

HALOALKANES & HALOARENES

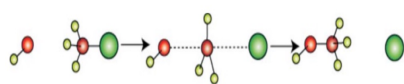
CLASS XII
BOARD EXAM

These notes
have been unified
by top families &
CBSE Science
Toppers

↳ Target 100
↳ Previous Year Q's
Integrated

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Amar
Chattarwal



Flow Chart

Methods of preparation

From Alcohols

From Hydrocarbons

Halogen Exchange

Physical Properties

B.P.

M.P.

Solubility

Reactions of Haloalkane

Nucleophilic Substitution

S_N1 and S_N2

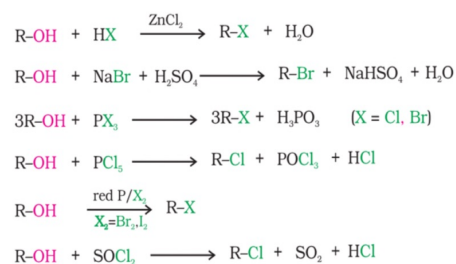
Elimination Reaction

Reaction with metals

Classification

Nomenclature

Nature of C-X bond



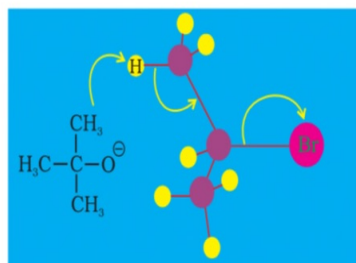
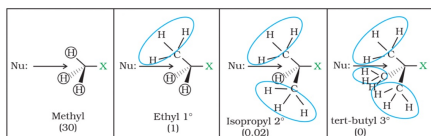
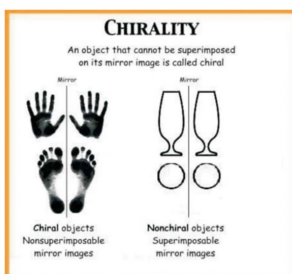
Haloalkanes and Haloarenes

Reaction of Haloarenes

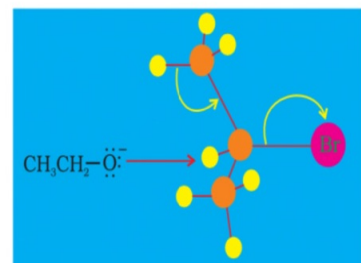
Nucleophilic Substitution

Electrophilic Substitution

Reaction with metals



Elimination



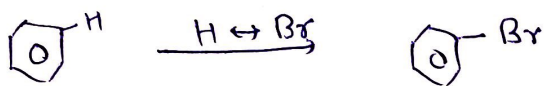
vs

Substitution

Haloalkanes and Haloarenes

→ Aliphatic hydrocarbon $\xrightarrow{H \leftrightarrow X}$ Alkyl halide [haloalkane]
 Aromatic hydrocarbon $\xrightarrow[\text{atom}]{\text{Replacement of hydrogen by halogen}}$ Aryl halide [haloarene]

Example - : $CH_4 \xrightarrow{H \leftrightarrow Cl} CH_3Cl$ Methyl chloride



Classification on basis of number of halogen atoms

- If one halogen atom is present in structure of alkanes/arenes : Monohaloalkane / Monohaloarene
- If two halogen atoms are present : Dihaloalkane / Dihaloarene
- similarly, If three halogen atoms are present : Trihaloalkane / Trihaloarene

Example - : C_2H_5X : Monohaloalkane ($X \rightarrow$ Halogen)



Monohalo compounds

Compounds containing sp^3 C-X bond

Compounds containing sp^2 C-X bond

① Alkyl halides : (R-X)

→ Primary Alkyl halide : $R'-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-X$

Example - : CH_3-CH_2-Br

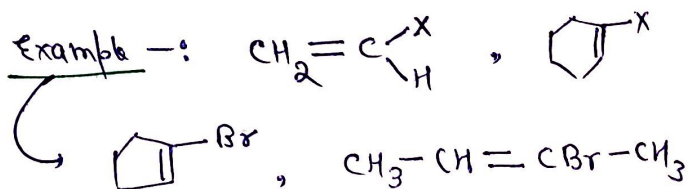
→ Secondary (2°) : $R'-\overset{\overset{R''}{|}}{\underset{\underset{X}{|}}{C}}-X$

Example - : $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-H$

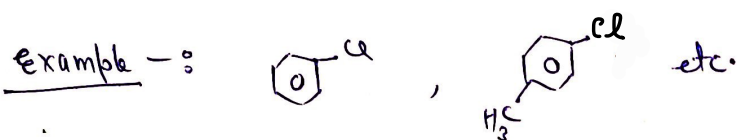
→ Tertiary (3°) : $R-\overset{\overset{R'}{|}}{\underset{\underset{R''}{|}}{C}}-X$

Example - : $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl$

① Vinyllic Halide :- X is bonded to carbon-carbon double bond.

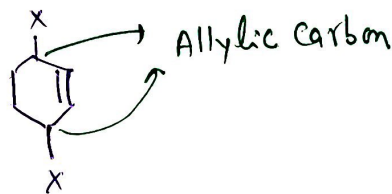
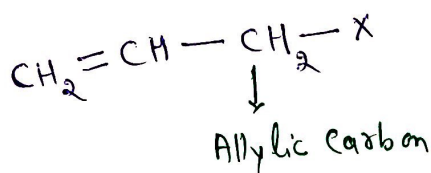


② Aryl halide :- X (halogen atom) is bonded to the carbon of aromatic ring (benzene)



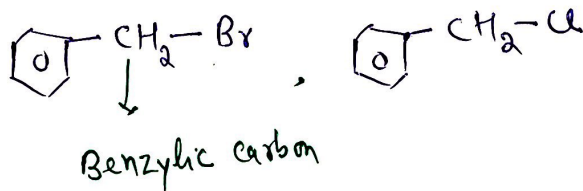
② Allylic Halides : X is bonded to sp^3 hybridised carbon atom next to carbon-carbon double bond.

Example -:



③ Benzylic halide -: Compounds in which the halogen atom is bonded to an sp^3 hybridised carbon atom next to benzene ring.

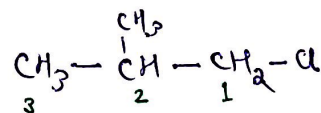
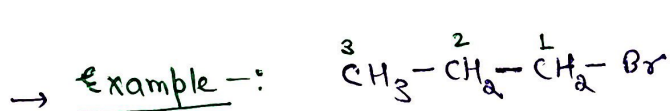
Example :



Nomenclature

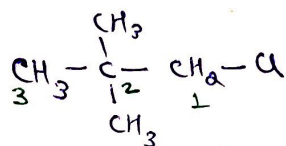
→ As we know about selection of main chain and numbering of hydrocarbon, same rule is here also (considering halogen atoms (F, Cl, Br, I) as substituents).

→ Rule : No. of carbon > Max. no. of substituent > Lowest set of locants > Alphabetical order

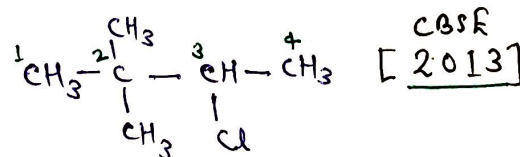


IUPAC → 1-Bromopropane

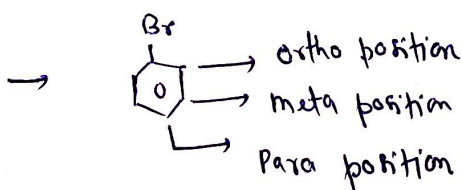
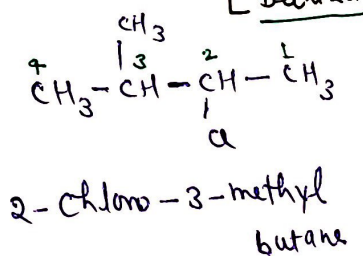
1-Chloro-2-methylpropane



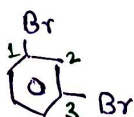
1-Chloro-2,2-dimethylpropane



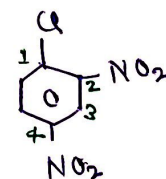
3-chloro-2,2-methylbutane



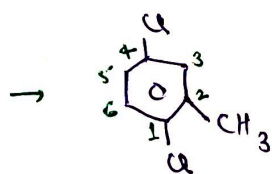
Bromobenzene



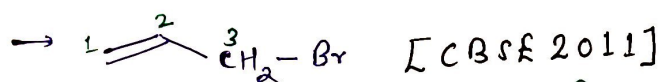
Common name : m-Dibromobenzene
IUPAC : 1,3-Dibromobenzene



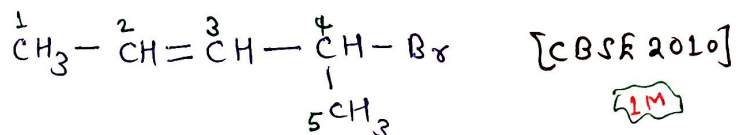
2,4-Dinitrochlorobenzene



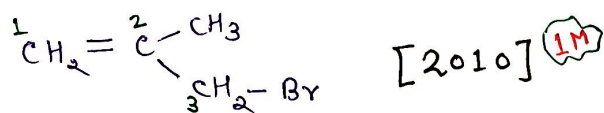
⇒ 1,4-Dichloro-2-methylbenzene
[CBSE 2013]



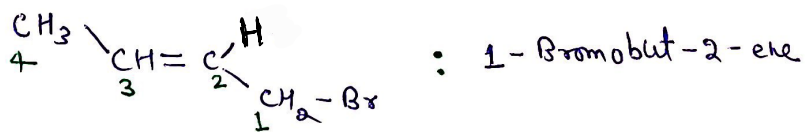
3-Bromopropene



4-Bromopent-2-ene

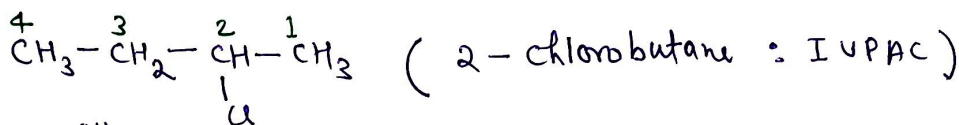


3-Bromo-2-methylpropene

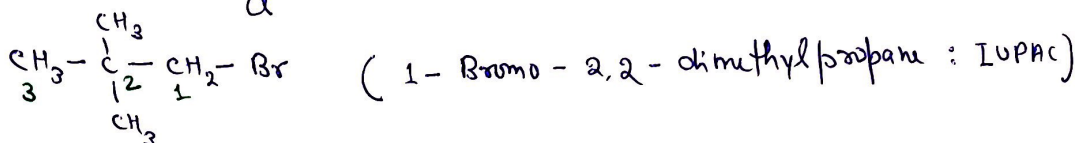


→ Draw the structure of following Compounds?

