

HALOALKANES &

HALOARENES

CLASS XII
BOARD EXAM

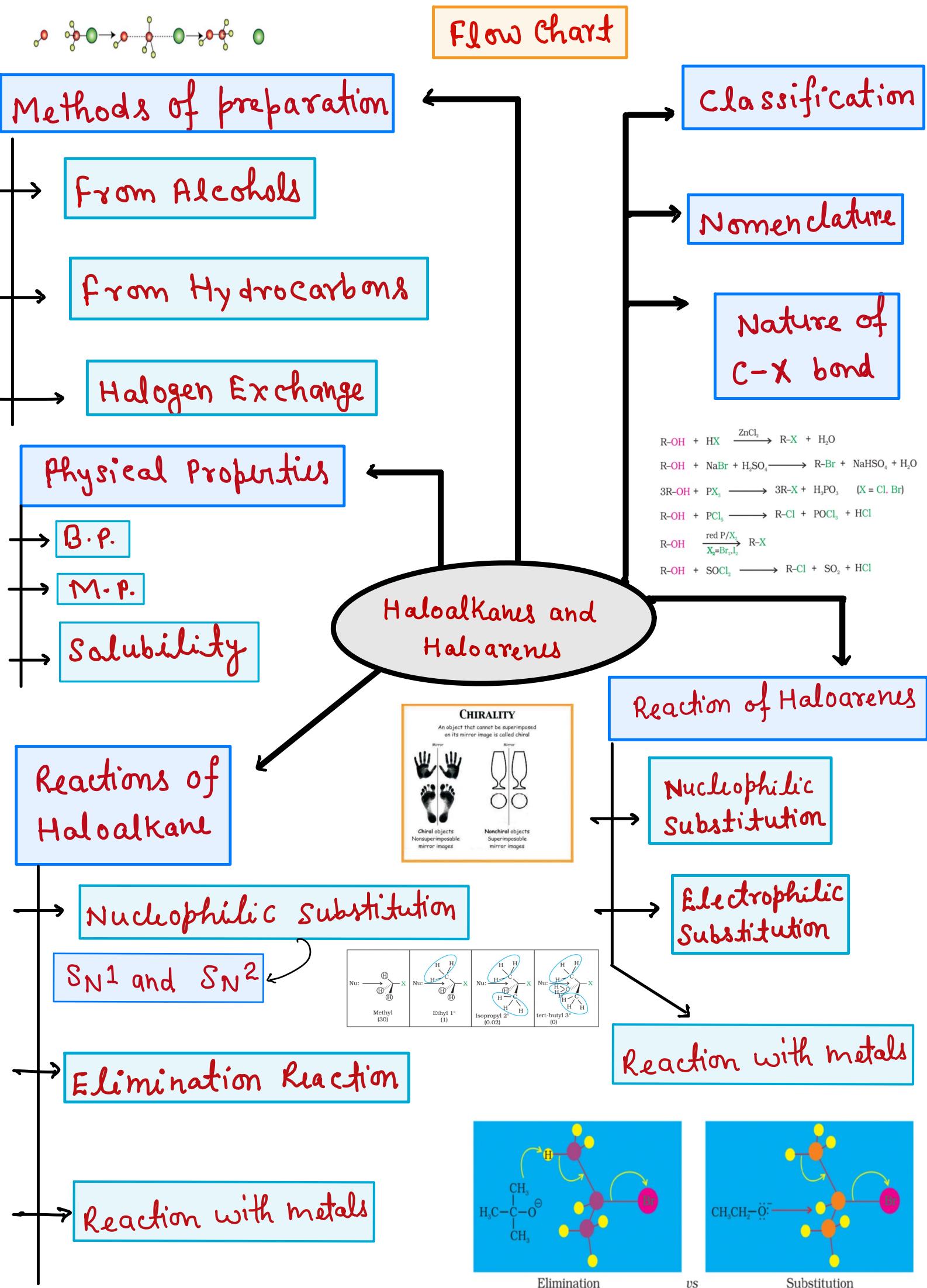
These notes
have been verified
by top faculties &
CBSE Science
Toppers

