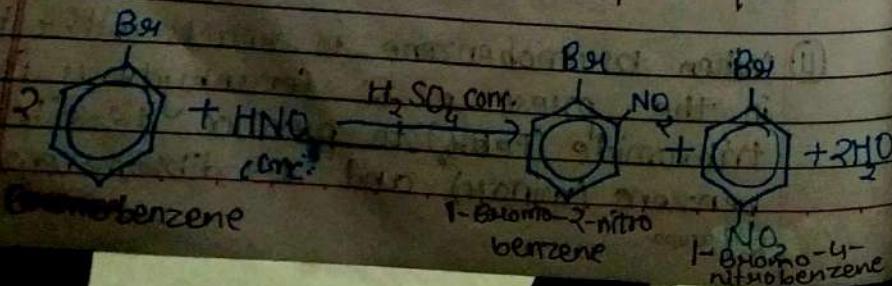
Nitrating mixture = conc. + conc.



1 : 2

#### Statement:

When chlorobenzene or bromobenzene is heated with concentrated nitric acid in the presence of concentrated sulphuric acid (nitrating mixture) to produce ortho and para product.

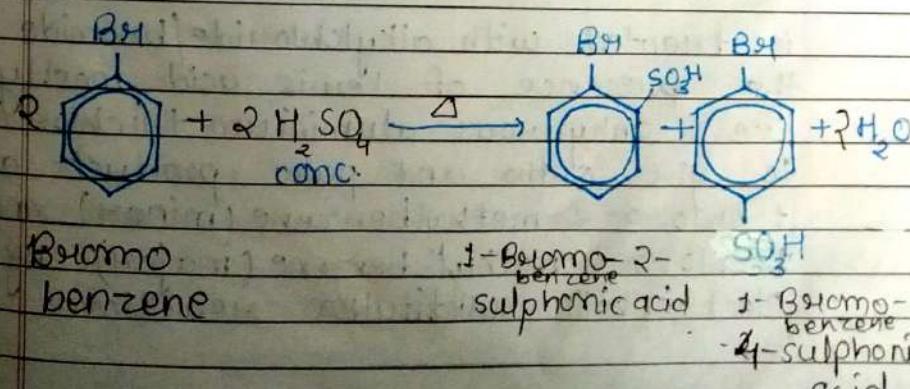


### ③ Sulphonation :-

-OH bond and produce sulphonic ion ( $-\text{SO}_3^-$ )

#### Statement:

When bromobenzene is heated with concentrated sulphuric acid to produce ortho and para product as 2-Bromobenzenesulphonic acid (minor) and 4-Bromobenzenesulphonic acid (major) by substitution reaction.

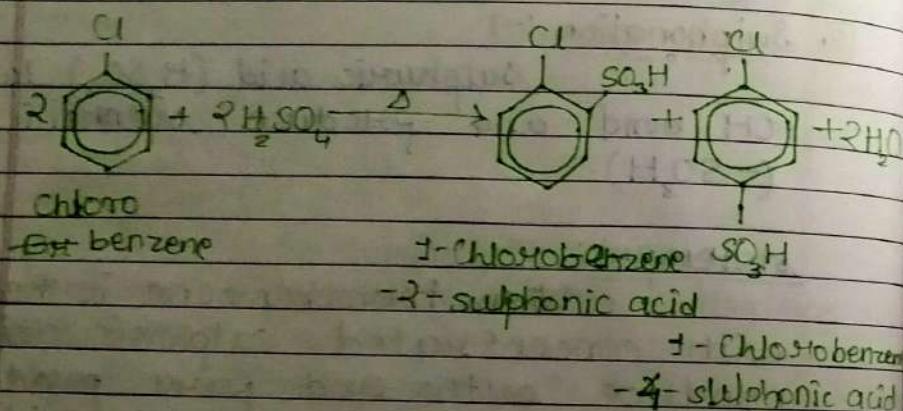


### Statement :

When chlorobenzene is heated with concentrated sulphuric acid to produce ortho and para product as:

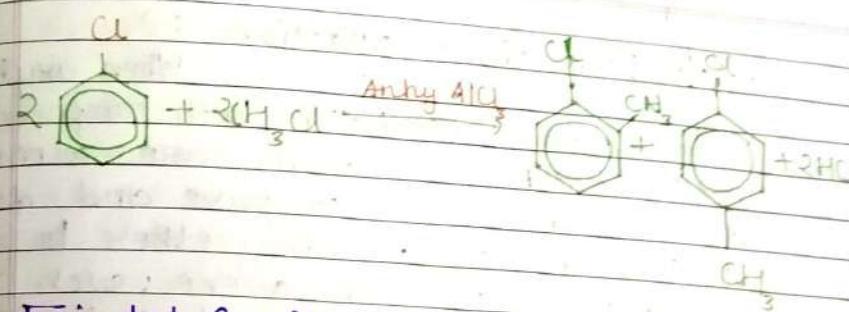
2-Chlorobenzene sulphonic acid (minor)  
 4-Chlorobenzene sulphonic acid (major)

by substitution reaction.