a.] sec-Butyl chloride

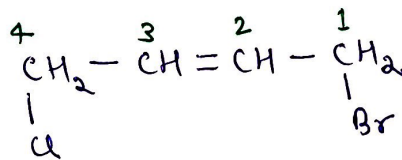


b.] Neo-Pentyl bromide



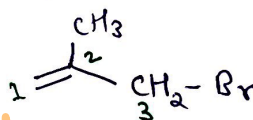
c.] 1-Bromo-4-chlorobut-2-ene

[Delhi 2017] (1M)



d.] 3-Bromo-2-methylprop-1-ene

[Delhi 2017] (1M)



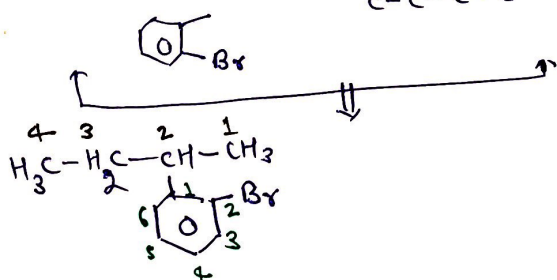
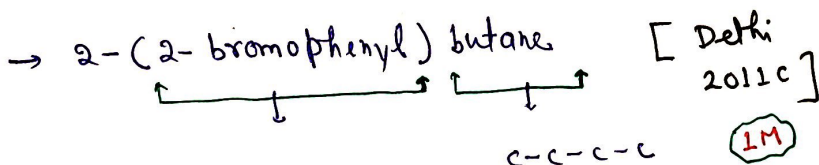
Apni Kaksha

NOTE : Benzene as substituent : Phenyl

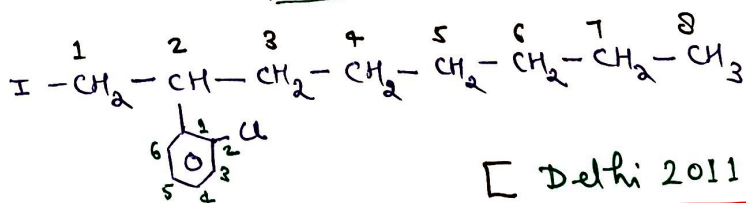
Example :- Chloromethyl benzene [X]

chlorophenylmethane is correct

name of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$



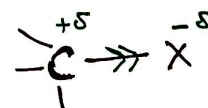
2-(2-chlorophenyl)-1-iodooctane



[Delhi 2011c]

Nature of C-X bond

→ Due to electronegative nature of halogens, C-X bond is polar.



→ size of halogen : $\text{I} > \text{Br} > \text{Cl} > \text{F}$

→ Carbon-halogen bond length : $\text{C-I} > \text{C-Br} > \text{C-Cl} > \text{C-F}$

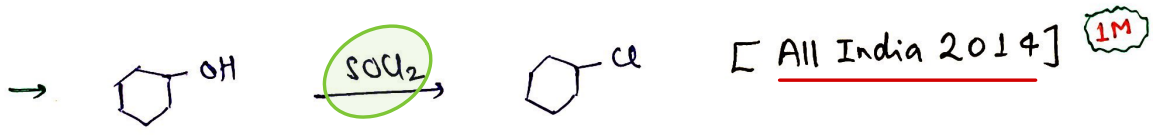
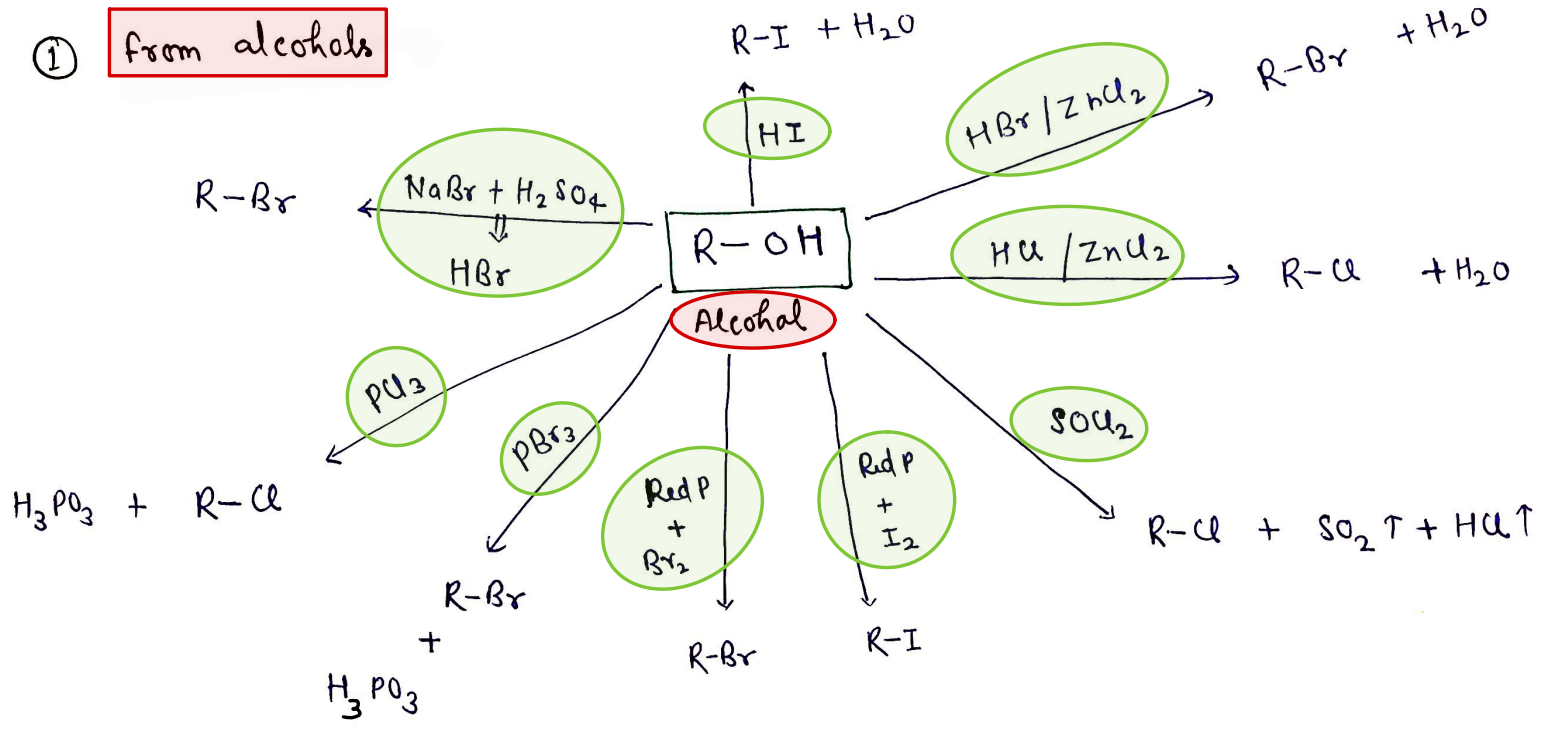
→ Bond Length of C-X $\propto$ $1/\text{C-X bond enthalpies}$

→ Bond Enthalpy : $\text{C-F} > \text{C-Cl} > \text{C-Br} > \text{C-I}$

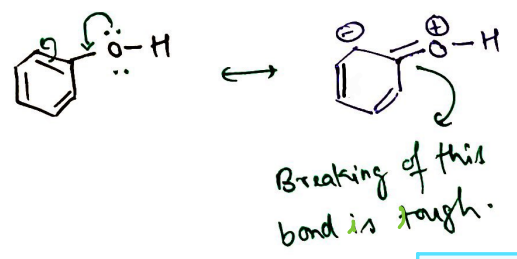
→ Order of dipole moment : $\text{CH}_3\text{-Cl} > \text{CH}_3\text{-F} > \text{CH}_3\text{-Br} > \text{CH}_3\text{-I}$

Methods of preparation

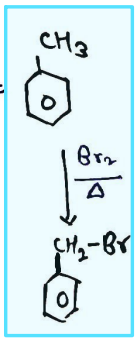
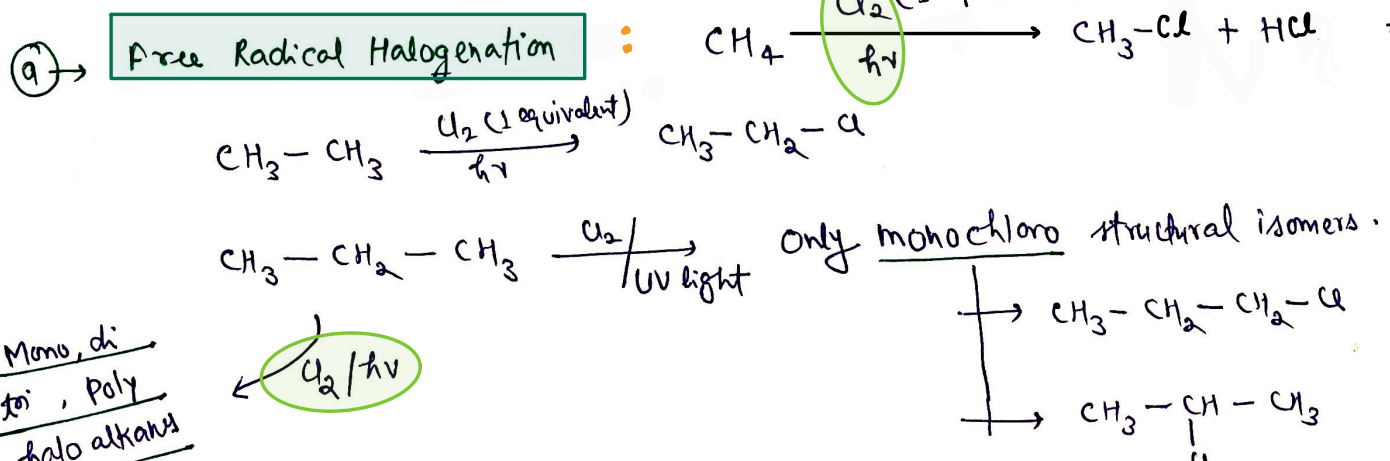
① from alcohols



→ Above method is not applicable for the preparation of aryl halides because the carbon-oxygen bond in phenol has partial double bond character.