- ↳ Target 100
- ↳ Previous Year Q's
Integrated

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Bharat Bhawan

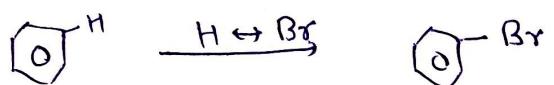
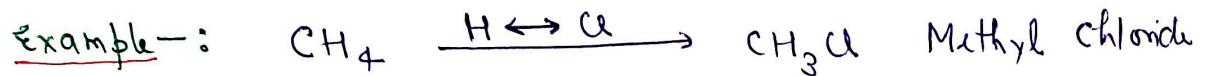
Flow Chart



Haloalkanes and Haloarenes

→ Aliphatic hydrocarbon $\xrightarrow{H \leftrightarrow X}$ Alkyl halide [haloalkane]

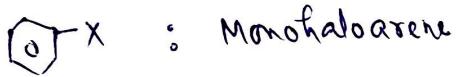
Aromatic hydrocarbon $\xrightarrow[\text{hydrogen by halogen atom}]{\text{Replacement of}}$ Aryl halide [haloarene]



Classification on basis of number of halogen atoms

- If one halogen atom is present in structure of alkanes / arenes : Monohalo alkane
- If two halogen atoms are present : Dihaloalkane / Dihaloarene
- Similarly, If three halogen atoms are present : Trihaloalkane
Trihaloarene

Example -: $\text{C}_2\text{H}_5\text{X}$: Monohaloalkane ($X \rightarrow \text{Halogen}$)



Monohalo compounds

Compounds containing sp^3 C-X bond



Compounds containing sp^2 C-X bond



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

Example -: $\text{CH}_2=\text{C}(X)\text{H}$, $\text{C}_6\text{H}_5\text{Br}$

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

Example -: $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ etc.

① Alkyl halides : (R-X)

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

Example -: $\text{CH}_3-\text{CH}_2-\text{Br}$

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

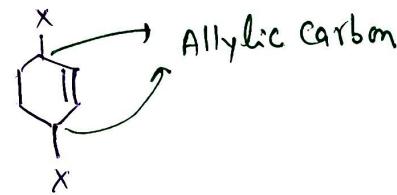
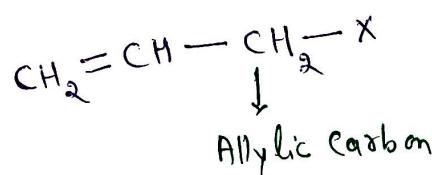
Example -: $\text{CH}_3-\underset{\substack{| \\ \text{CH}_3 \\ | \\ \text{Br}}}{\text{C}}-\text{H}$

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

Example -: $\text{CH}_3-\underset{\substack{| \\ \text{CH}_3 \\ | \\ \text{CH}_3}}{\text{C}}-\text{Cl}$

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

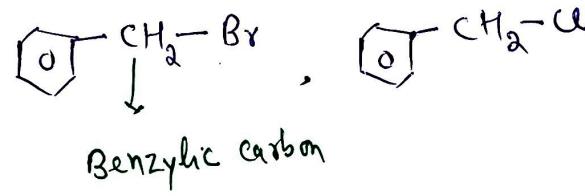
Example - :



Allyl bromide :- $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Br}$

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

Example :



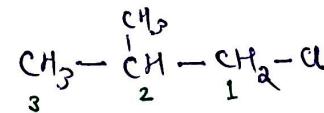
Nomenclature



→ 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).

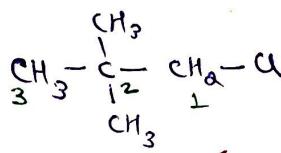
→ Rule : No. of carbon > Max. no. of substituent > Lowest set of locants > Alphabetic order

→ Example - : $\text{CH}_3-\overset{3}{\text{CH}_2}-\overset{2}{\text{CH}_2}-\overset{1}{\text{CH}_2}-\text{Br}$

