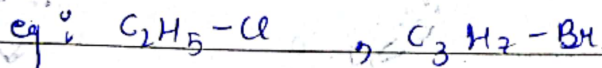
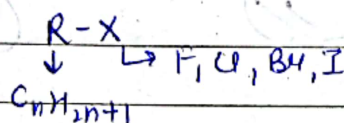


Halalkanes and Haloarenes

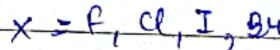
* The halogen derivatives of aliphatic hydrocarbons are called haloalkanes.
 eg. $\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{H}-\text{C}-\text{C}-\text{H} \\ | & | \\ \text{H} & \text{H} \end{array} \xrightarrow{\text{X}_2} \begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{H}-\text{C}-\text{C}-\text{X} \\ | & | \\ \text{H} & \text{H} \end{array}$

* The halogen derivatives of aromatic hydrocarbons are called as haloarenes.
 eg. $\text{Benzene} \xrightarrow{\text{X}_2} \text{Aryl halide} + \text{HX}$

* Haloalkanes are also known as "Alkyl halide".



* Haloarenes are also known as "Aryl halide".



* Classification.

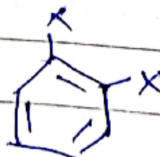
On the basis of no. of Halogen atoms.

$\text{C}_2\text{H}_5\text{X}$
Mono haloalkane



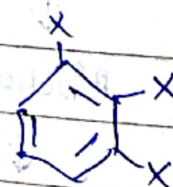
Monohaloalkane

$\text{X}-\text{CH}_2-\text{CH}_2-\text{X}$
Dihaloalkane



Dihaloalkane

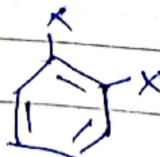
$\text{CH}_2\text{X}-\text{CHX}-\text{CH}_2\text{X}$
Trihaloalkane



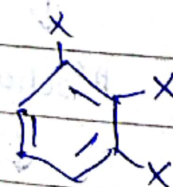
Trihaloalkane



Monohaloarene



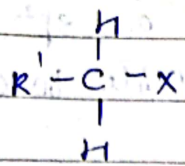
Dihaloarene



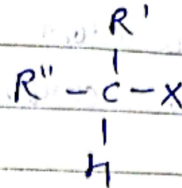
Trihaloarene

• On the basis of compounds containing sp^3 C-X Bond.
 $\Rightarrow$ Monohalogen.

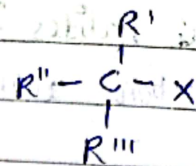
(a) Alkyl halides
 or haloalkanes
 [R-X]



1° Alkyl halide



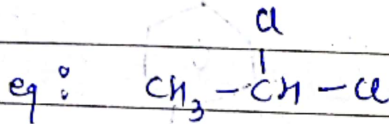
2° Alkyl halide



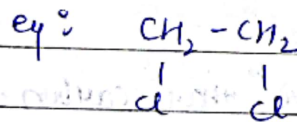
3° Alkyl halide

$\Rightarrow$ Dihalogen.
 $\rightarrow$ दोन ही carbon से Halogen atom जुड़े हैं।

• Geminal dihalide = Halogen atoms are attached to same carbon atom. These are kha "alkylidene dihalides".

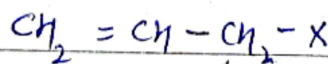


• Vicinal dihalide = Halogen atom are attached to adjacent carbon atoms. These are kha "alkylene dihalides".

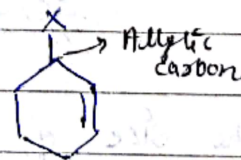


(b) Allylic halides

$\Rightarrow$ These are the compounds in which halogen is bonded to sp^3 hybridised carbon next to C-C double bond [C=C]

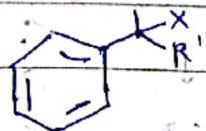
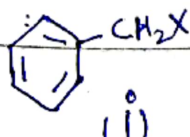


↓
 Allylic carbon



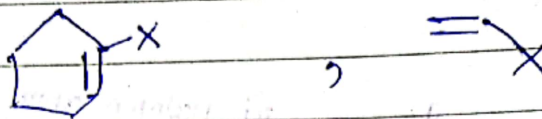
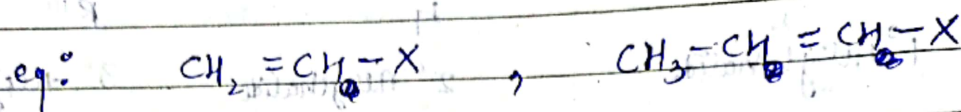
(c) Benzyl Halide

[इसमें भी carbon से halogen जुड़ा है वो carbon Benzene से जुड़ा है]
 $\Rightarrow$ These are the compounds in which halogen is bonded to sp^3 hybridised carbon atom next to an aromatic ring.

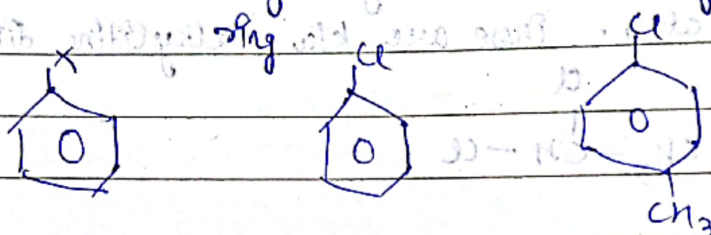


On the basis of compounds containing sp^2 C-X bond.

a) **Vinyl halides**: Halogen atom is bonded to an sp^2 hybridised carbon atom of a carbon-carbon double bond $[C=C]$



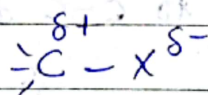
b) **Aryl halides**: Halogen atom is directly bonded to benzene



4-methylchlorobenzene

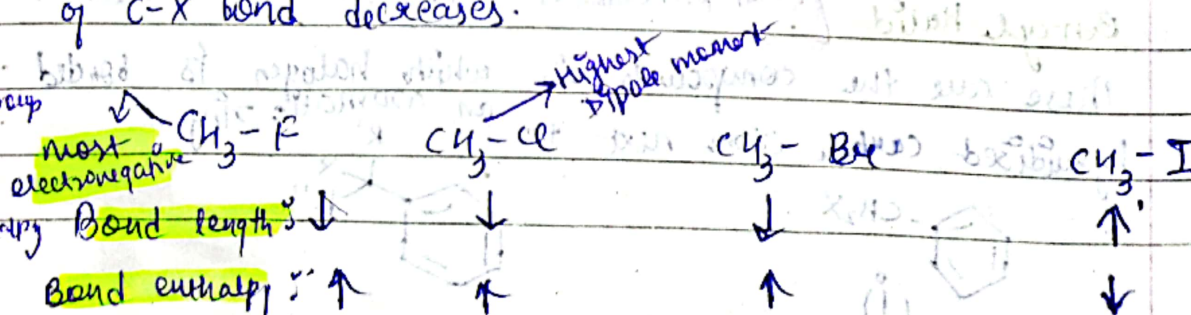
* Nature of C-X Bonds.

Halogens are more "electronegative" than carbon. So, the carbon halogen bond is a polar bond. The carbon bears a small positive charge whereas the halogen bears a partial negative charge.



As the size of halogen atom increases on moving down the group, the C-X bond length also increases and polarity of C-X bond decreases.

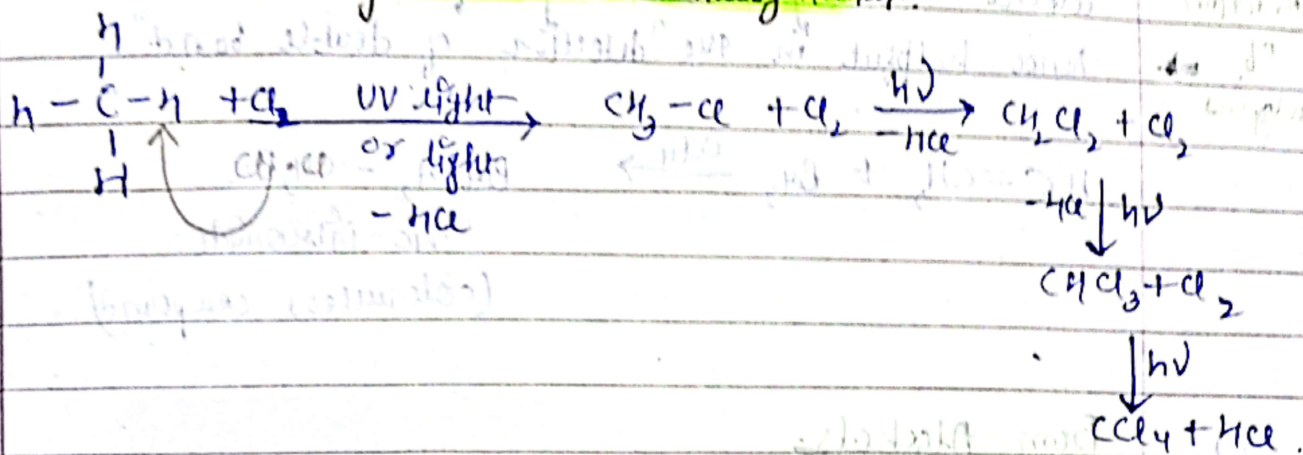
Down the group
size of Bond
length $\uparrow$
Bond enthalpy $\downarrow$



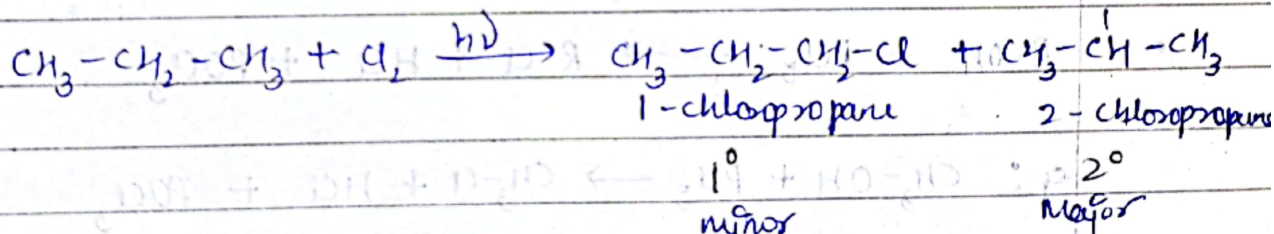
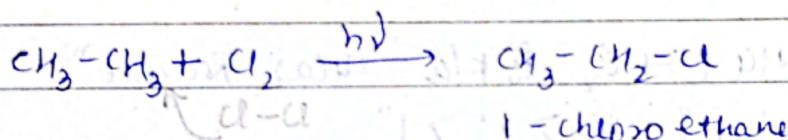
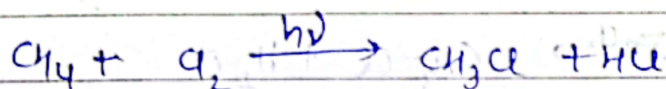
* Methods of preparation.