2.] From Hydrocarbon

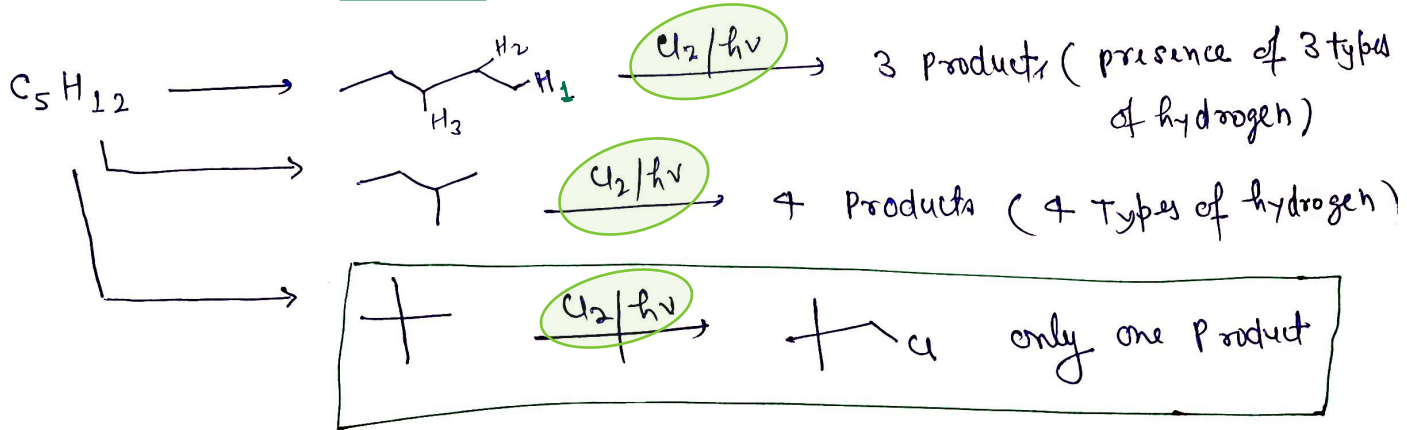


A hydrocarbon C_5H_{12} gives only one monochlorination product. [Delhi 2013C]

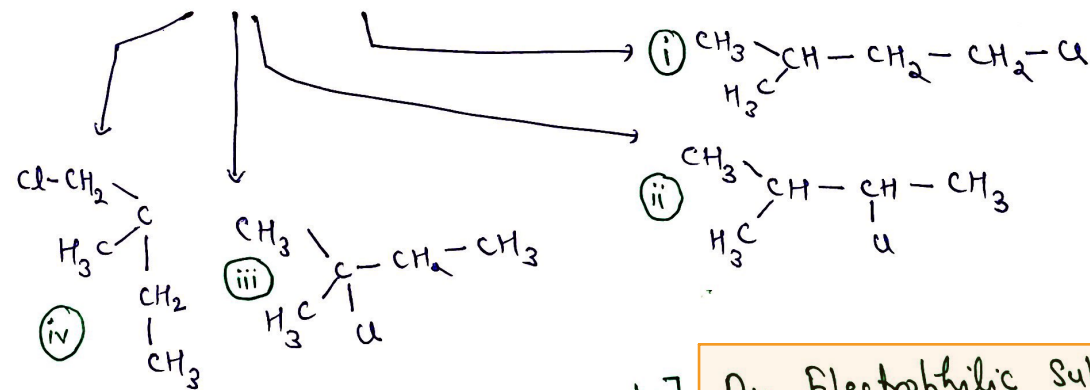
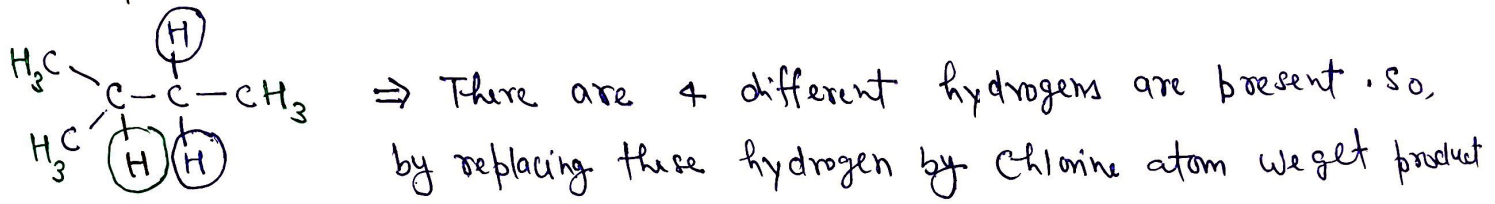
2 M

Identify the hydrocarbon.

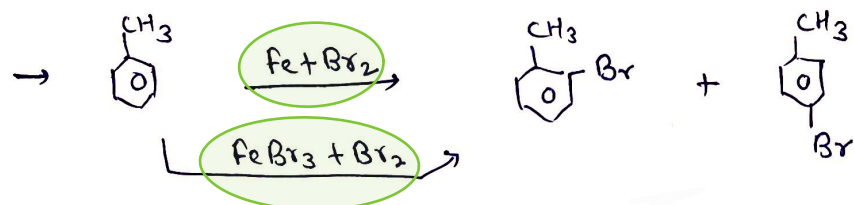
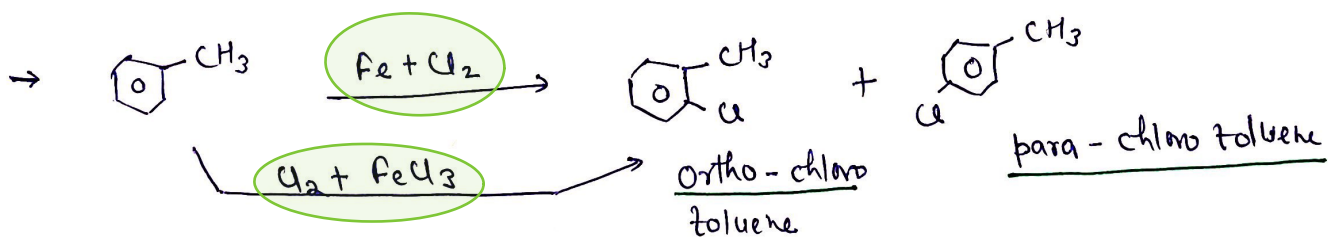
Isomers



→ Find possible monochloro structural isomers of $(CH_3)_2CH-CH_2-CH_3$.

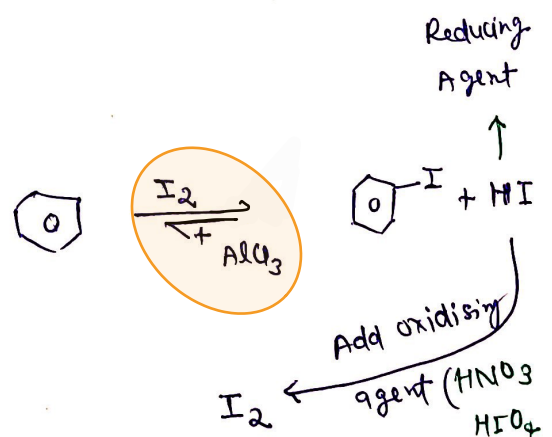


b.] By Electrophilic Substitution :-



→ Reactions with I_2 are reversible in nature.

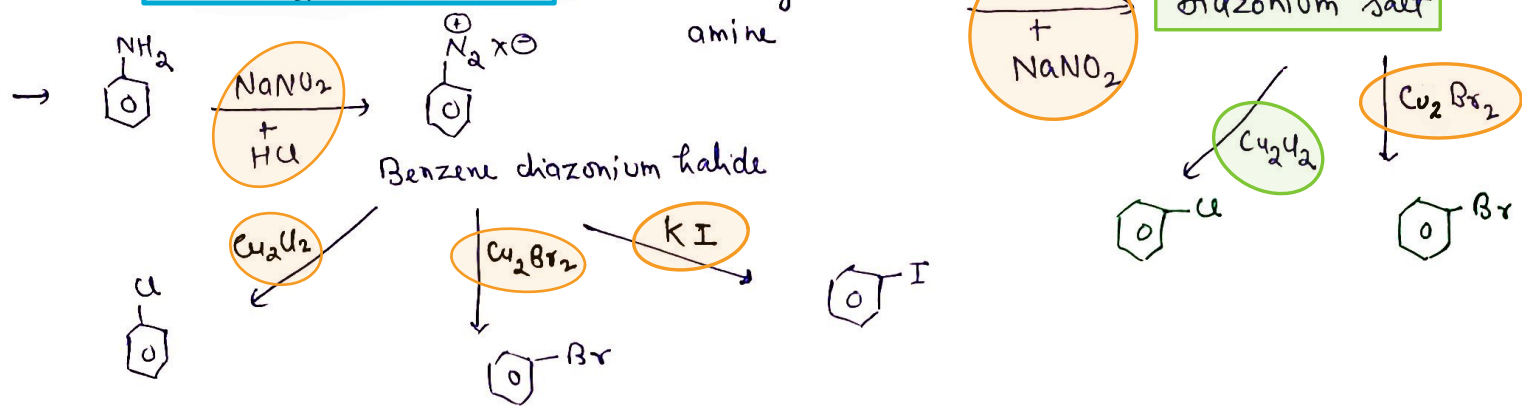
This reaction requires presence of oxidising agent to oxidise HI formed during iodination.



→ Due to high reactivity of fluorine (there is probability of explosion)

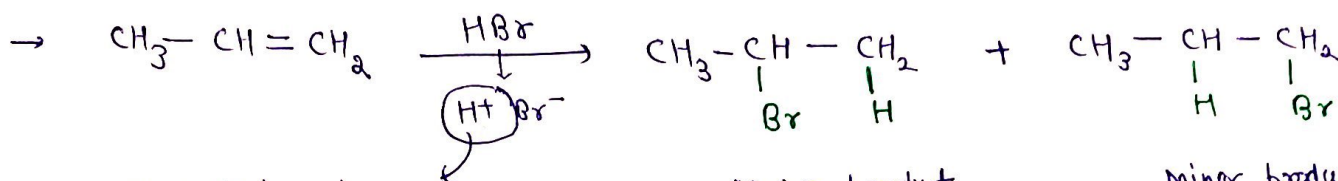
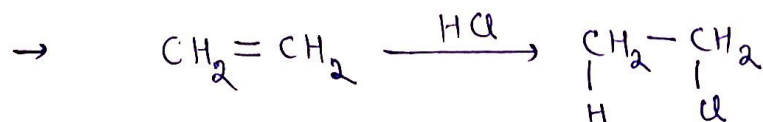
fluoro compounds are not prepared by this method.

c.] Sandmeyer's Reaction :- Primary aromatic amine



d.] From alkenes :-

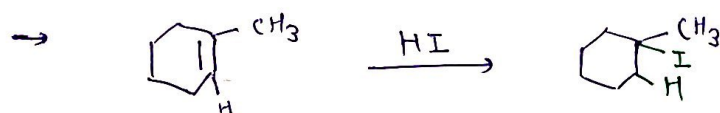
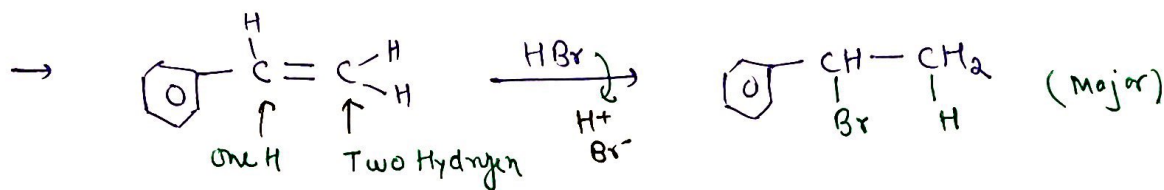
(i) Addition of hydrogen halide ($\text{HCl}, \text{HBr}, \text{HI}, \text{HF}$)



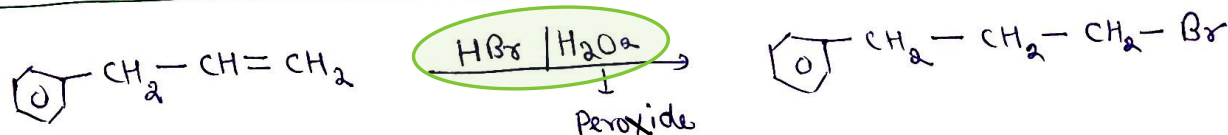
Add to that carbon which has more no. of hydrogen.