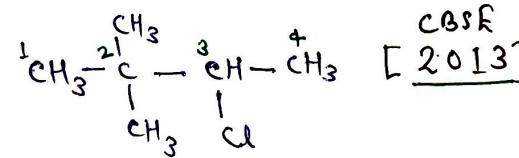


1 - Chloro - 2 - methyl propane

IUPAC → 1 - Bromopropane

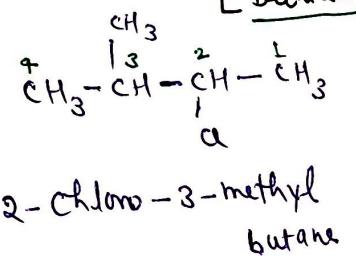


1 - Chloro - 2,2 - dimethyl propane



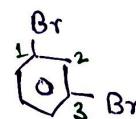
[CBSE
2013]

3 - chloro - 2,2 - methylbutane



2 - Chloro - 3 - methyl butane

→



Common name : m - Dibromo benzene

IUPAC : 1,3 - Dibromo benzene

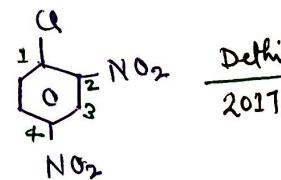
Bromobenzene

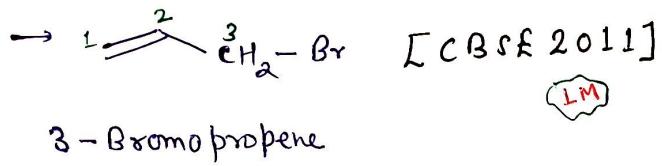
→

\Rightarrow 1,4 - Dichloro - 2 - methyl benzene

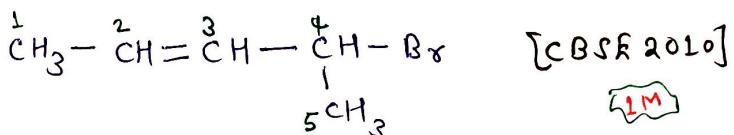
[CBSE 2013]

2,4 - Dinitro chloro benzene





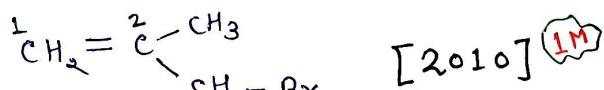
3-Bromo propene



5
CH₃

1M

4-Bromopent-2-ene

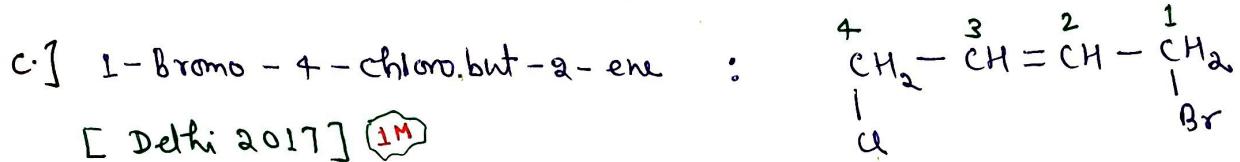
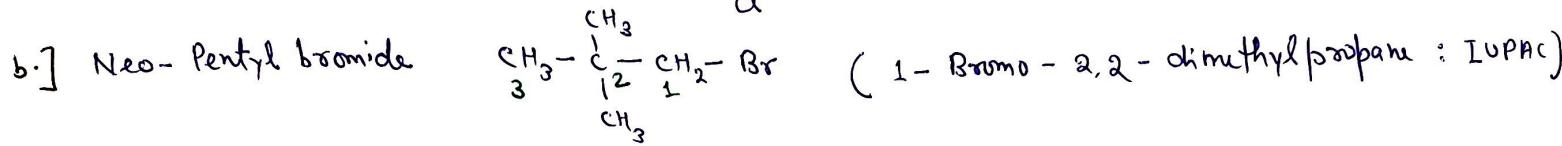
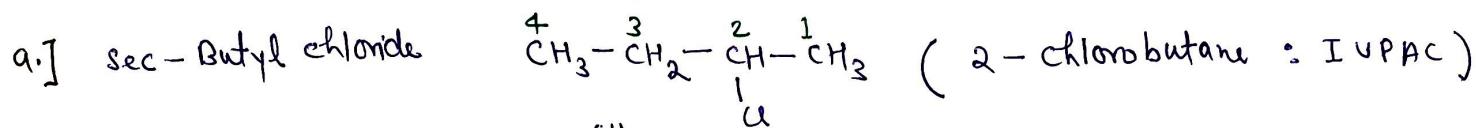