1. From hydrocarbon.

(i) From alkanes by Free radical halogenation.

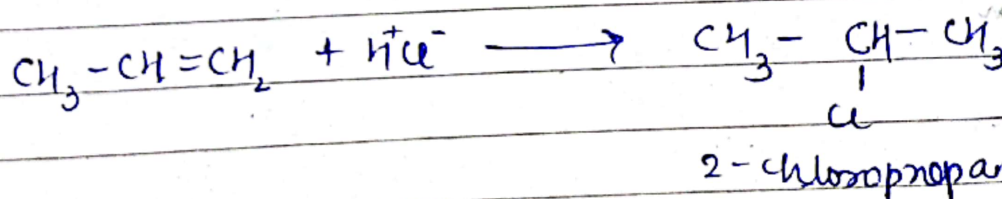
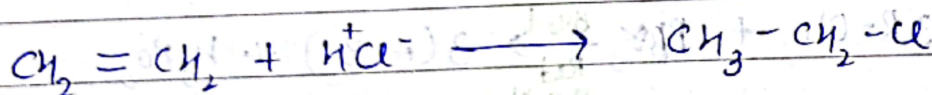


monohalogenation.



(ii) From alkenes.

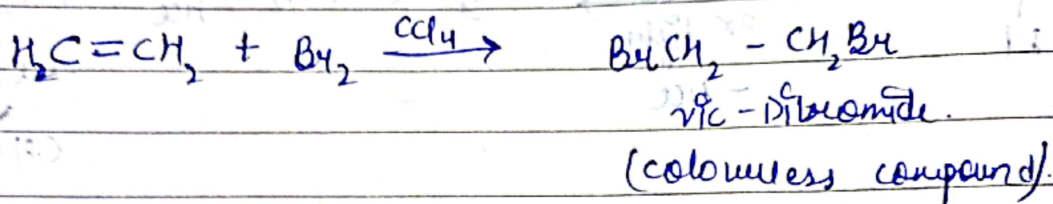
Alkenes give haloalkanes by electrophilic addition of Halogen



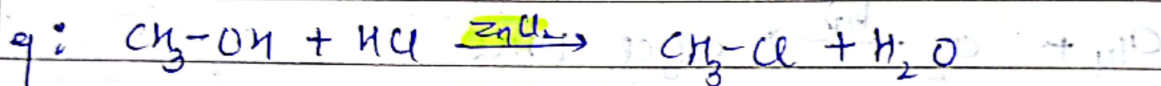
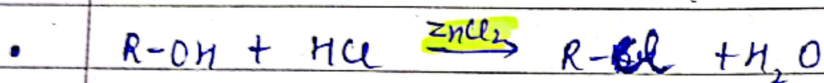
(i)
Addition
of Hydrogen
halide
[H-X]

(ii)
Addition
of
halogens $\rightarrow$

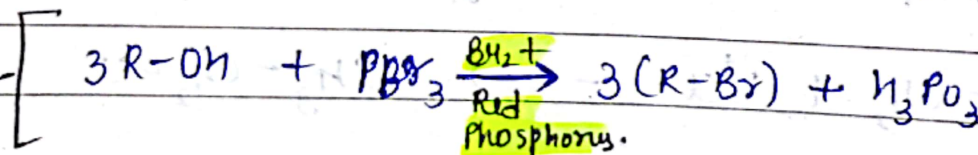
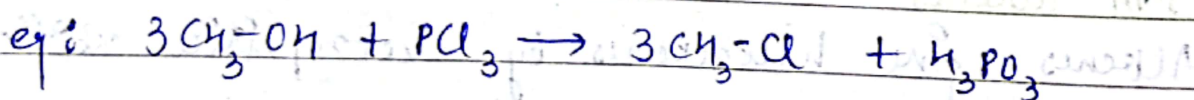
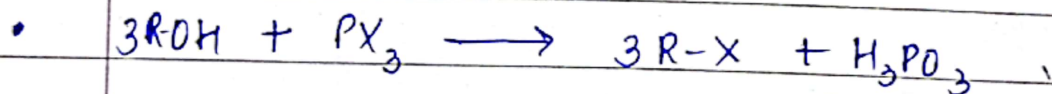
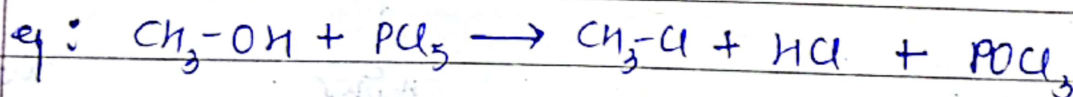
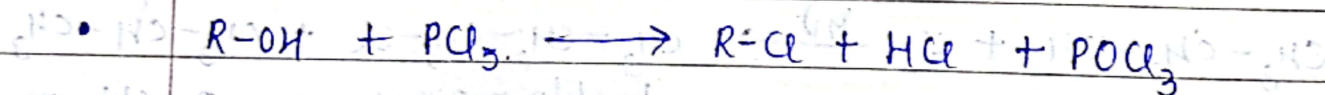
Detection of Double Bond: Addition of bromine in CCl_4 to an alkene resulting in discharge of reddish brown colour of bromine hence helpful in the "detection of double bond".



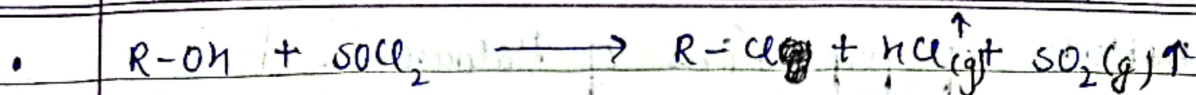
2) From Alcohols:



$\Rightarrow$ Mixture of $\text{HCl} + \text{ZnCl}_2$ is k/a "Lucas Reagent"
 $\Rightarrow$ Reactivity order: $3^\circ > 2^\circ > 1^\circ$



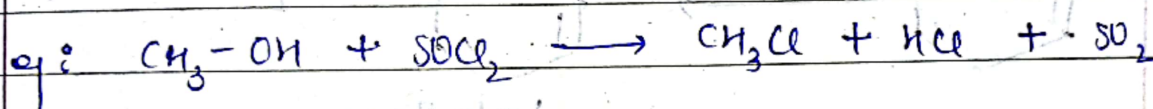
Alkyl bromide compounds are formed during the rxn [Fresh]



Also k/a "Darzen Process" or "Thionyl chloride method".

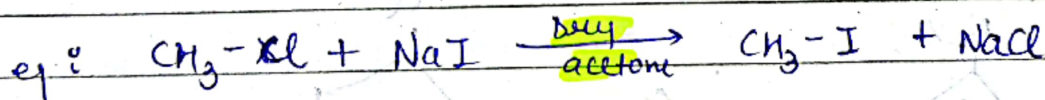
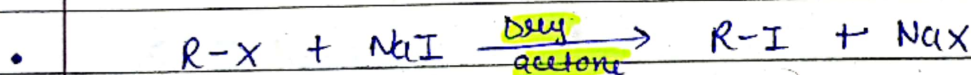
Q why Darzen Process is best process to make Halobalkanes from Alcohol?

Ans Because the side products are gaseous in nature & easily escapable.

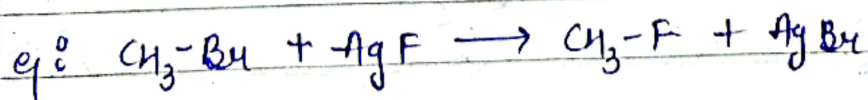
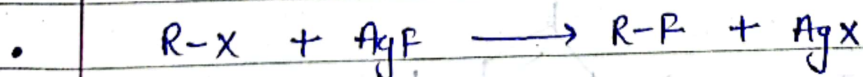


3) Halogen Exchange Method

a) **Finkelstein Reaction**: Alkyl Iodides are often prepared by the rxn of alkyl chlorides / Bromides with NaI in dry acetone.



b) **Swarts Reaction**: The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride / Bromide in the presence of metallic fluoride.



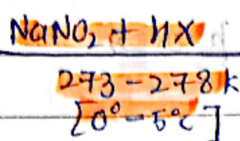
=> metallic fluoride such as AgF, Hg₂F₂, CoF₂ or SbF₃.

*

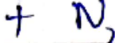
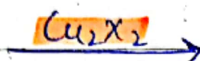
Methods of preparations of Halobenzene.

1) From amines by sandmeyer's reaction.

Step I

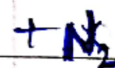
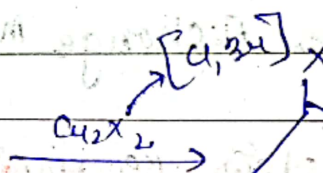
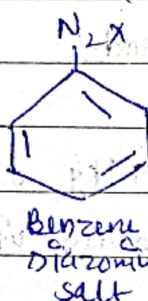
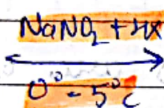
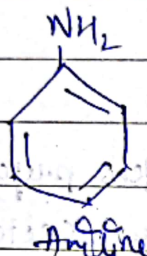


Step II



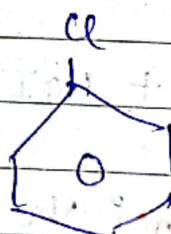
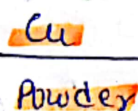
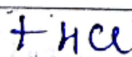
Halo Benzene

Overall

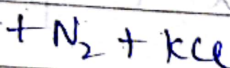
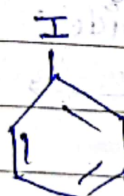
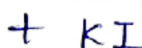


Halo Benzene

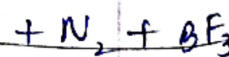
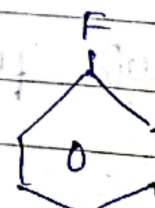
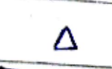
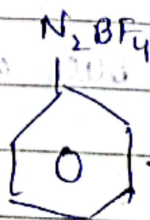
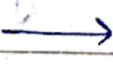
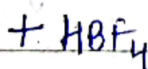
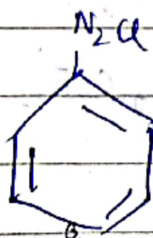
2) Gattermann Rxn.