Major product
Markovnikov's

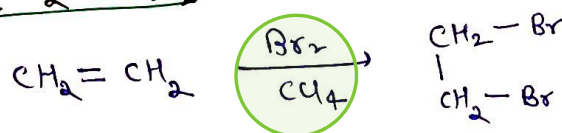
Minor product
Anti-Markovnikov's



But in presence of peroxide only addition of HBr $\Rightarrow$ Anti markovnikov's fashion



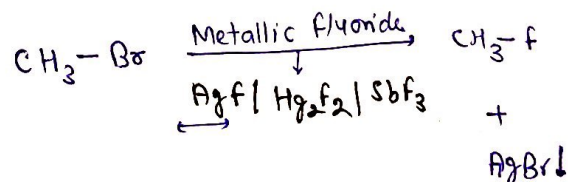
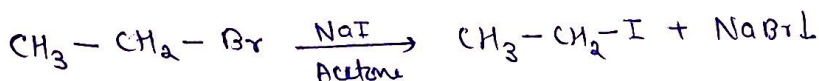
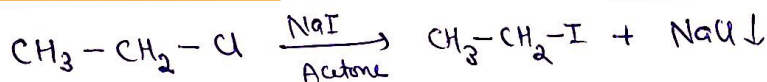
(ii) Addition of Halogens (Cl_2, Br_2) :-



Finkelstein Reaction

Halogen Exchange

Swarts Reaction

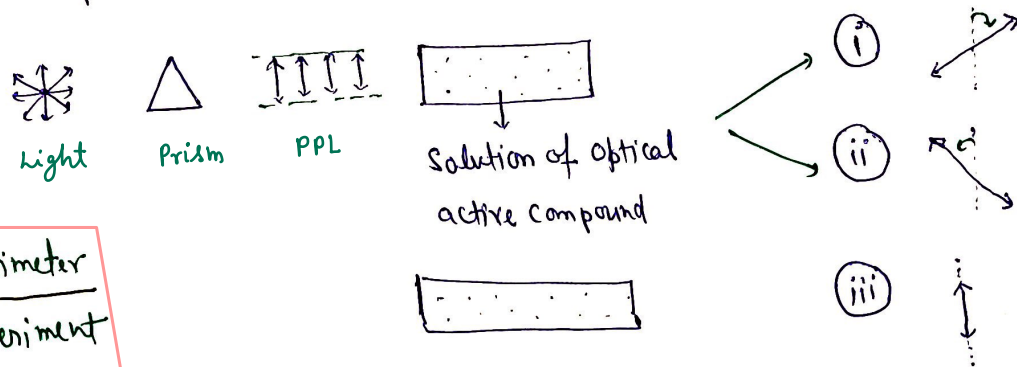


In Acetone : NaI is soluble but not NaCl/NaBr.

In water Agf is soluble but not AgCl/AgBr.

Optical active compound -:

"The compound which can rotate the plane polarised light"



Rotation in right direction } dextro-rotatory

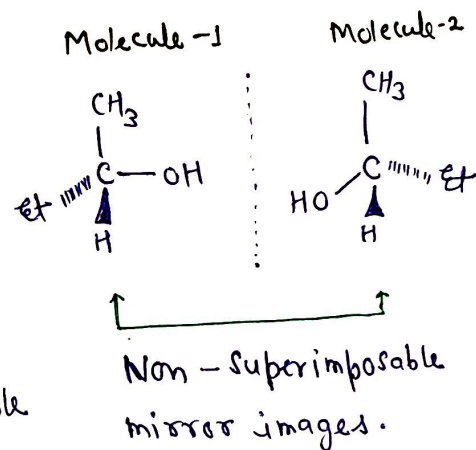
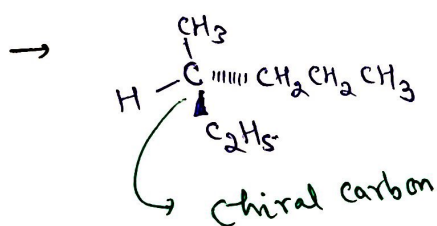
Rotation in left direction } laevo-rotatory

No Rotation → optically inactive

Polarimeter Experiment

→ dextro-rotatory compound and laevo-rotatory compounds are optical isomers. This phenomenon is known as **optical isomerism**.

→ **Asymmetric Carbon** [chiral carbon] -: sp^3 hybridised carbon attached with 4 different substituents is known as chiral carbon.



→ **Chiral** -: The objects which are non-superimposable on their mirror image are said to be chiral.

"molecule having a chiral carbon is always optical active."

chiral molecule
↓
Optical active compound.

→ **Enantiomers** -: Stereoisomers with non-superimposable mirror image character.

→ **Diastereomer** -: Stereoisomers which are not mirror image of each other.

→ In above example molecule-1 & molecule-2 are enantiomer of each other as they are non-superimposable mirror images.

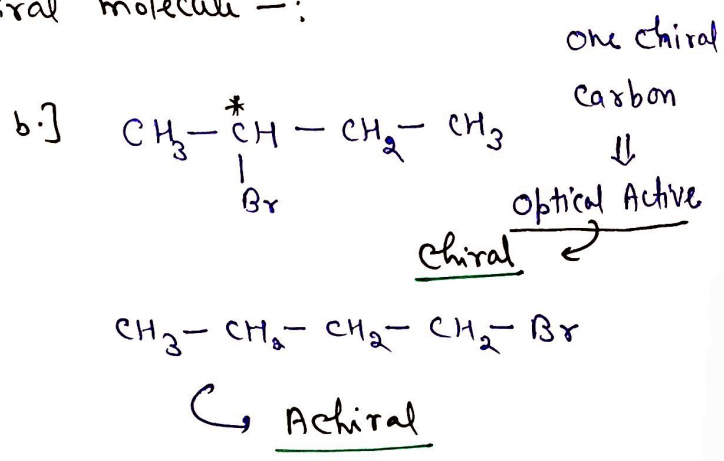
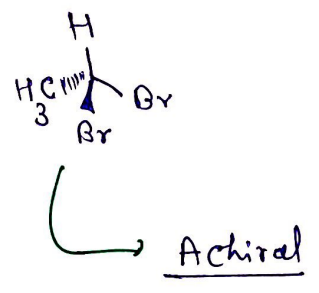
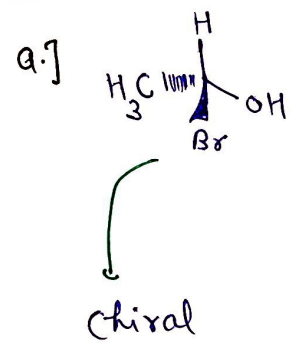
→ **Racemic mix** -: A mixture containing two enantiomers in equal proportions is known as racemic mixture.



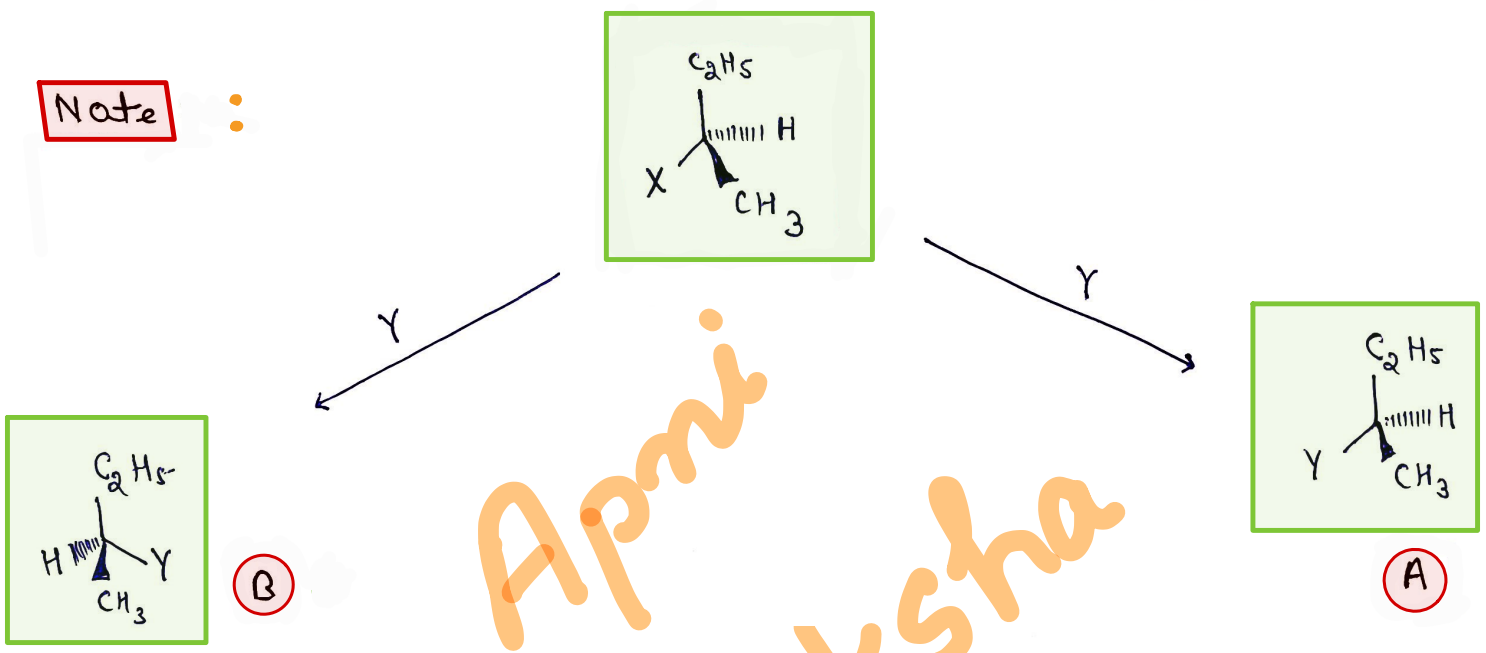
→ It is represented by dl or (+).

→ The process of forming racemic mixture is known as racemisation.

Question :- Identify chiral and achiral molecule -:



Note :



→ Retention :- If A is the only product in reaction. Then this process is called retention.

→ Inversion :- If B is the only product in reaction, then this process is called inversion.

→ Racemisation :- If A and B both are 50%. then this process is called racemisation. And mixture of A+B : Racemic mixture.

→ Mixture of A and B with 50-50% concentration is optically inactive. As one isomer will rotate light in the direction opposite to another.