3-Bromo - 2-methylpropene

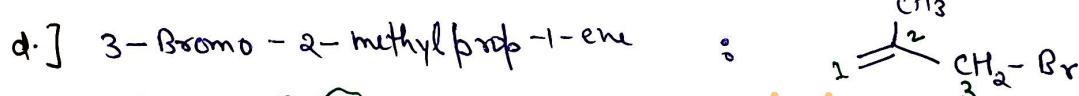


Apni Kaksha

→ Draw the structure of following compounds?



[Delhi 2017] 1M



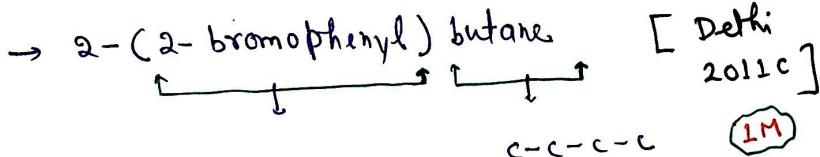
[Delhi 2017] 1M

Apni Kaksha

NOTE : Benzene as substituent : Phenyl

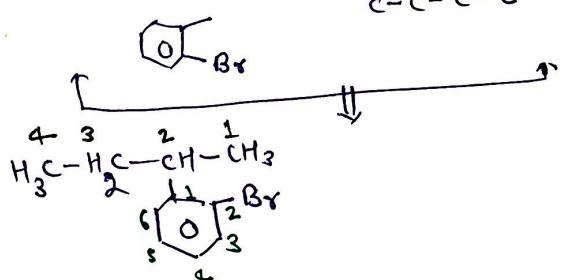
Example -: Chloromethyl benzene [X]
chlorophenylmethane [Y] is correct

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

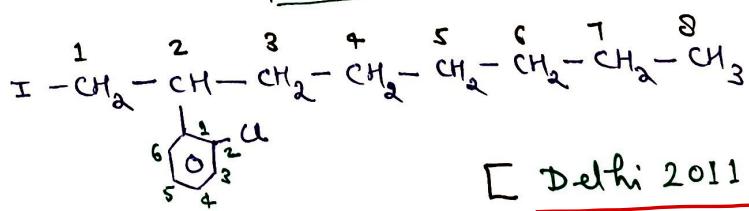


[Delhi 2011c]

1M



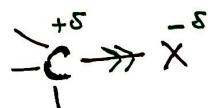
2-(2-chlorophenyl)-1-iodooctane



[Delhi 2011c]