3)



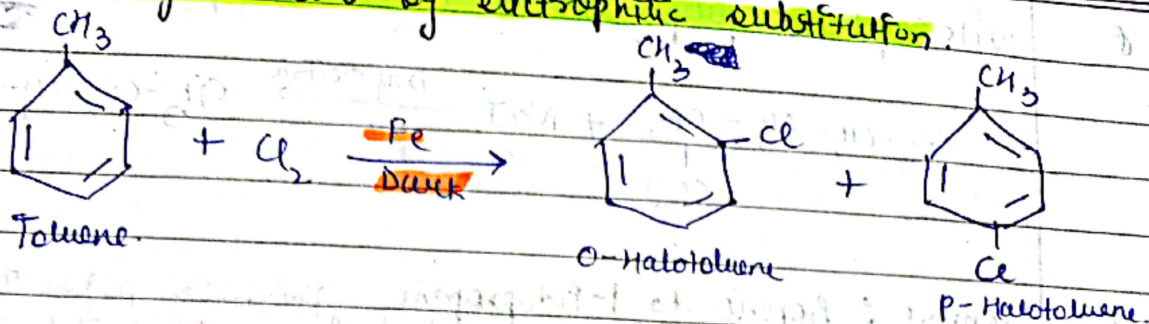
4)



This is Balz-Schiemann Rxn.

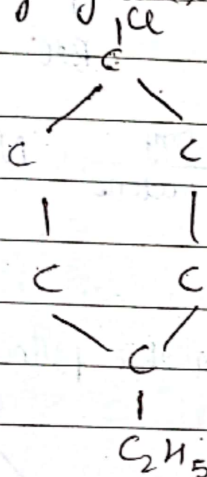
Q)

From hydrocarbon by electrophilic substitution.



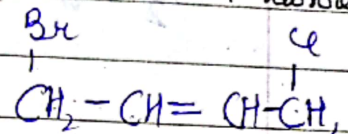
Q

1-chloro-4-ethylcyclohexane.



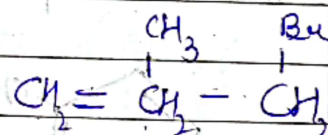
Q

1-bromo-4-chlorobut-2-ene

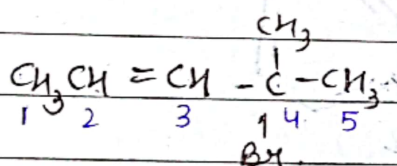


Q

3-bromo-2-methylprop-1-ene

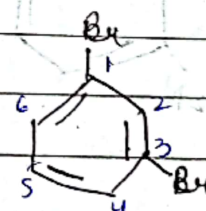


Q



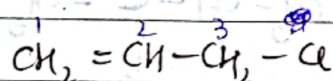
4-bromo-4-methylpent-2-ene.

Q



1,3-dibromobenzene.

Q

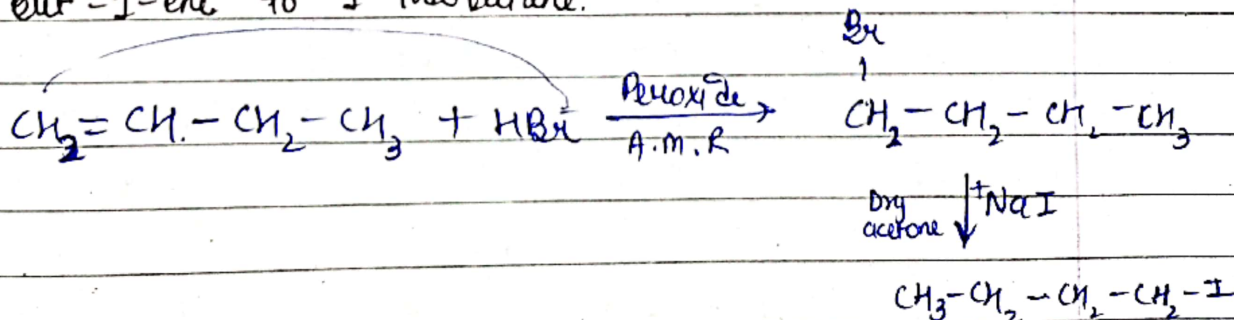


3-chloroprop-1-ene

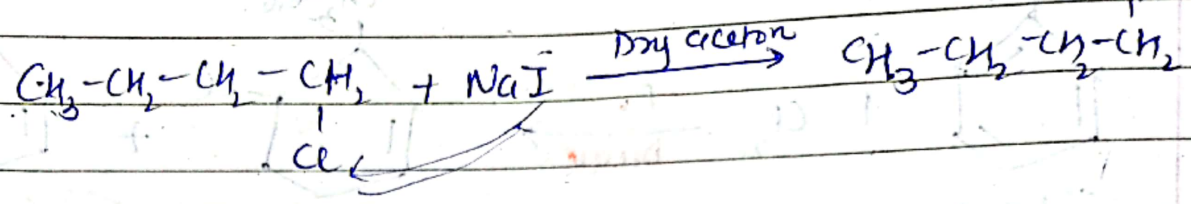
Q

How can you convert the following?

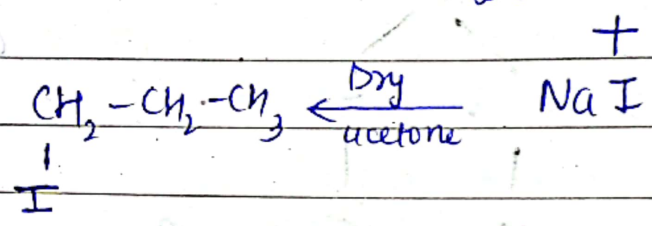
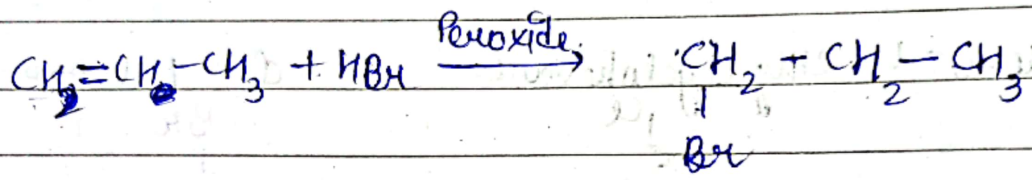
But-1-ene to 1-iodobutane.



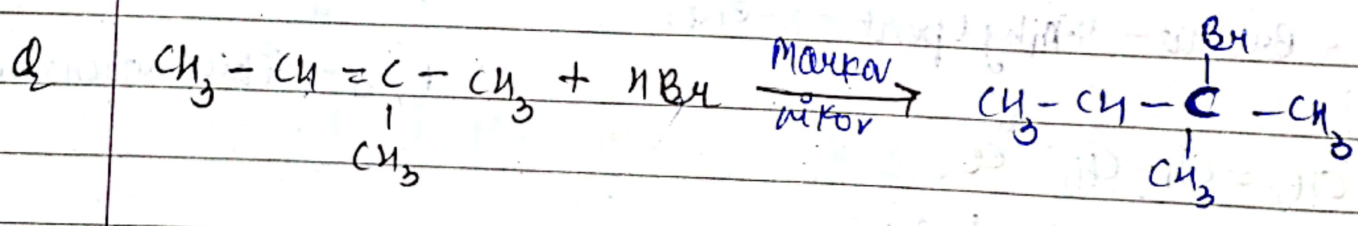
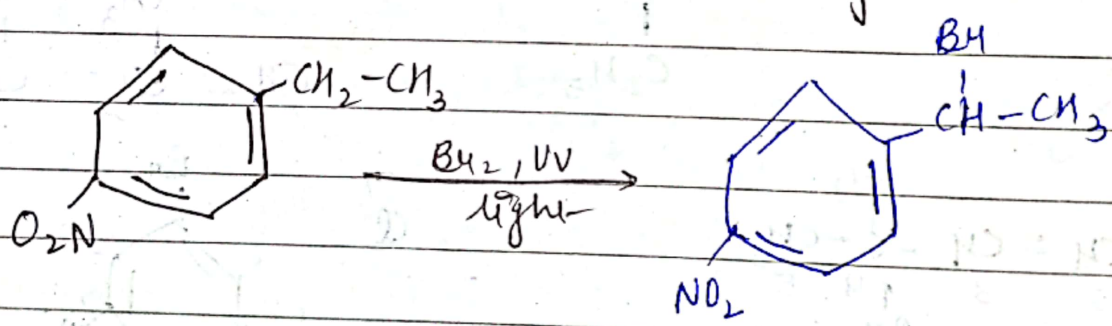
Q write eqn for preparation of 1-iodobutane from 1-chlorobutane



Q Convert: Propene to 1-iodopropane origiⁿ at Terminal position of group
मूलतः एत^न ही Anti Markov
rule follow
ह^नग^नी



Q write the major product in the following



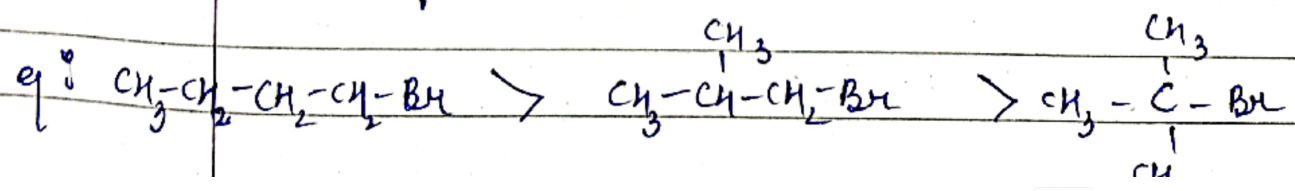
* Physical properties of Haloalkanes

- Colour: Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light.
- Smell: many volatile halides ~~are~~ have sweet smell.
- Nature: Lower haloalkanes are gaseous in nature while higher haloalkanes and Halocenes are liquid and solid in nature.
- Boiling point: B.P $\propto$ molecular mass $\propto$ Branching
 - $\Rightarrow$ B.P of alkyl halides increases with the increase in no. of carbon atoms in alkyl group.