Physical Properties

B.P. & M.P.

→ Molecules of organic halogen compounds are generally polar, due to greater polarity as well as higher molecular mass as compared to parent hydrocarbon, the dipole-dipole and van der Waals force of attraction are stronger in halogen derivatives.

So. B.P. : Halogen Derivative compound > Parent hydrocarbon.



→ For a given halogen atom —: B.P. : $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} > \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

→ For a given alkyl group —: B.P. : $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$

→ B.P. $\propto \frac{1}{\text{Branching}}$ —: B.P. : $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3 > \text{CH}_3\text{C}(\text{Br})_2\text{CH}_3$

→ Melting point : $\text{p-Cl-C}_6\text{H}_5 \gg \text{o-Cl-C}_6\text{H}_5 / \text{m-Cl-C}_6\text{H}_5$: Due to symmetry of para isomer that fits in crystal lattice better as ortho/m.

[CBSE 2019]

Solubility :— The solubility of haloalkanes in water is low. Because force of attraction between haloalkanes is greater than haloalkanes-water interaction.

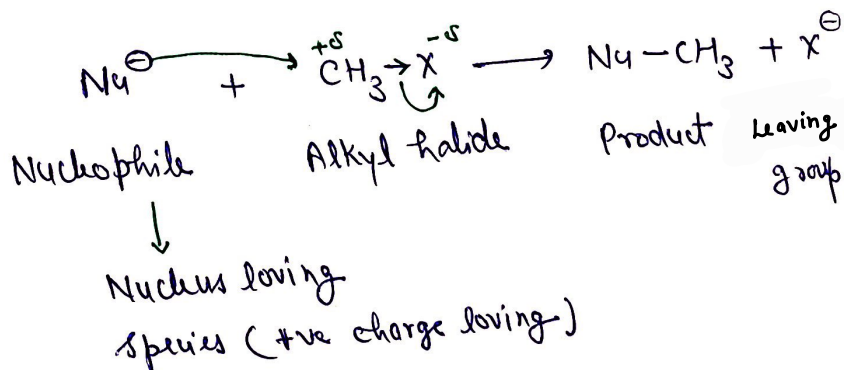
Chemical Reactions of Haloalkanes

Nucleophilic substitution Reaction

Elimination Reaction

Reaction with metals

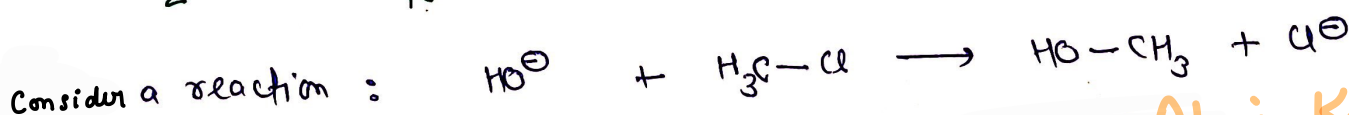
Nucleophilic substitution Reaction —:



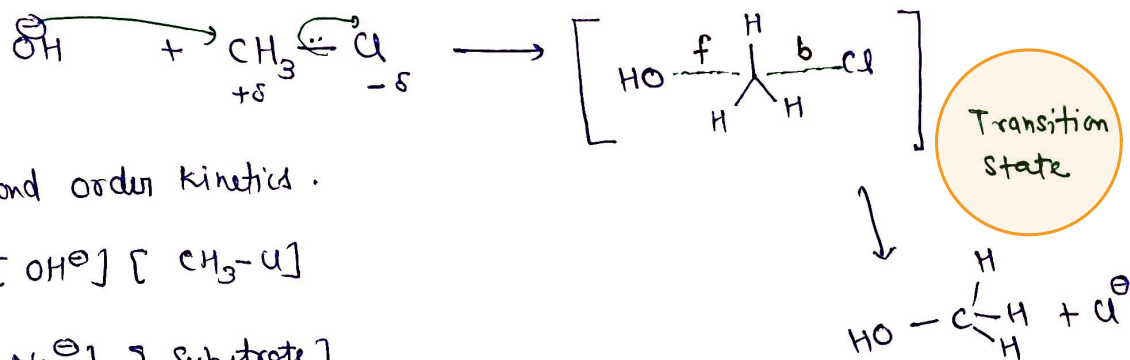
In this reaction, substitution reaction is initiated by a nucleophile so, it is called NSR.

→ Two different mechanisms can explain above reaction $\begin{cases} \text{S}_\text{N}2 \\ \text{S}_\text{N}1 \end{cases}$

Bimolecular Nucleophilic Substitution —: $\text{S}_\text{N}2$



Mechanism -:



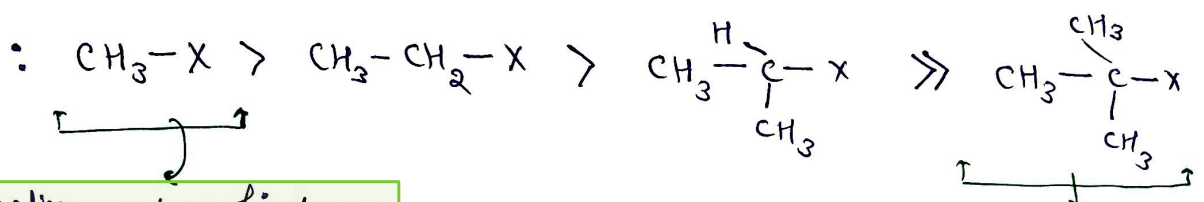
→ It follows second order kinetics.

$$\text{Rate} = k [\text{OH}^-] [\text{CH}_3\text{-Cl}]$$

$$\text{Rate} \propto [\text{Nu}^-] [\text{Substrate}]$$

→ It is a single step (concerted) reaction.

→ Order of reactivity: Primary halide > secondary halide >> Tertiary halide

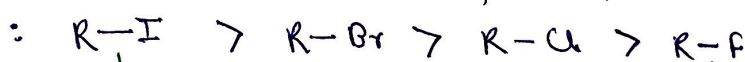


Most reactive: less hindrance

Least reactive because

bulky groups hinder the approaching of nucleophile towards carbon.

→ Order of reactivity with different halogen atoms

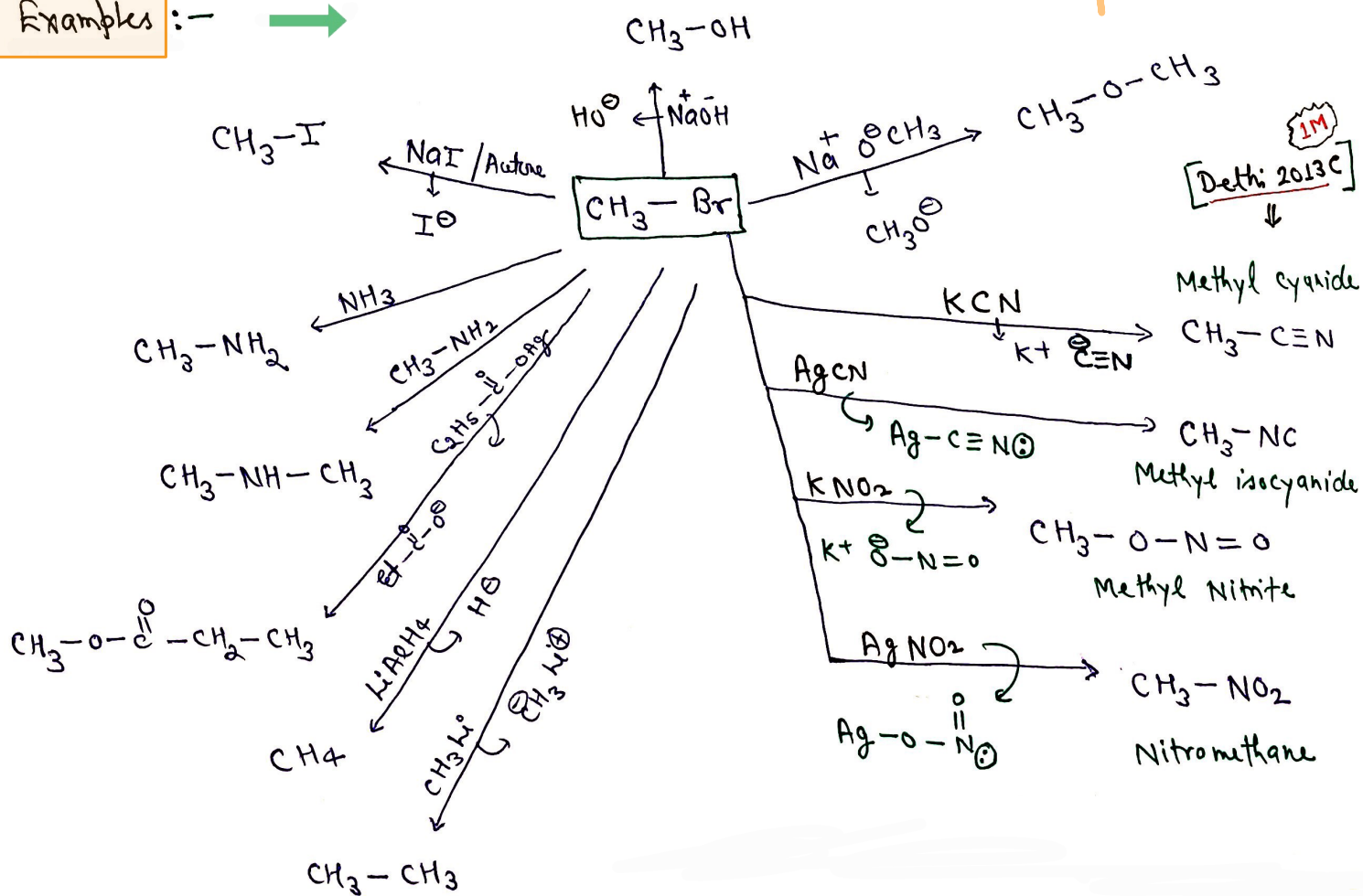


Weak Bond strength
So, easy to break.

Strong Bond, so tough
to break.