Nature of C-X bond

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



→ Size of halogen : I > Br > Cl > F

→ Carbon-halogen bond : C-I > C-Br > C-Cl > C-F
length

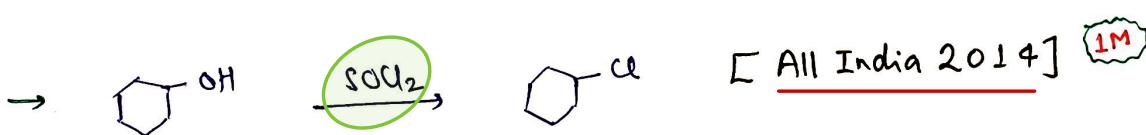
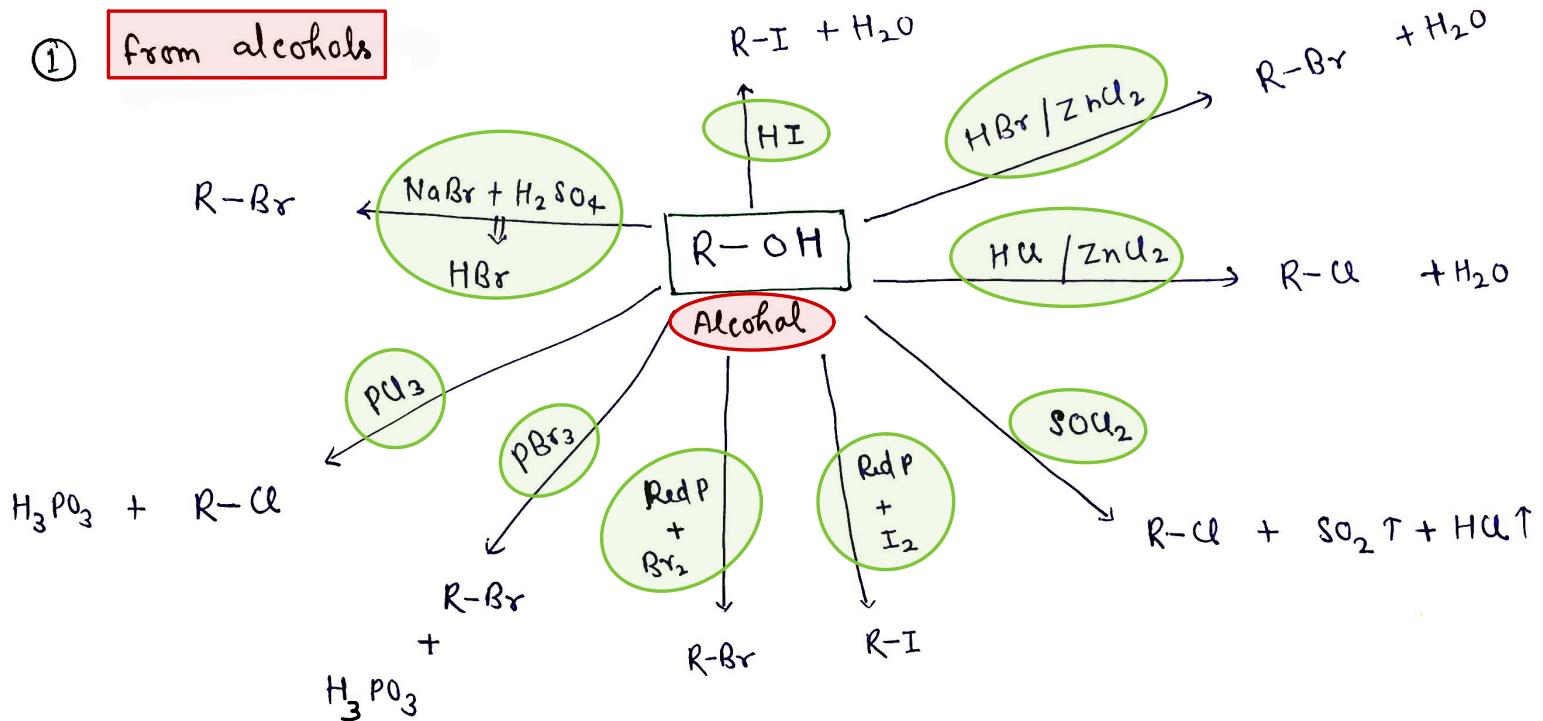
Bond length of C-X & 1/C-X bond enthalpies

→ Bond Enthalpy : C-F > C-Cl > C-Br > C-I

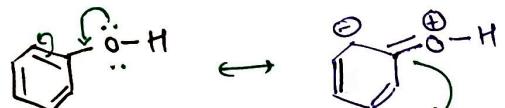
→ Order of dipole moment : CH₃-Cl > CH₃-F > CH₃-Br > CH₃-I