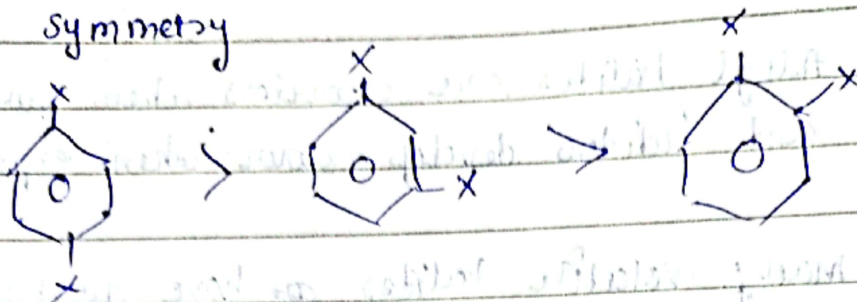
eg: $\text{CH}_3\text{Cl} < \text{C}_2\text{H}_5\text{Cl} < \text{C}_3\text{H}_7\text{Cl} < \text{C}_4\text{H}_9\text{Cl}$
 - $\Rightarrow$ Due to polar nature of C-X bond, Haloalkanes exert dipole-dipole interactions. Hence, Haloalkanes have higher boiling point compared to hydrocarbons with same molecular mass.

eg: $\text{CH}_3\text{Cl} > \text{CH}_4$
 - $\Rightarrow$ For a given alkyl group the boiling point and densities of different alkyl halides are $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$. This is because with the increase in atomic size, the magnitude of Van der Waal forces also increases.

eg: $\text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$
 - $\Rightarrow$ In alkyl halides the increase in branching decreases the boiling point. This is because increase in branching decreases its surface area which weakens intermolecular forces.



- In case of haloarenes, m.p. is directly proportional to symmetry



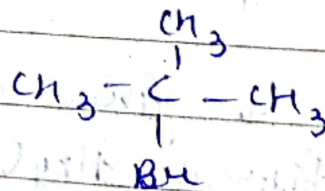
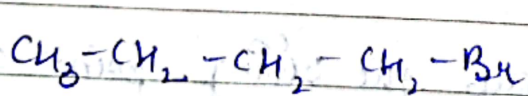
- Solubility**: Alkyl halides are insoluble in water. This is because they can neither form hydrogen bond with water nor can break hydrogen bonding of water molecules.

Q why p-dichlorobenzene has higher melting point than that of ortho or meta isomer?

Ans Due to symmetry they have better closed packing.

Q Alkyl halides, though polar, are immiscible with water?
Ans Because they can't make hydrogen bond with water & can't break the hydrogen bond of water molecule.

Q Give Reason: ^{chain} n-Butyl bromide has higher b.p than t-butyl bromide



In Branching B.P. decreases because surface area decreases due to which van der Waal forces

α carbon = the carbon to which functional group is attached

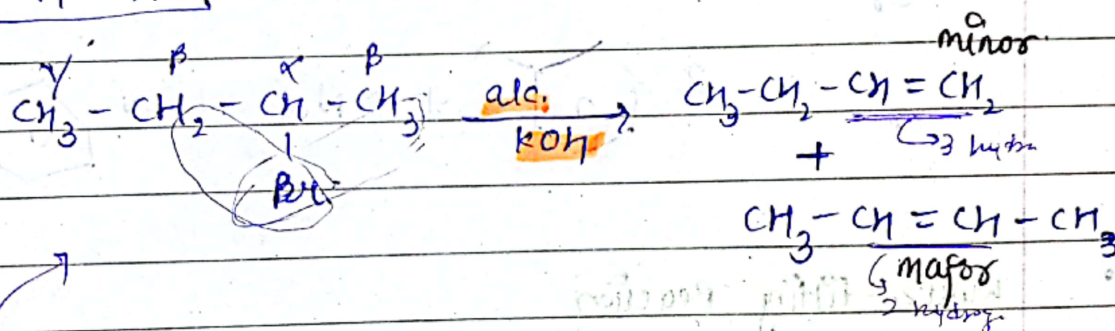
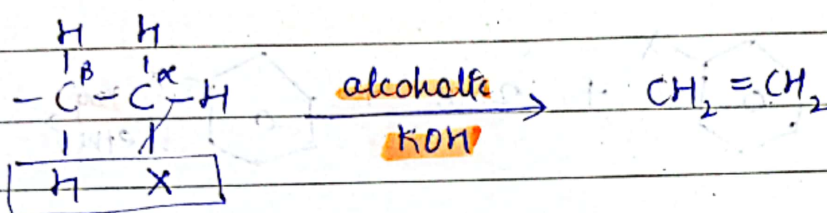
β carbon = the carbon next to α -carbon on either side

Page No.	
Date	

* Chemical properties of Haloalkanes

1) Elimination Reaction / Dehydrohalogenation / β -elimination

- When alkyl halide is treated with alcoholic potassium hydroxide then hydrogen at β -carbon is eliminated along with halogen. A saturated compound is changed into unsaturated compound and alkene are formed.



Saytzeff Rule :

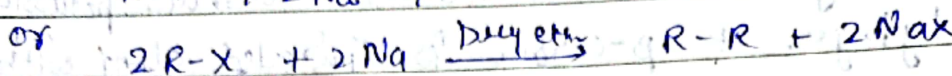
- ⇒ In β -elimination of alkyl halide; major product will be the alkene in which double bonded carbon have least no. of hydrogens.

OR

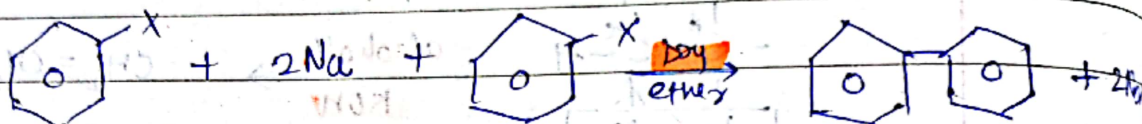
- ⇒ more alkylated alkene will be the major product.

2) Reaction with metal.

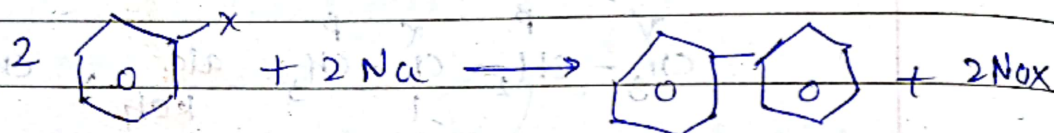
Wurtz Reaction.



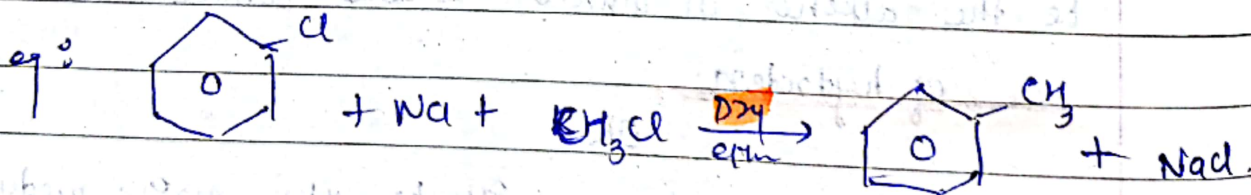
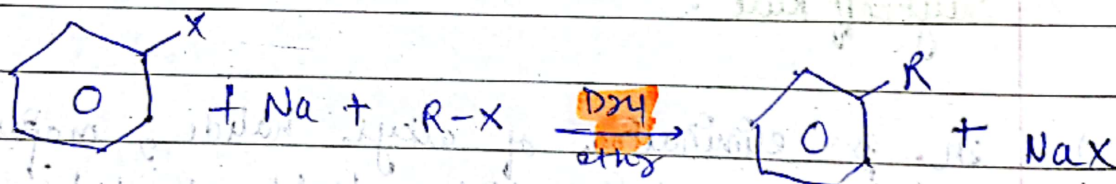
Fittig Reaction.



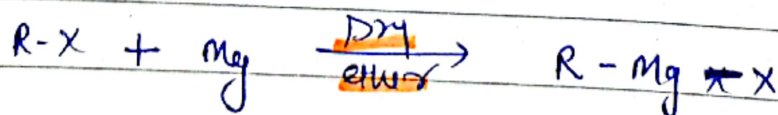
or



Wurtz-Fittig Reaction

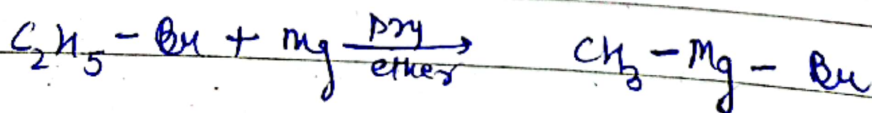


Reaction with magnesium metal.

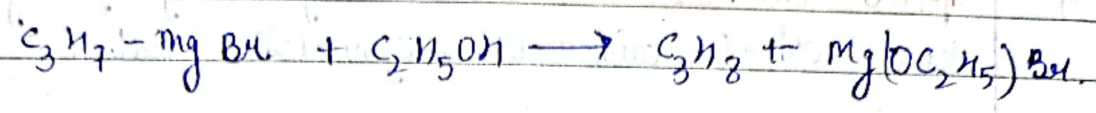
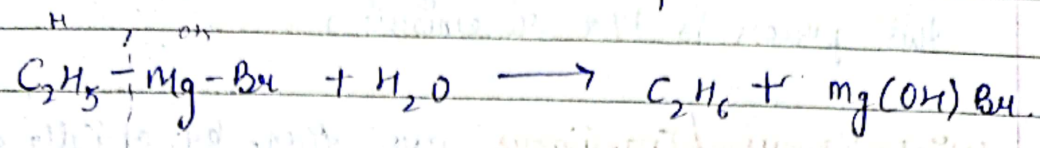


Grignard reagent
or

organo metallic compound.