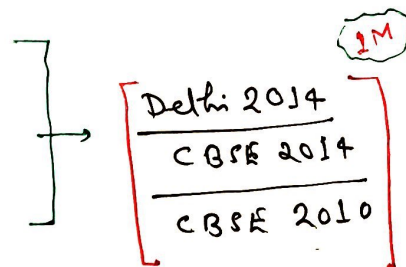
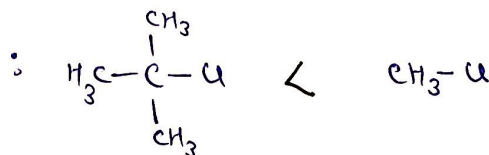
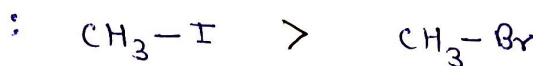
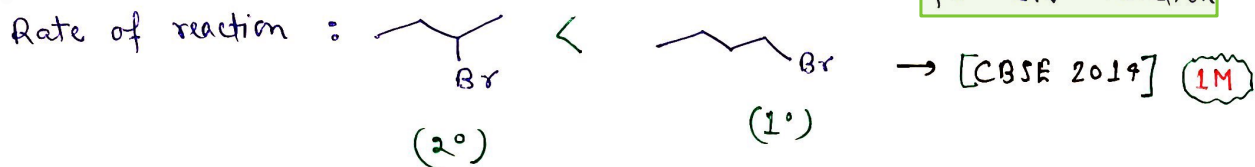
Apni Kaksha

Examples :-

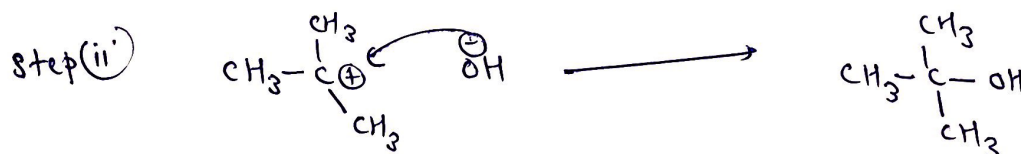
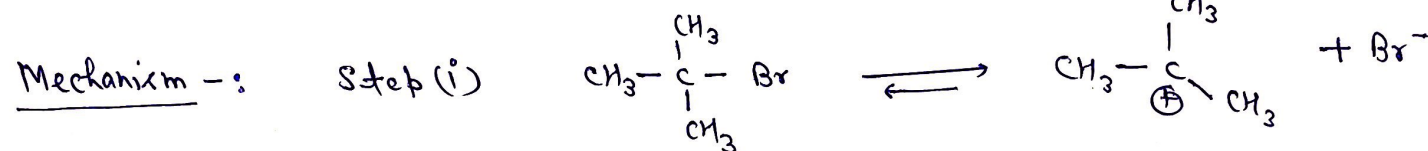
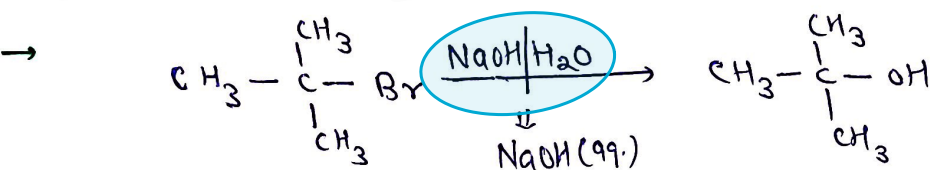


Substrate having less crowding is more effective than more crowding substrate.

Example -:



Unimolecular Substitution nucleophilic reaction : $\text{S}_\text{N}1$

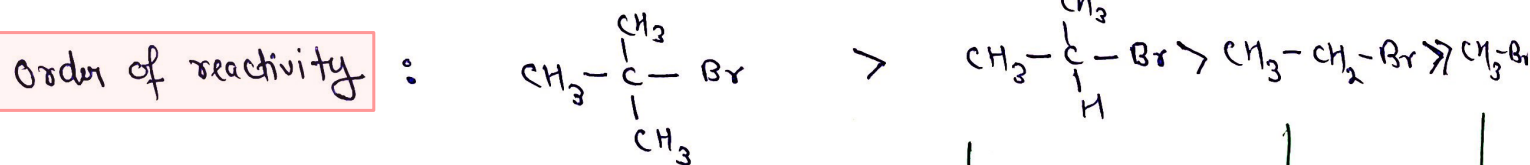


→ Above reaction follows first order kinetics.

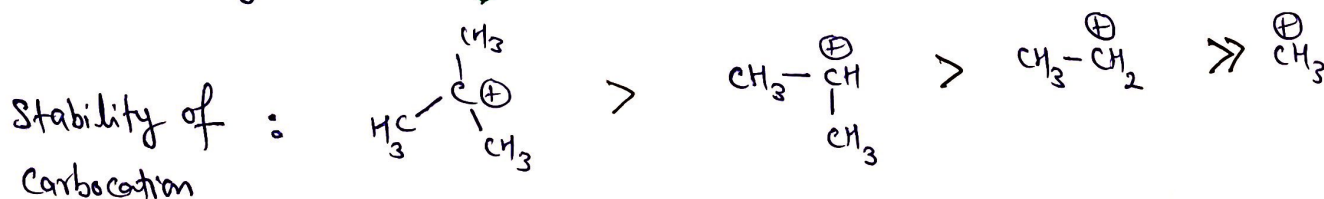
Rate $\propto$ [Alkyl halide]

→ It is a two step reaction and carbocation reaction intermediate is formed.

→ Step (i) is slow and reversible & Rate of reaction depends on slowest step.



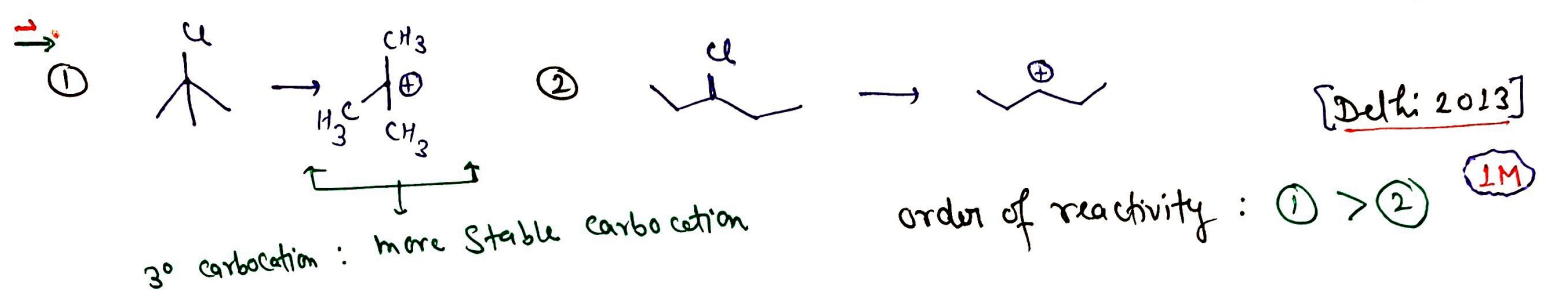
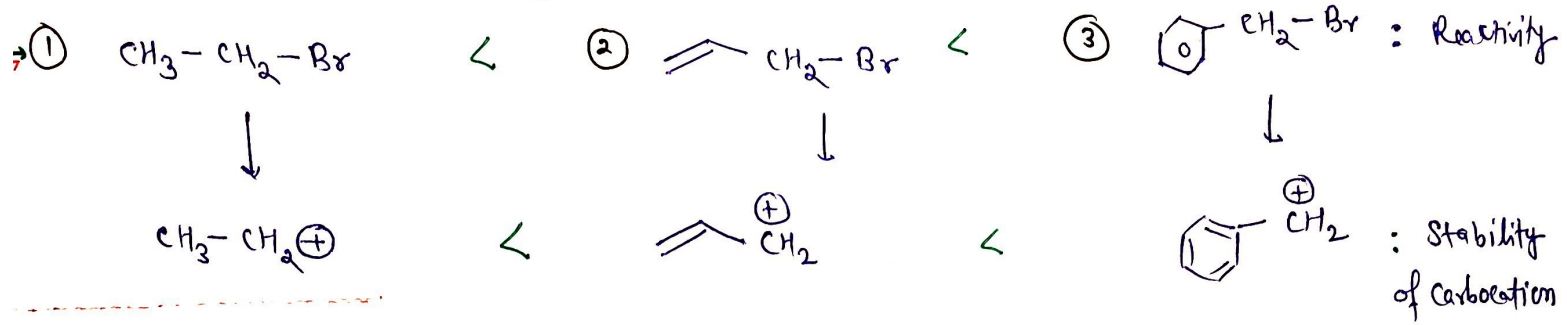
During reaction $\rightarrow$



→ If carbocation intermediate is stable then that substrate gives fast $\text{S}_\text{N}1$ reaction

→ Order of reactivity : $R-I > R-Br > R-Cl > R-F$

→ Find the order of reactivity for S_N1 reaction ?

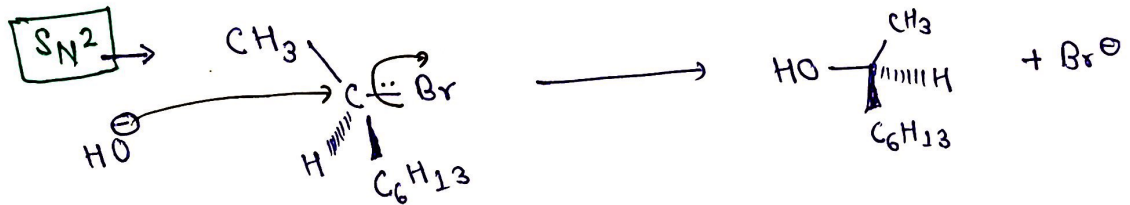


Stereochemistry of S_N1 vs S_N2 :-

S_N2 reaction gives inverted product.

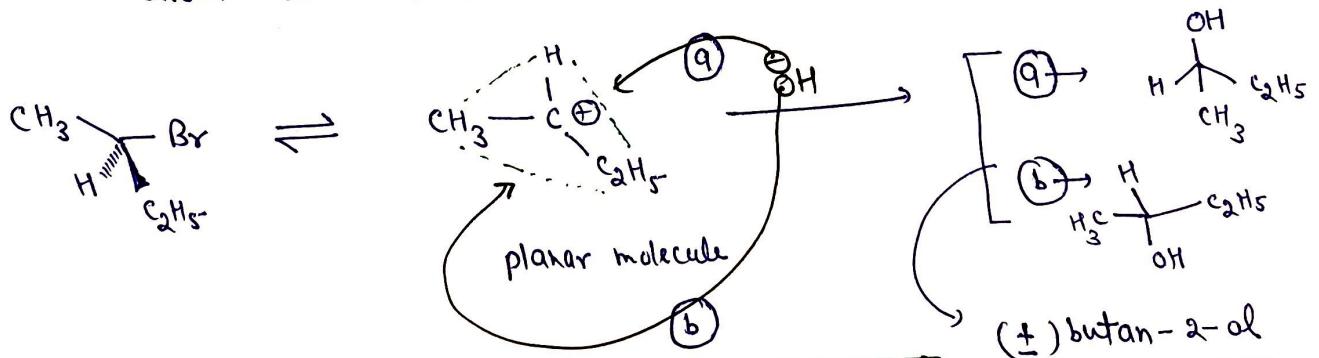
But S_N1 reaction gives racemic mixture (It goes through racemisation)

Example :-



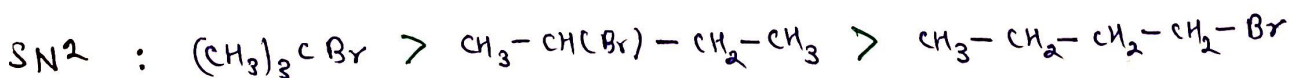
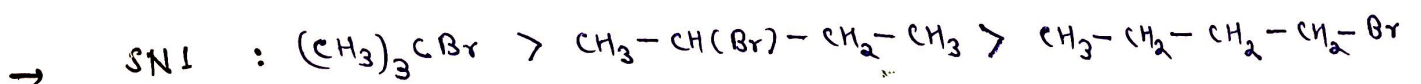
OH^- attacks on the opposite side of carbon-bromine bond. So inversion of configuration happens.