Methods of preparation

① from alcohols



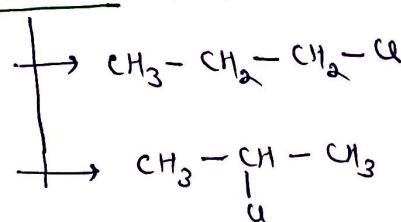
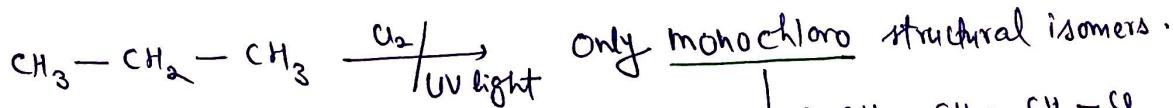
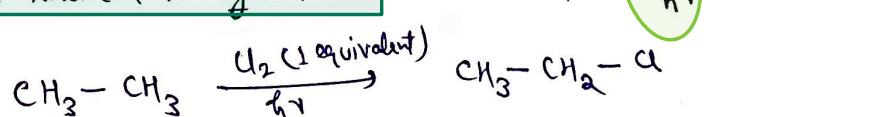
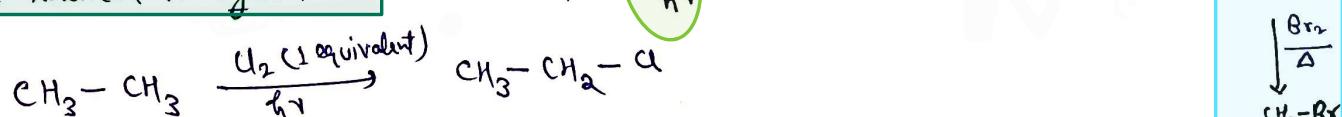
→ Above method is not applicable for the preparation of aryl halides because the carbon - oxygen bond in phenol has partial double bond character.



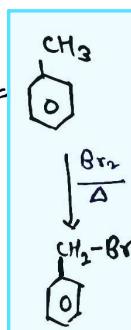
Breaking of this bond is tough.

2.] from Hydrocarbon

① Free Radical Halogenation :