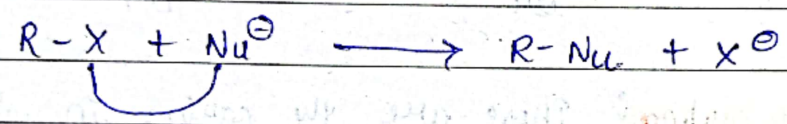


⇒ Grignard Reagent should be prepared under anhydrous condition because it is protonophile [proton lover] with any source of proton $[H^+]$ it form hydrocarbon.



d) **Nucleophilic substitution Rxn**

These substitution rxn in which an atom or group of atom is substituted by a nucleophile [nucleus lover] $\rightarrow Nu^-$



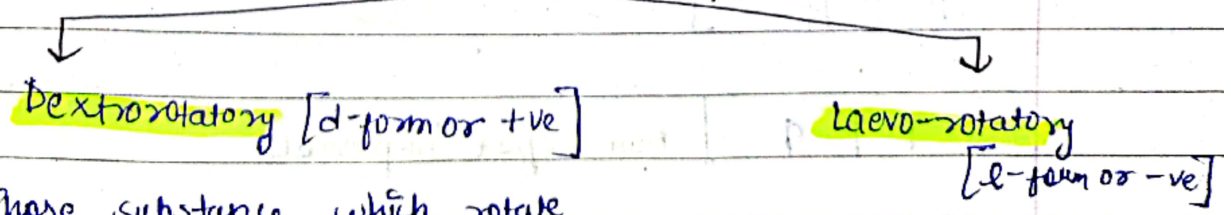
a) **Stereochemistry**. [Stereochemical aspects of nucleophilic substitution rxn]

Optical activity:

⇒ **Plane polarised light**: when an ordinary light passed through Nicol prism, it travel in single plane called PPL

⇒ **Optically active compound**: optically active substance are those, which can rotate plane polarised light.

Two types of optically active



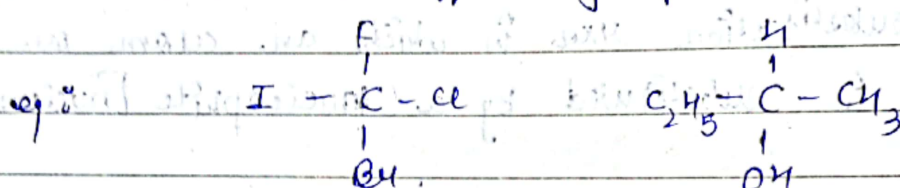
⇒ These substance which rotate PPL towards right are clockwise is k/a Dextrorotatory

⇒ These substance which rotate PPL towards left are anticlockwise is k/a

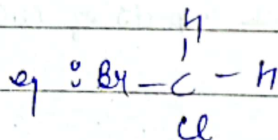
1) **Racemic mixture**: Equimolar mixture of dextro-rotatory and laevorotatory substance so that net rotation of PPL is zero. Called racemic mixture represented by dl or $\pm$. This process is called racemisation.

2) **Optical Isomers / Enantiomers** are given by optically active compounds have chiral carbon or asymmetric carbon.

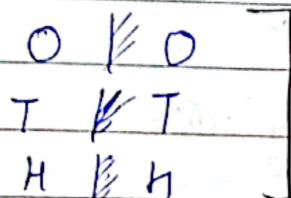
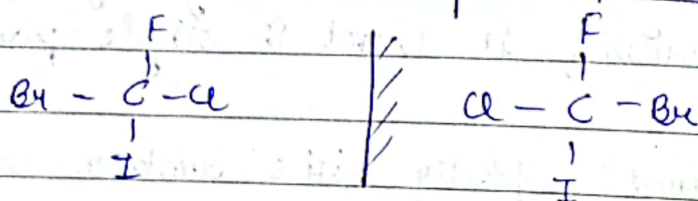
3) **Chiral carbon**: These are the carbon in which all four bonds of carbon are with different group.



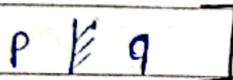
4) **Achiral carbon**: These are the carbon in which all four bonds of carbon are not with different group.



5) **Optical Isomers**: Non-super imposable mirror image.

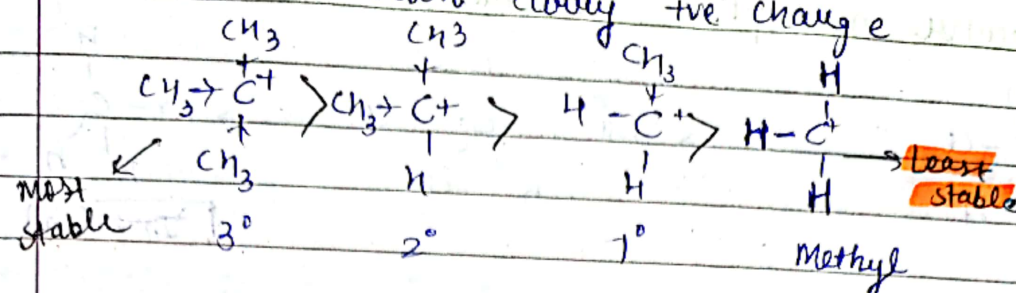


Super imposable



Non-super imposable

Carbocation : Carbon carry +ve charge



alkyl group are e^- donating in nature

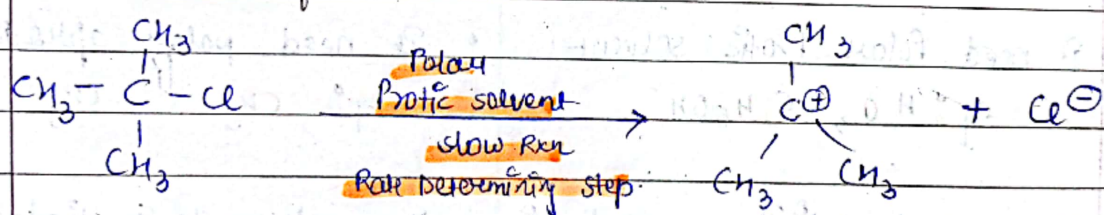
Types of nucleophilic substitution Rxn [2 Types]

1) **Unimolecular**

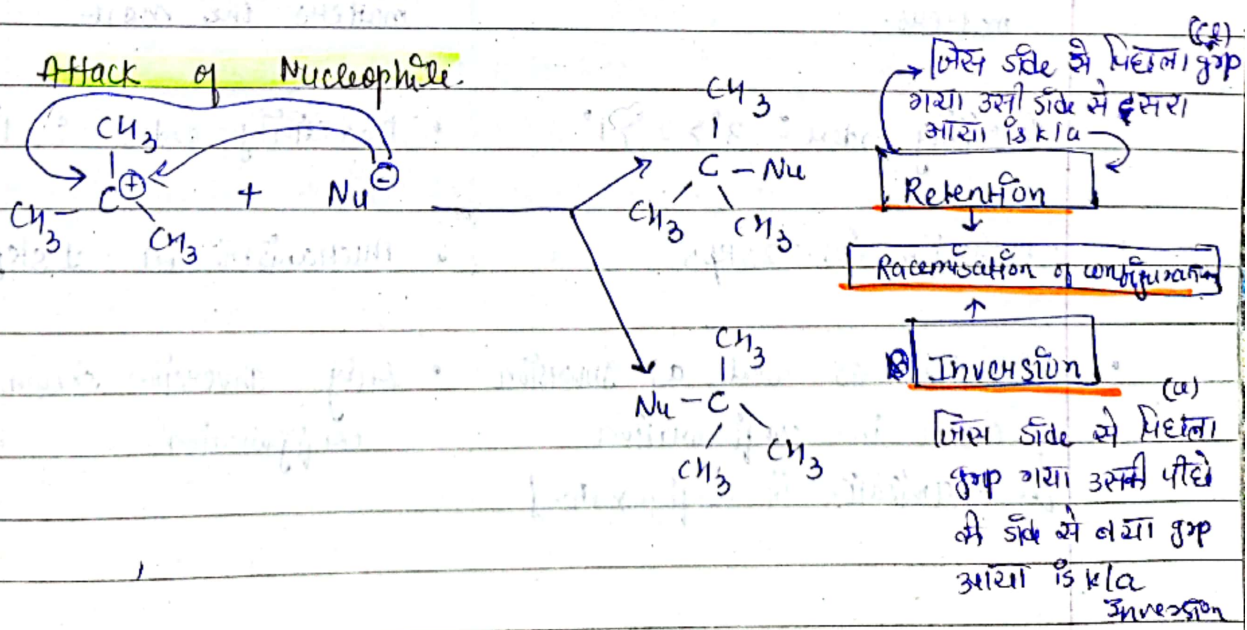
Nucleophilic substitution Rxn [S_N1]

It occurs in two steps:

Formation of Carbocation

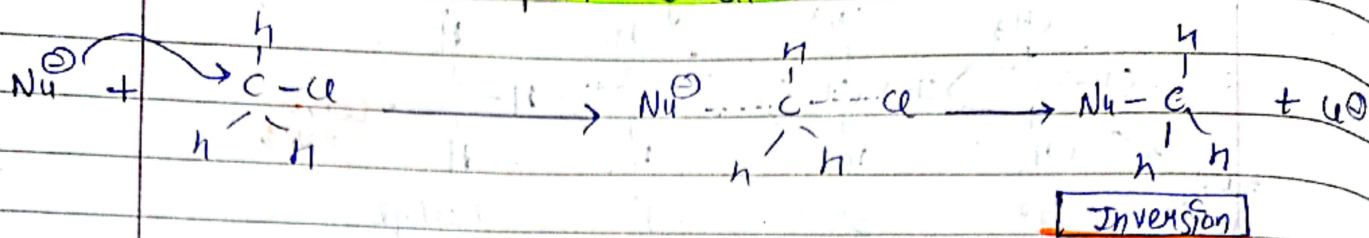


Attack of Nucleophile

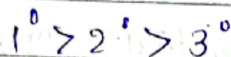


Stability of Carbocation
 Reactivity Order $\rightarrow 3^\circ > 2^\circ > 1^\circ$

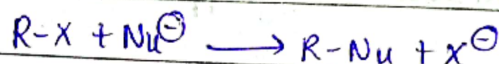
2)

Bimolecular nucleophilic substitution [S_N2]

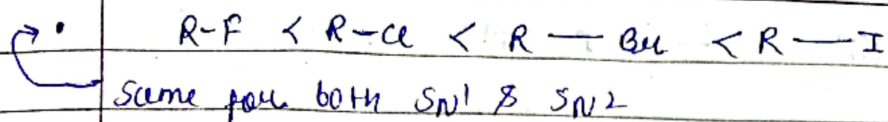
⇒ Less steric hindrance
 ↳ faster



★

S_N1 [unimolecular]S_N2 [Bimolecular]