S_N1 :-



Order of reactivity for S_N1 : $\text{tert. Halide} > \text{sec. Halide} > 1^\circ \text{ Halide} > CH_3X$

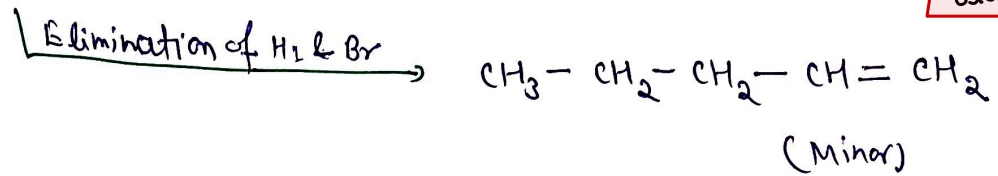
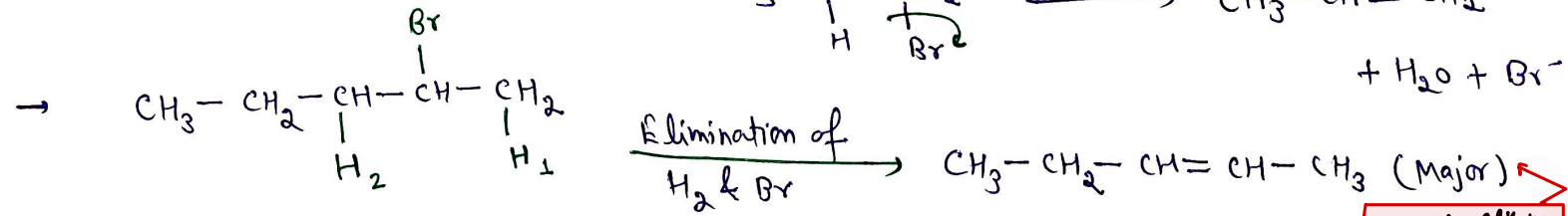
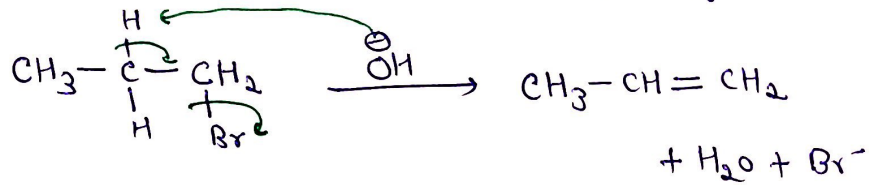
for S_N2 : $CH_3-X > 1^\circ \text{ Halide} > \text{sec. Halide} >> \text{ter. Halide}$



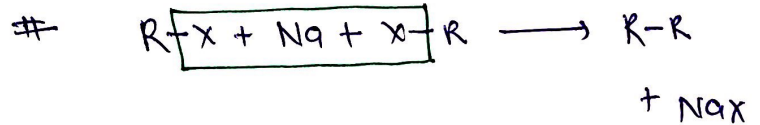
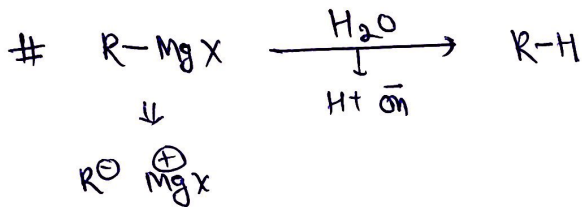
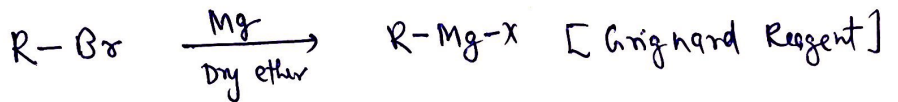
Elimination Reaction :-

Haloalkane with β -hydrogen atom $\xrightarrow[\text{(alcoholic)}]{\text{KOH}}$ Alkene

Dehydrohalogenation Reaction



Reaction with metals :-



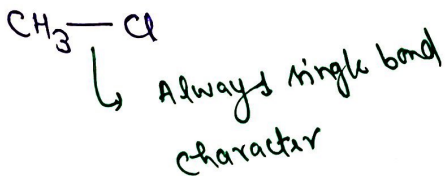
Reactions of haloarenes

Nucleophilic Substitution :- Aryl halides are extremely less reactive toward [Delhi 2013] (2M)

NSR due to following reasons :-

(i) Resonance effect :-

[Delhi 2013] (1M)

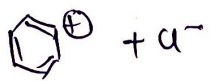


C-Cl bond acquires a partial double bond character due to resonance as a result

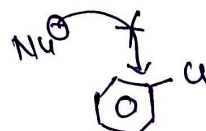
bond breaking in haloarene is difficult than haloalkane. Therefore haloarenes are less reactive than haloalkane towards NSR.

(ii) Instability of phenyl cation :- Haloarenes can not follow $\text{S}_\text{N}1$ path because

during first step we get phenyl cation which is not stable.

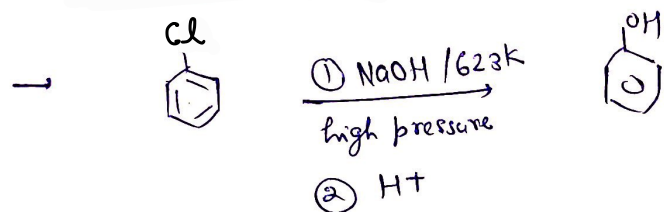


(iii) Because of possible repulsion, it is less likely for electron rich nucleophile to approach electron rich arenes.

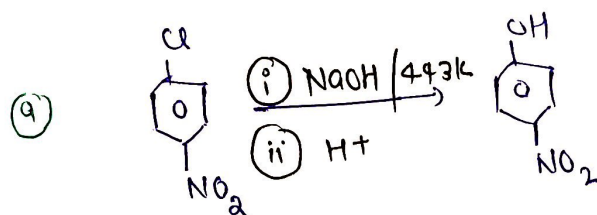


Apni Kaksha :-

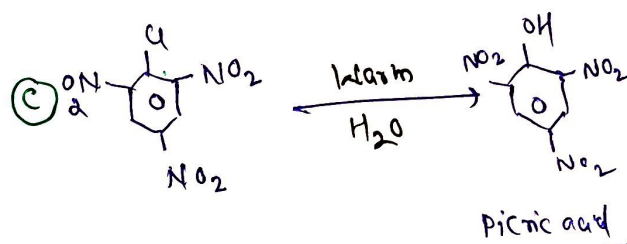
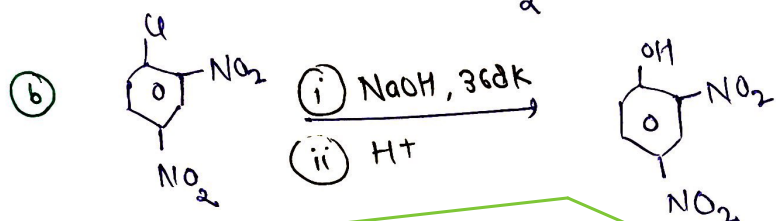
→ Replacement by hydroxyl group :-



The presence of an electron withdrawing group ($-\text{NO}_2$ / $-\text{CN}$) at ortho and para positions increases the reactivity of halo-arene.



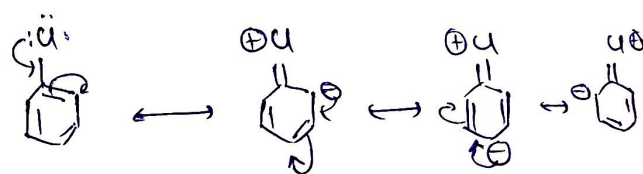
[Delhi 2019] 1M



Electrophilic Substitution Reaction :-

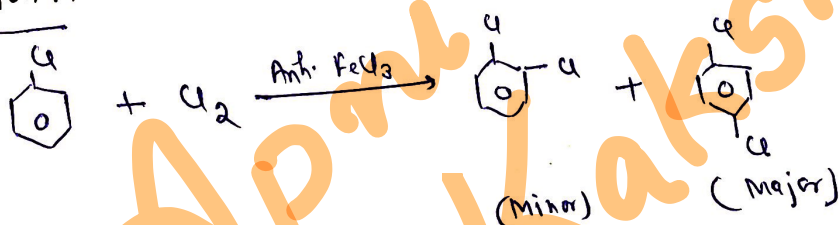
→ Halogens are ortho - para directing in nature for ESR. [Delhi 2012]

3M



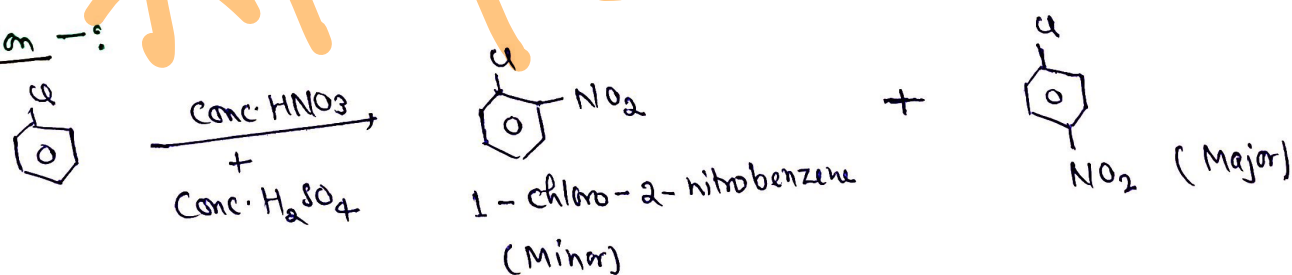
Due to resonance, the electron density increases more at ortho and para position.

i) Halogenation :-

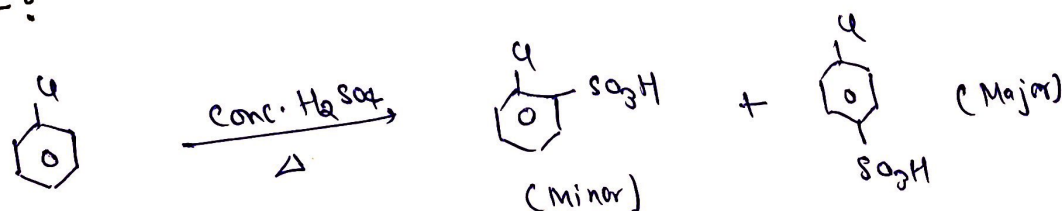


→ [CBSE 2015] 1M

ii) Nitration :-



iii) Sulphonation :-



(iv)