## ④ Friedel-Crafts alkylation :-

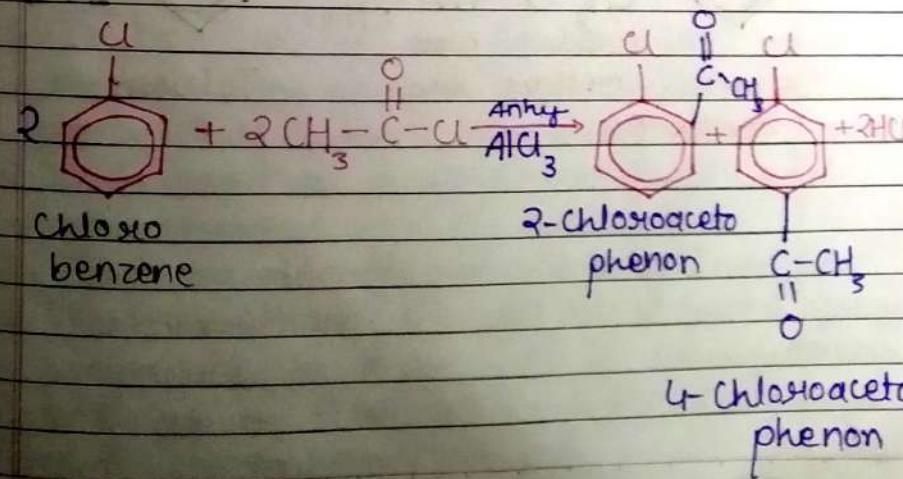
When chlorobenzene is treated with alkylchloride/bromide in the presence of Lewis acid mostly use anhydrous aluminium trichloride to give ortho and para product as 1-chloro-2-methylbenzene (minor) and 1-chloro-4-methyl benzene (major) by electrophilic substitution reaction.



Friedel-Crafts alkylation gives maximum yield (product) by using anhydrous  $\text{AlCl}_3$  at the place of Lewis acid.

⑤ Friedel-Crafts acylation :-

-ne reacts with acetylchloride ( $\text{CH}_3\text{COCl}$ ) in the presence of Lewis acid specially anhydrous aluminium trichloride ( $\text{AlCl}_3$ ) to give ortho and para product as 2-chloroacetophenone (minor) and 4-chloroacetophenone (major).

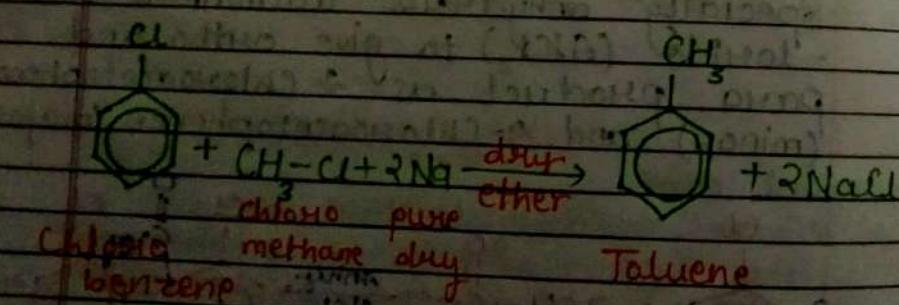


### ⑥ Wurtz - Fittig Reaction :-

When aryl halide reacts with alkyl halide (both compounds containing halogen atoms are same) in the presence of pure and dry sodium metal in dry ether to give arylalkane or arylarene; such a reaction called as Wurtz - Fittig reaction.