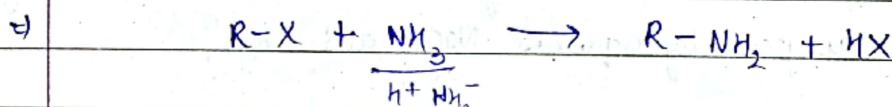
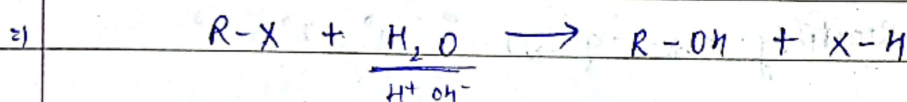
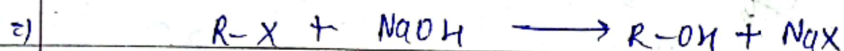
- | | |
|---|--|
| <ul style="list-style-type: none"> • Rate of Rxn depends on: $k [\text{R-X}]$ • It need Polar Protic solvent
eg: H_2O, $\text{C}_2\text{H}_5\text{OH}$ • Here low stability of carbocation matters. • Reactivity order: $3^\circ > 2^\circ > 1^\circ$ • Mechanism in 2 steps • Retention as well as inversion shown in configuration
[∴ Racemisation in configuration] | <ul style="list-style-type: none"> • Rate = $k [\text{R-X}] [\text{Nu}^-]$ • It need polar aprotic solvent
eg: CH_3COCH_3 • Here less steric hindrance matters the most • Reactivity order: $1^\circ > 2^\circ > 1^\circ$ • Mechanism in 1 step. • Only Inversion shown in the configuration. |
|---|--|



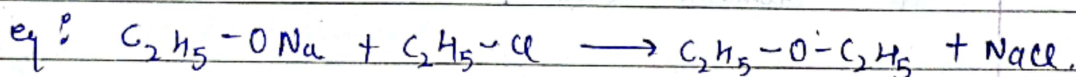
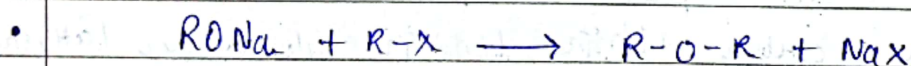
• Benzyl and allyl prefer to undergo S_N1 reaction.

• Order for S_N1 : Benzyl & Allyl $> 3^\circ > 2^\circ > 1^\circ$

* some examples of nucleophilic substitution rxn.

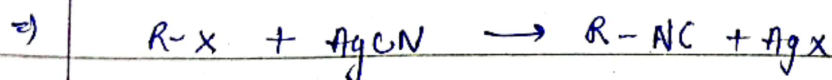
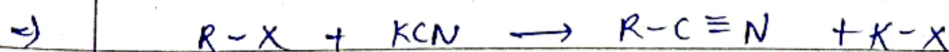


⇒ Williamson synthesis: This rxn follows S_N2 mechanism.

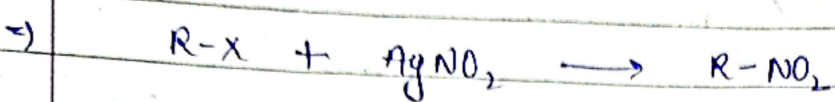
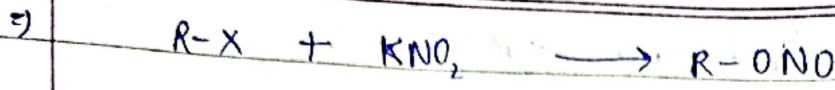


Note: Alkyl halide should be primary, so that ether will be formed. If alkyl halide is 3° then elimination rxn takes place & alkene is formed.

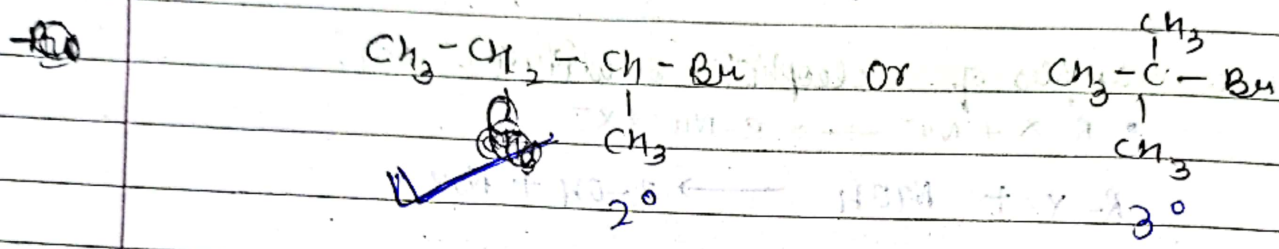
• Reactivity order of elimination rxns $3^\circ > 2^\circ > 1^\circ$



• Ambidentate Nucleophile: which have two attacking centre is K/a amb---



Q. which alkyl halide from the following pair would you expect to react more rapidly by an S_N2 mechanism?



Reactivity order of S_N2 : $1^\circ > 2^\circ > 3^\circ$

Q. Out of chlorobenzene (C_6H_5Cl) and benzyl chloride ($C_6H_5CH_2Cl$), which one gets easily hydrolysed by aqueous NaOH and why?

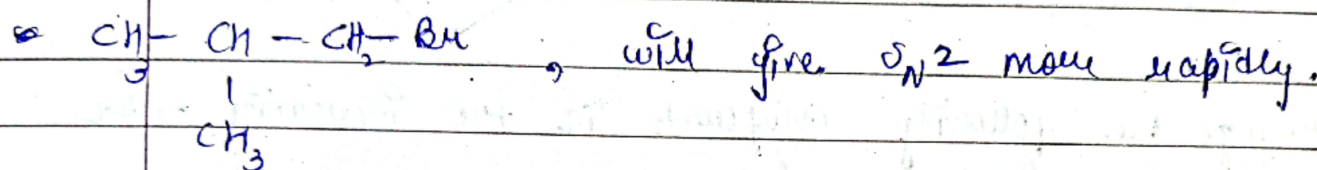
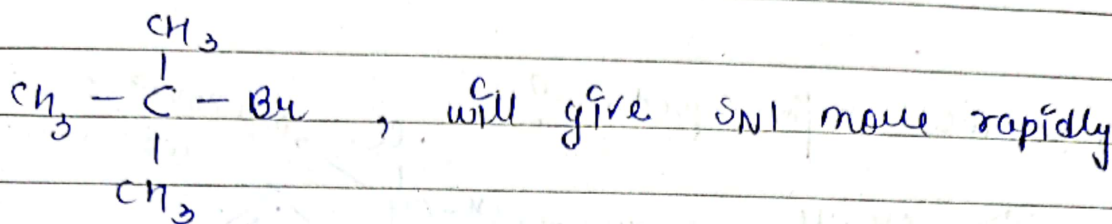
Benzyl chloride will get easily hydrolysed by aqueous NaOH because the carbon-chlorine bond in benzyl chloride [attached to an aliphatic carbon] is weaker & more reactive than the carbon-chlorine bond in chlorobenzene [attached to an aromatic carbon].

Q. Out of $CH_3-\overset{1^\circ}{CH}-CH_2-Cl$ and $CH_3-\overset{2^\circ}{CH}-CH_2-Cl$ which is more reactive towards S_N1 rxn & why?

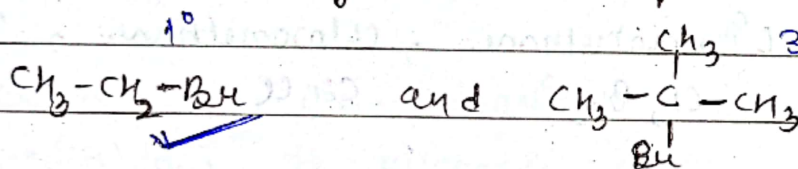
Ans. Reactivity order of S_N1 : $3^\circ > 2^\circ > 1^\circ$

Q Write the structure of an isomer of compound C_4H_9Br which is most reactive towards S_N1 Rxn & S_N2 Rxn?

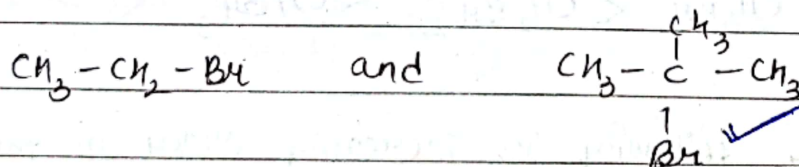
Ans C_4H_9-Br isomer.



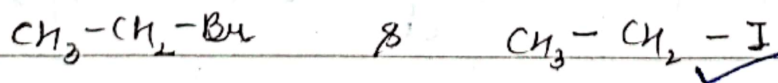
Q which would undergo S_N2 Rxn faster in the following pair & why?



Q " " " S_N1 " " " " " ?

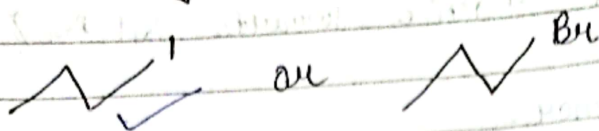


Q which would undergo S_N2 Rxn faster in the following

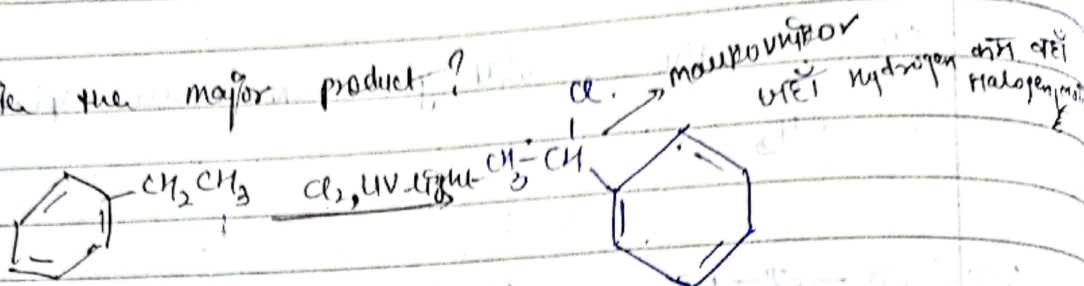


→ Because, $R-F < R-Cl < R-Br < R-I$
 I^- is a better leaving group.