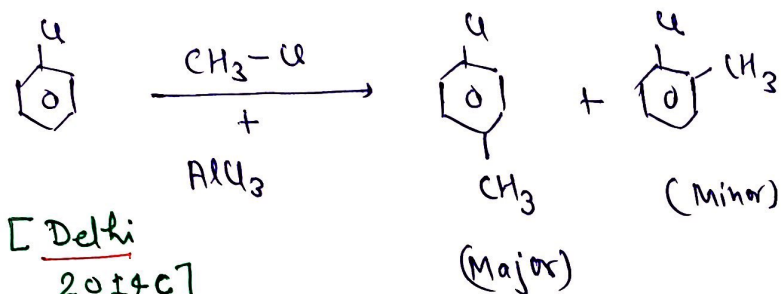
Friedel - craft's Reaction

[Delhi 2010]

1M

Alkylation

Addition of alkyl group on benzene

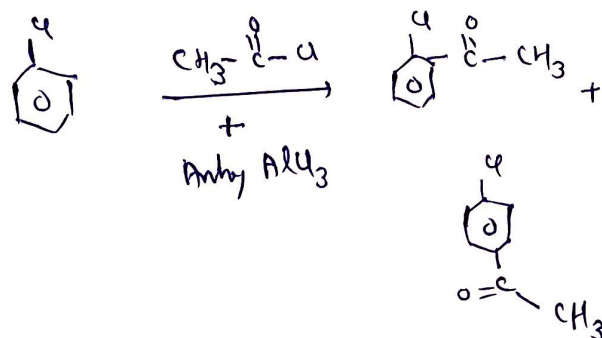


[Delhi 2014C]

1M

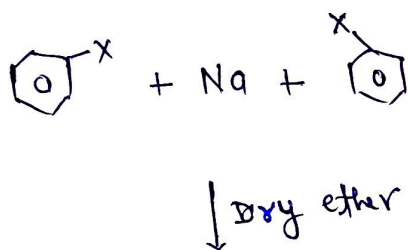
Acylation

Addition of acyl group on benzene

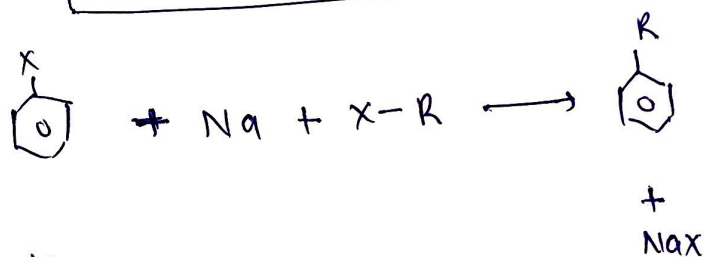


Reaction with metal :-

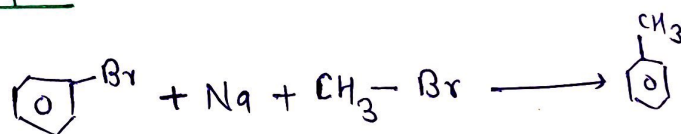
Fittig Reaction



Wurtz - Fittig Reaction



Example:-

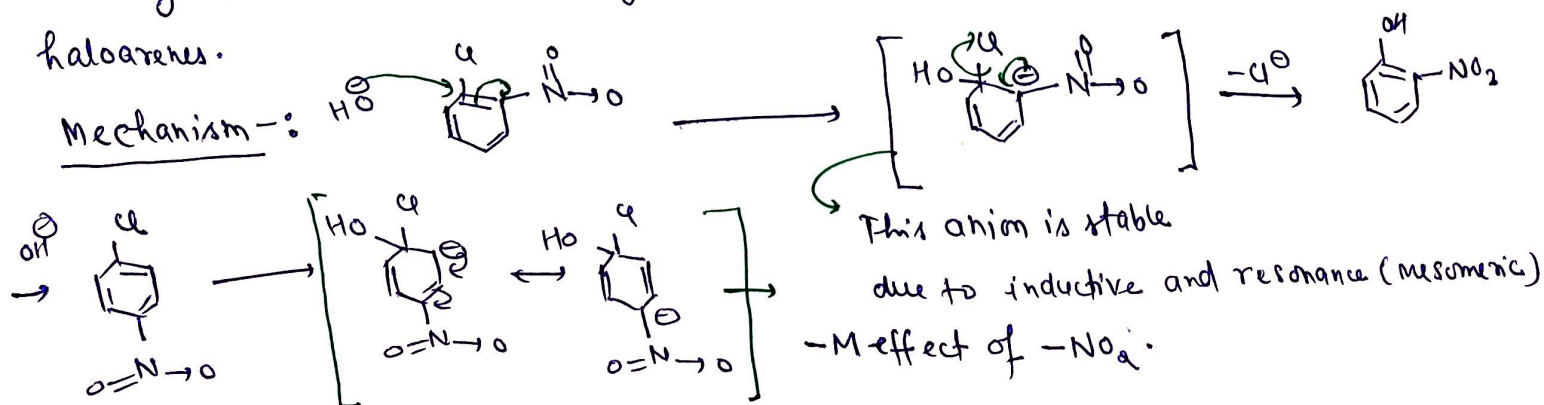


Question :- The presence of nitro group at ortho - para positions increase the reactivity of haloarenes towards NSR, Why?

[CBSE 2019]

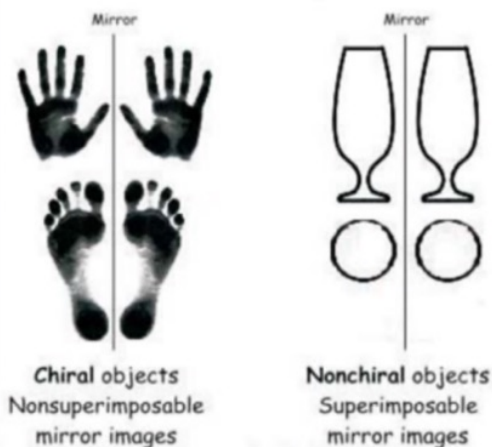
1M

Answer :- Because $-\text{NO}_2$ group at ortho and para positions withdraw electron density from the benzene ring and thus facilitates the nucleophilic attack on haloarenes.

Mechanism:-

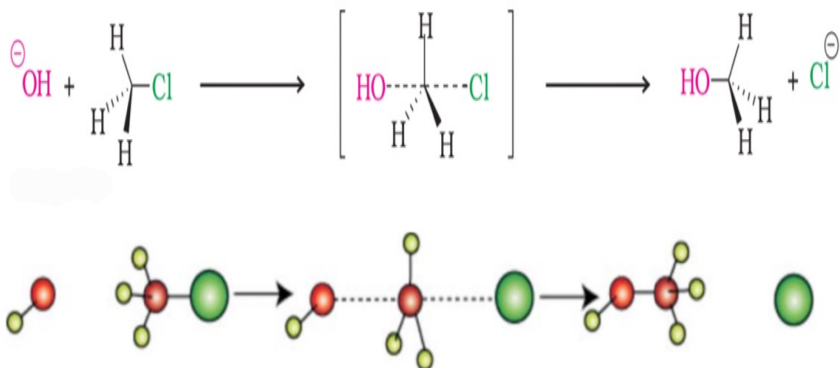
CHIRALITY

An object that cannot be superimposed on its mirror image is called chiral

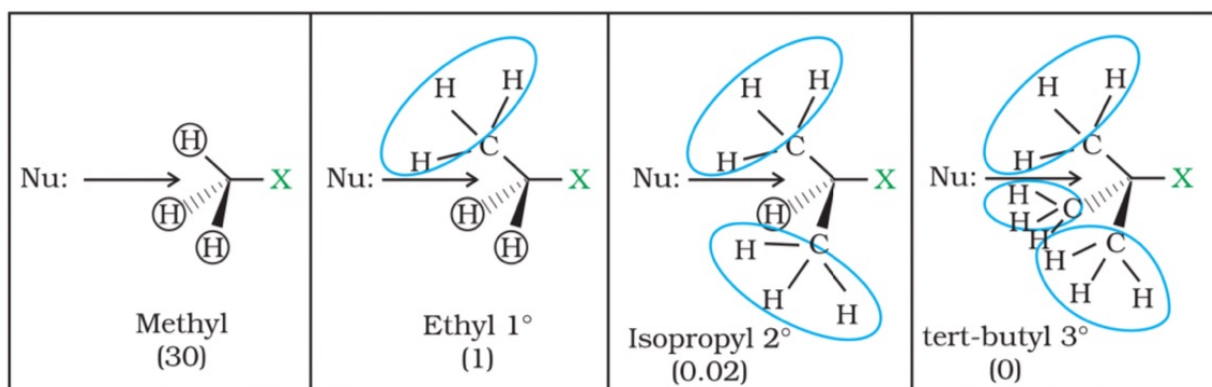


Some common examples of chiral and achiral objects

S_N2 Reaction



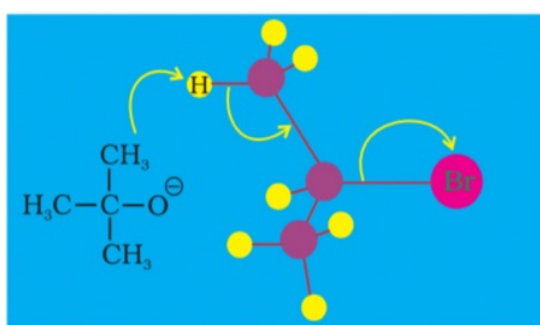
Red dot represents the incoming hydroxide ion and green dot represents the outgoing halide ion



Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis

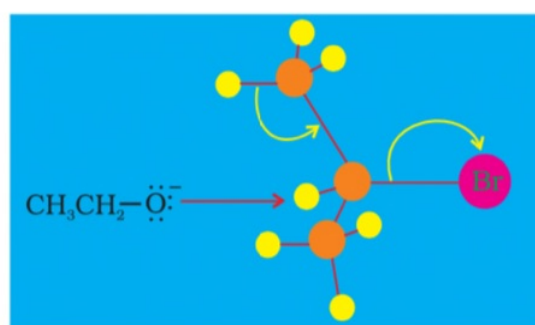
Elimination versus substitution

A chemical reaction is the result of competition; it is a race that is won by the fastest runner. A collection of molecules tend to do, by and large, what is easiest for them. An alkyl halide with α -hydrogen atoms when reacted with a base or a nucleophile has two competing routes: substitution (S_N1 and S_N2) and elimination. Which route will be taken up depends upon the nature of alkyl halide, strength and size of base/nucleophile and reaction conditions. Thus, a bulkier nucleophile will prefer to act as a base and abstracts a proton rather than approach a tetravalent carbon atom (steric reasons) and *vice versa*. Similarly, a primary alkyl halide will prefer a S_N2 reaction, a secondary halide- S_N2 or elimination depending upon the strength of base/nucleophile and a tertiary halide- S_N1 or elimination depending upon the stability of carbocation or the more substituted alkene.



Elimination

vs



Substitution