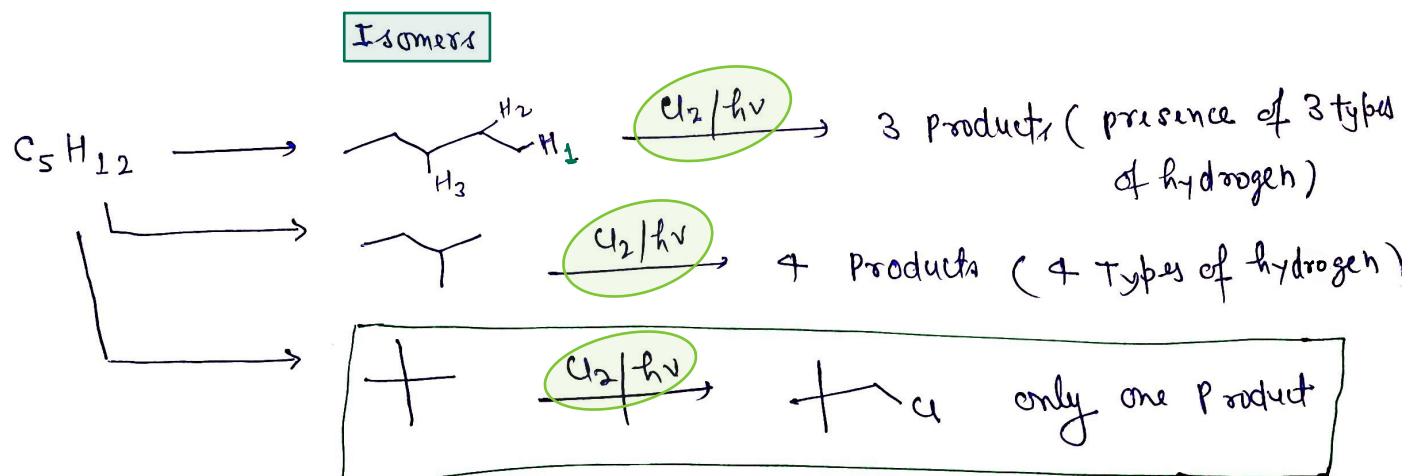


Mono, di, tri, poly halo alkanes

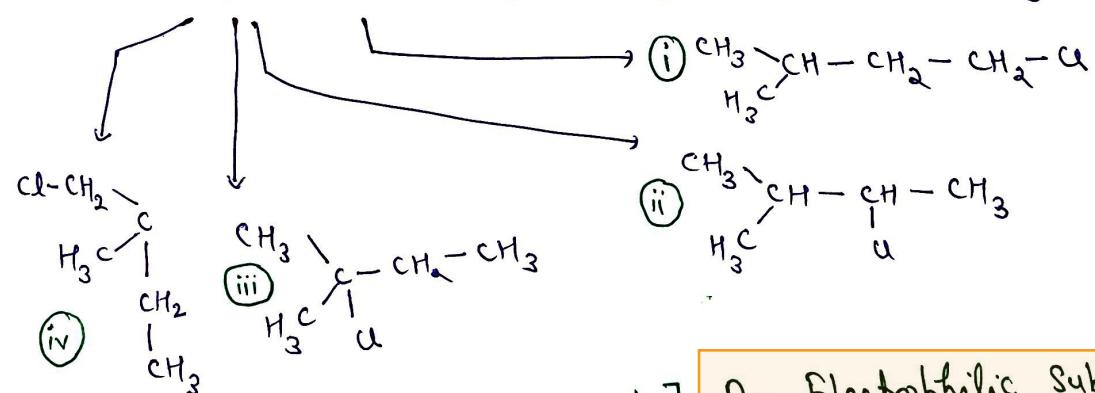
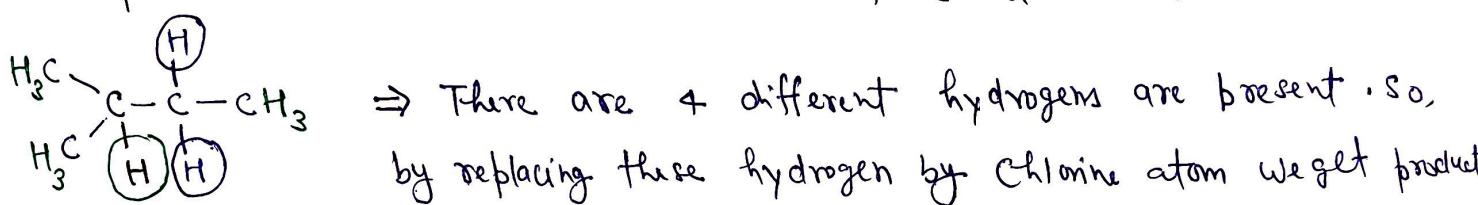


A hydrocarbon C_5H_{12} gives only one monochlorination product . [Delhi 2013C] 2 M

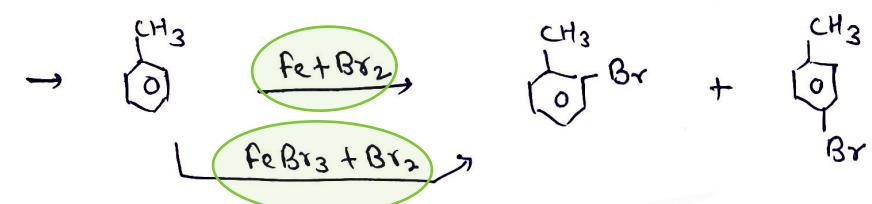
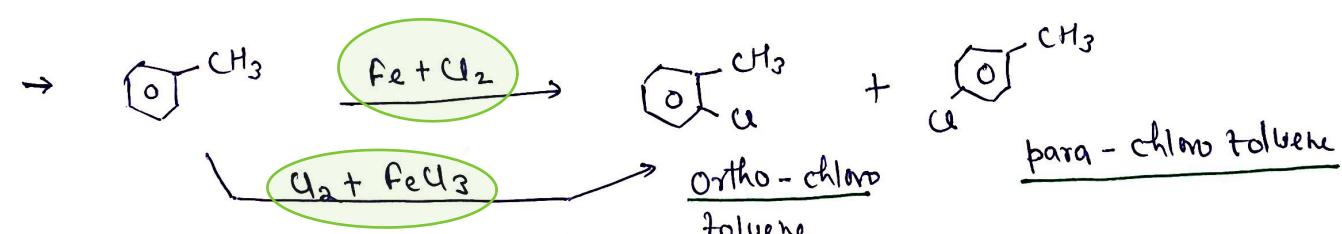
Identify the hydrocarbon.