Q. which will give faster S_N2 ?



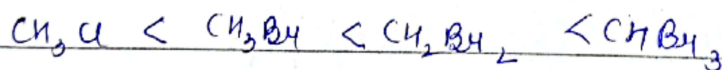
Q. write the major product?



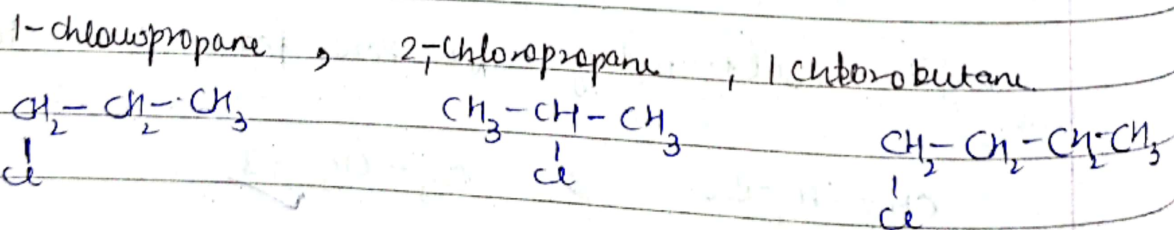
Q. Arrange the following compounds in the increasing order of their boiling points:

Bromoform, Dibromomethane, chloromethane, Bromomethane
 $CHBr_3$ CH_2Br_2 CH_3Cl CH_3Br

Ans. B.P & molecular weight.



Q. Arrange the following in increasing order of their B.P

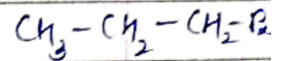
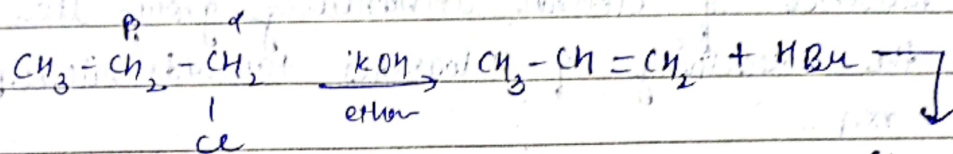
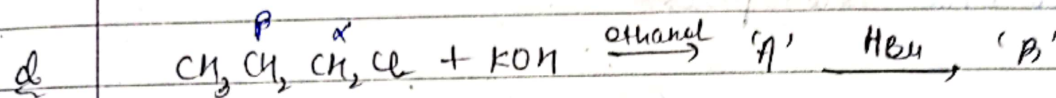
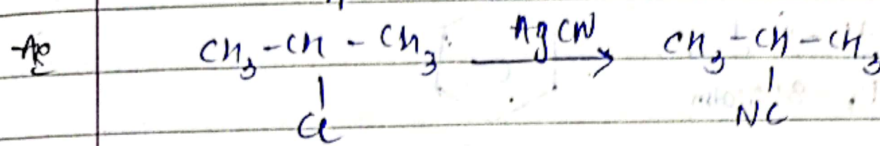
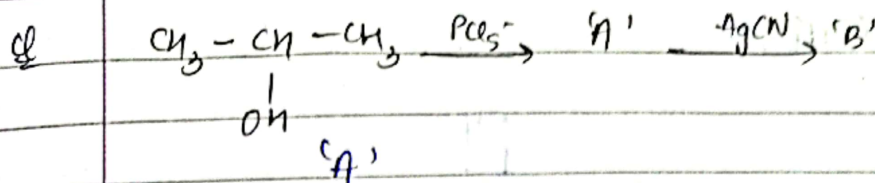


Ans. 2-chloropropane $\times$ 1-chloropropane $<$ 1-chlorobutane

Q. what is an ambident nucleophile? Give eg:

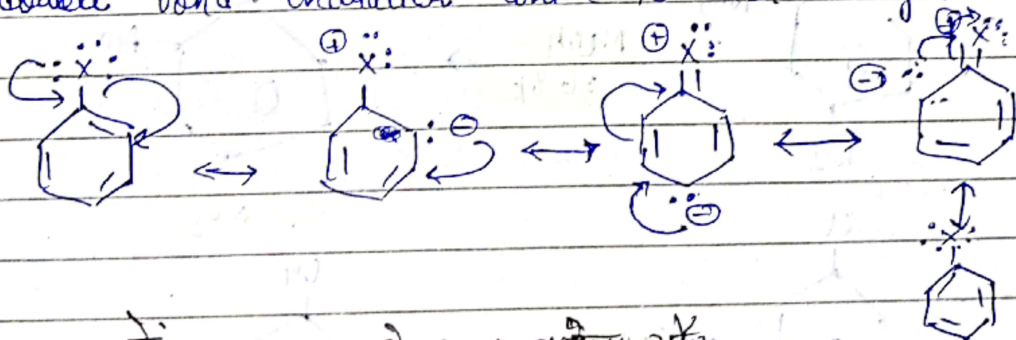
2) Those nucleophile which have two attacking centre.





* Chemical Properties of Haloarenes.

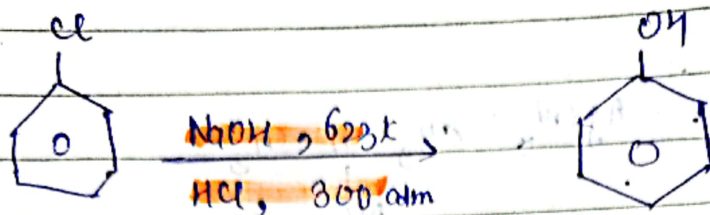
- 1) Haloarenes are less reactive towards nucleophilic substitution reaction. due to resonance C-X bond have partial double bond character which is not easy to break.



Resonance में, electron से Bond बनता है
Bond से electron:

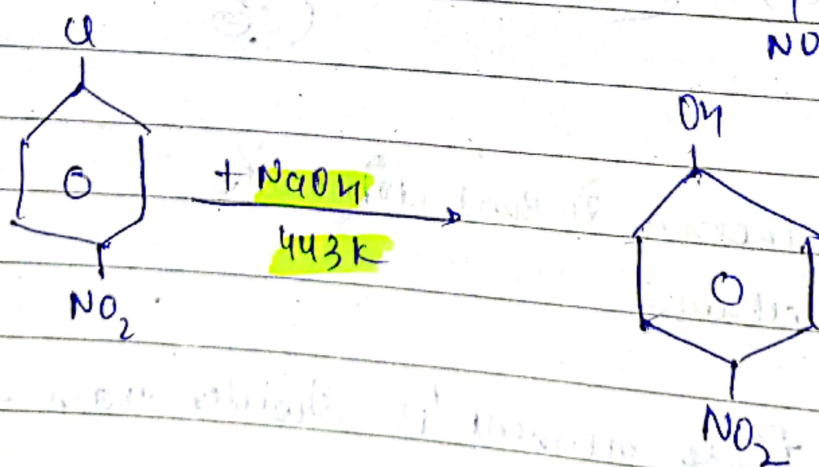
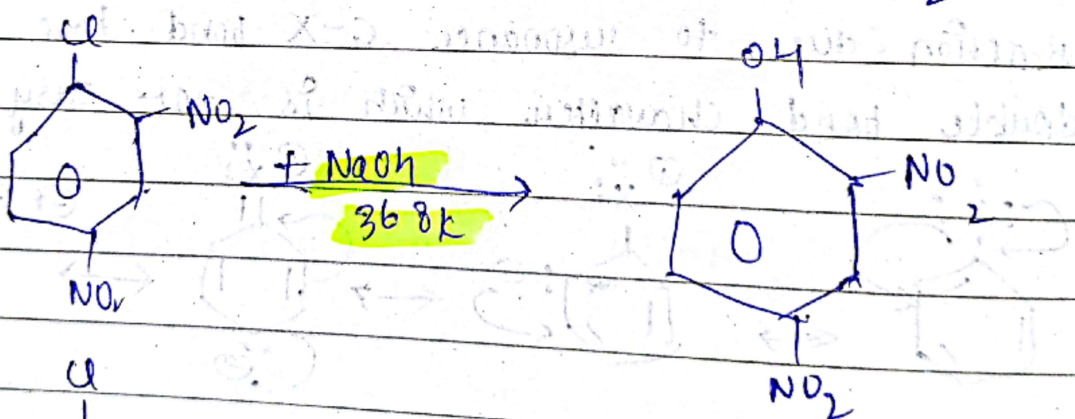
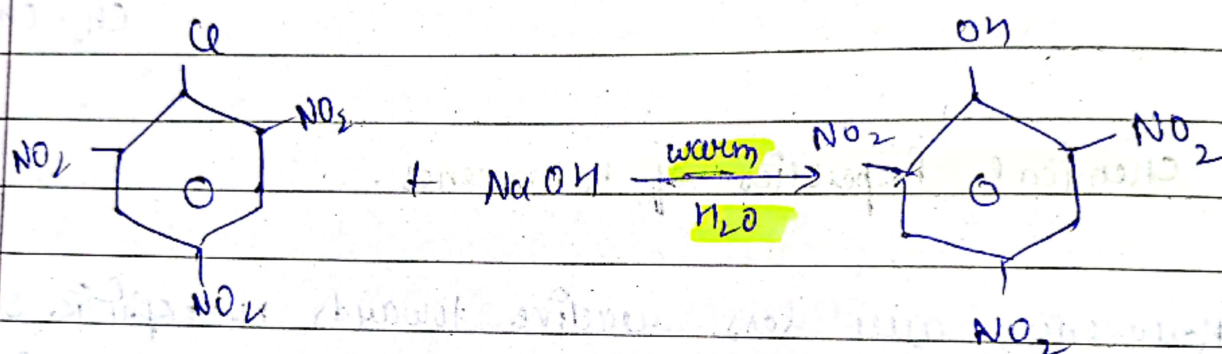
- 2) Haloarene dipole moment is smaller than alkyl halides.