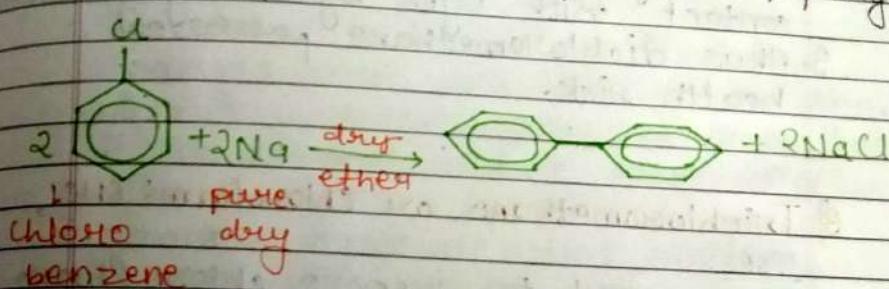
#### Example:

When chlorobenzene reacts with chloroethane in the presence of pure dry sodium metal in dry ether to give toluene (methylbenzene).



### ⑦ Fittig reaction :-

When the two molecule of chloro or bromo benzene reacts with pure and dry sodium metal in the presence of dry ether to produce diphenyl.



Uses and environmental effects of some alkyls or aryl halides :-

#### i) Dichloromethane : $\text{CH}_2\text{Cl}_2$

##### Uses :

- It has ability to dissolve wide range of organic compounds hence it is used as an ideal solvent for many chemical reactions.
- It is used as a degreaser and paint remover.
- Used to decaffeinate tea and coffee.
- Dichloromethane is used as aerosol spray propellant as it is volatile causes nausea and as a fumigant pesticide for grains and strawberries.

Environmental effects:

1. When mixed in air in high amount, as it is highly volatile causes nausea, numbness in fingers and toes, dizziness and if in less amount causes impaired vision and hearing.
2. It is highly dangerous if it comes in contact with eyes by damaging cornea.
3. Thus dichloromethane possesses health risk.

B) Trichloromethane or chloroform:  $\text{CHCl}_3$ Uses:

1. It is used to prepare chlorofluoro methane, a Freon refrigerant R-22.
2. Used as a solvent in pharmaceutical industry and for producing pesticides and dyes.
3. Used as a source of dichloro carbene ( $\text{CCl}_2$ ) group.

Environmental effects:

1. Previously chloroform was used as anaesthetic but now it is replaced by ether due to its toxicity.
2. Chloroform when exposed to air and sunlight forms a poisonous compound phosgene, hence it is stored in dark, well stoppered bottles.
3. If mixed with air it is hazardous and causes headache and fatigue and if inhaled for long time affects central nervous system.

C) Tetrachloromethane or carbon tetrachloride:  $\text{CCl}_4$ Uses:

1. It is used as a dry cleaning agent and as a pesticide to kill insects in stored grains.
2. It is also used as a solvent, in the production of refrigerants.

Environmental effects:

1. On contact it causes eye irritation, damages nerve cells, vomiting sensation, dizziness, unconsciousness or death, thus it has severe adverse health effects.
2. When mixed with air it causes ozone depletion, which affects human skin leading to cancer.

D) Iodoform:  $\text{CHI}_3$ Uses:

1. It is used in medicine as a healing agent and antiseptic, dressing of wounds and sores. The antiseptic property is due to liberation of free iodine.
2. On small scale Iodoform is used as disinfectant.

Environmental effects:

It has strong smell.

## F) Freons:

Mostly widely used Freons are  
 Dichloro difluoro methane  $\text{CCl}_2\text{F}_2$ ,  
 Trichloro difluoro methane  $\text{CCl}_3\text{F}$ ,  
 Chloro difluoro methane  $\text{CHCl}_2\text{F}$ , etc.

## Uses:

- They are widely used as propellants in aerosol products of food, cosmetics and pharmaceutical industries.
- Freons containing bromine in their molecules are used as fire extinguishers.
- They are also used in aerosol insecticides, solvent for cleaning clothes and metallic surfaces, as foaming agents in preparation of foamed plastics and in production of certain fluoro carbons.
- They are used as refrigerants (which causes depletion).
- Freons are also used for air conditioning, as are noncorrosive.

## Environmental effect:-

- refrigerant causes ozone depletion.
- the freons have low toxicity
- biological activity.
- from propane getting more
- inertive.

## Trichloro ethane:

It is used as a solvent in paint.

## Uses:

- DDT is used as insecticide against malaria.
- It is used to kill various insects like housefly and mosquitoes due to its high and specific toxicity.

## Environmental effects:

- It is not readily metabolized and not destroyed by environmental destructive forces.
- It is deposited and stored in fatty tissues.
- If it exists for a long time in soil, plants and animals as well, it produces unforeseen ecological effects.

It is replaced by better and safer insecticides due to its ecological problems.