①

Nucleophilic Substitution

⇒ This is called S_N1 process

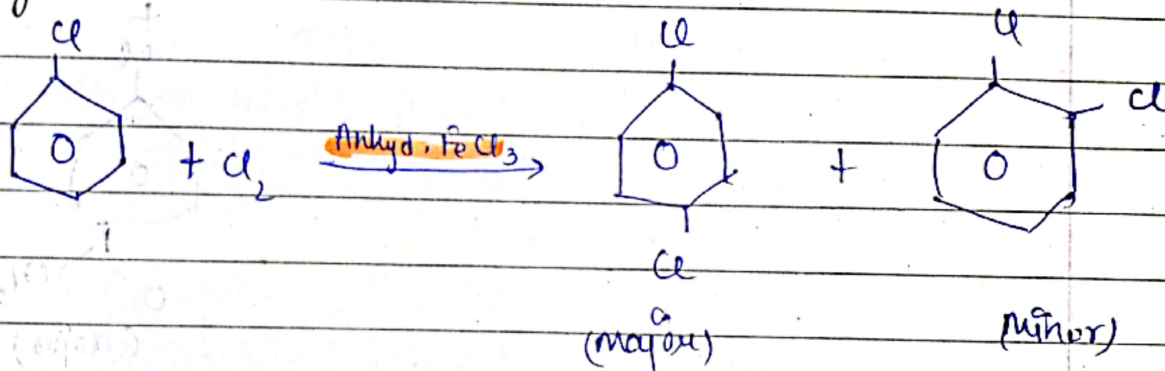
⇒ Presence of electron withdrawing group like NO_2 increases the reactivity of Haloarenes towards nucleophilic substitution.



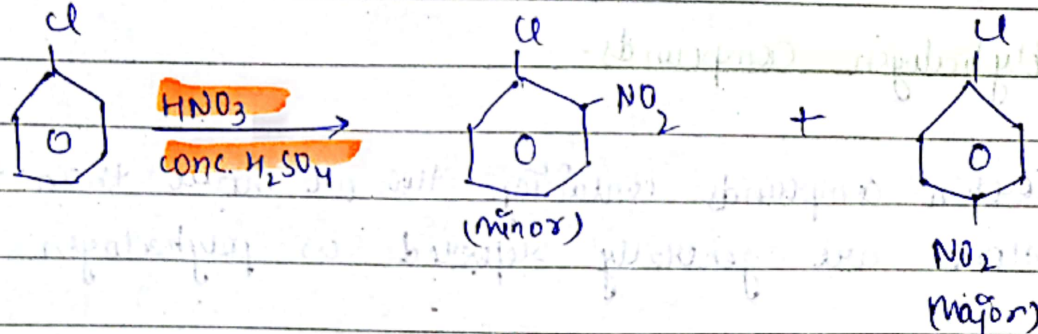
② Electrophilic substitution rxn :

- Halobenzenes undergo electrophilic substitution rxn due to benzene ring. Halogen group is ortho & para directing. So, the substitution takes place at ortho and para positions.
- Although halogen group is 'o' 'p' directing but it also has deactivating effect due to -I effect.

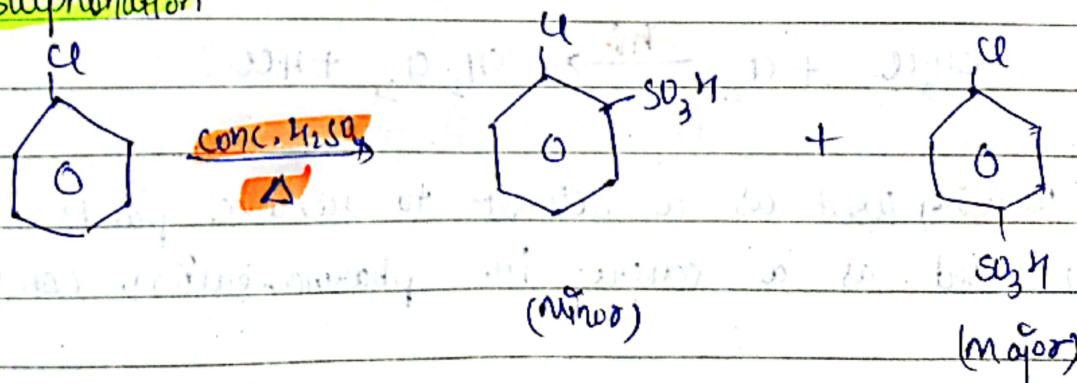
i) Halogenation :



(ii) Nitration :



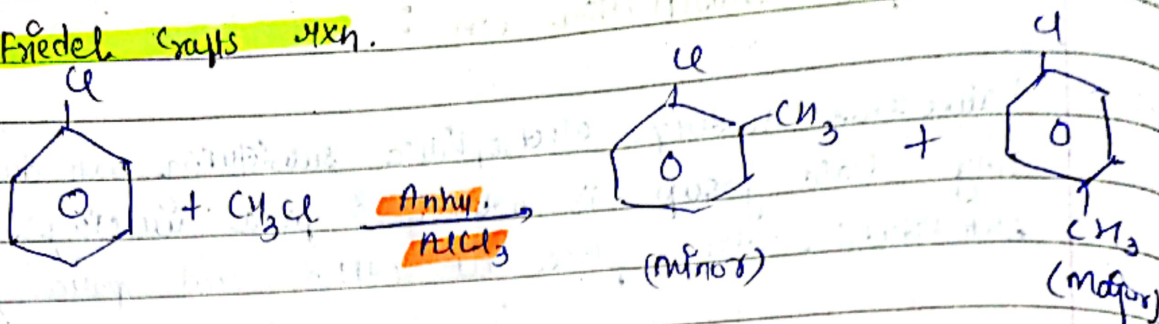
(iii) Sulphonation



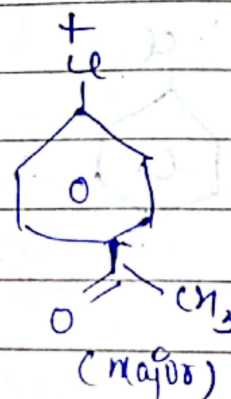
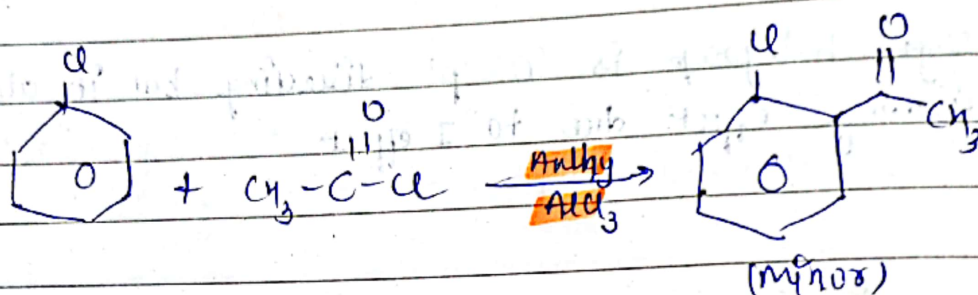
α
(M)

Friedel Crafts rxn.

Alkylation



Acylation

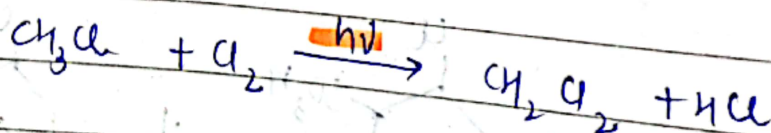


*

Polyhalogen Compounds

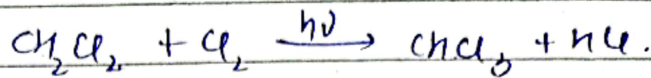
Carbon compounds containing two or more than two halogen atoms are generally referred as polyhalogen.

1) Dichloromethane [methylene chloride]



- uses i) used as a solvent to remove paints
- ii) used as a solvent in pharmaceutical companies

2) Bichloromethane [Chloroform].



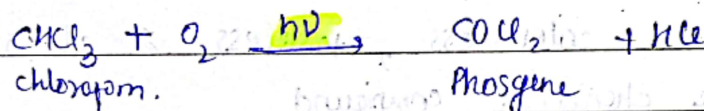
→ chloroform carbon

uses: ⇒ used in production of the Freon. [CFC]

⇒ used as anesthetic in cough syrup.

⇒ used as preservative for anatomical specimens.

⇒ chloroform should be kept in air tight dark bottles because, it undergoes atmospheric oxidation in the presence of sunlight & form a poisonous gas called "phosgene".



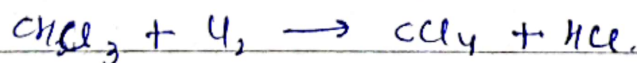
3) Iodoform [Iodoform].

⇒ It was earlier used as an antiseptic but the antiseptic properties are due to liberation of free iodine & not due to iodoform itself.

uses: ⇒ It is used to manufacture pharmaceutical products.

⇒ used as antiseptic, when it comes in contact with skin it liberates free iodine which act as an antiseptic.

4) Tetrachloromethane [Carbon tetrachloride].

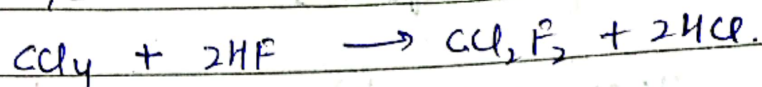


uses: ⇒ used as an fire extinguisher

⇒ used in manufacture of chloroform

⇒ used in dry cleaning.

• **Freons** - 1, 2



uses: used as refrigerants in refrigerator & air conditioners.

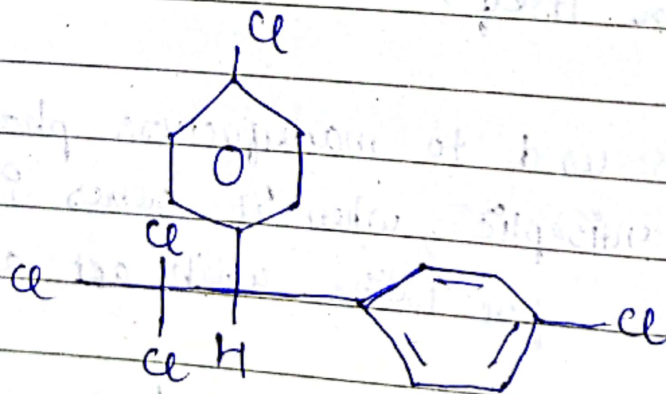
Harm: these freons are responsible for the depletion of ozone layers.

• **p,p'-Dichloro Diphenyl Trichloroethane [DDT]**

⇒ DDT is a colourless, tasteless & almost odourless crystalline chemical compound.

⇒ It is very effective against the mosquitoes that spread malaria and lice that carry typhus.

Harm: It is very toxic for fishes. It is not metabolised by animals. Instead it is stored in fatty tissues.



DDT.

Q Identify A, B, C, D, E and F :