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



b.] **By Electrophilic Substitution :-**



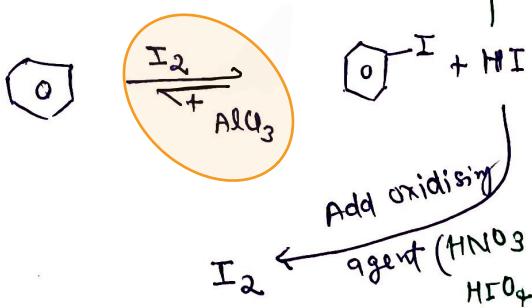
Reducing Agent

→ Reactions with I_2 are reversible in nature .

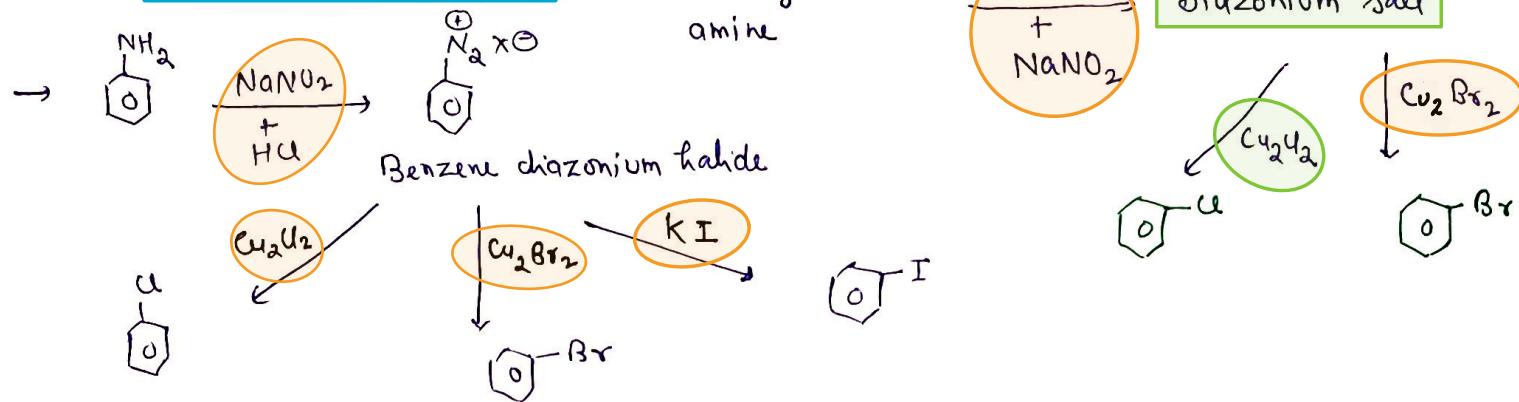
This reaction requires presence of oxidising agent to oxidise HI formed during iodination .

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

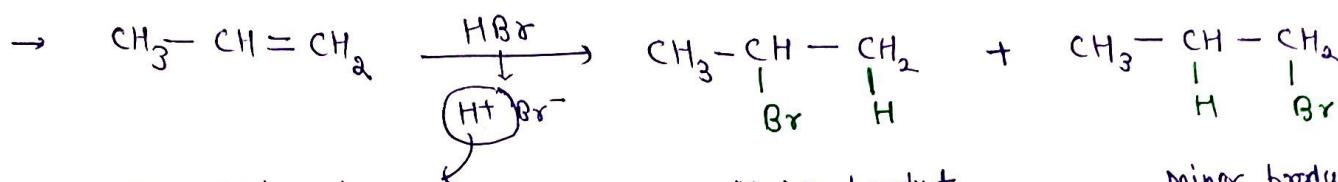
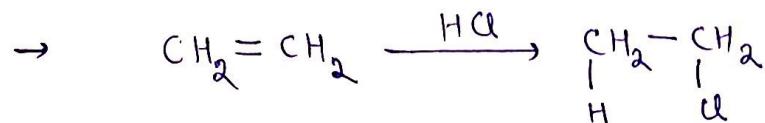
fluoro compounds are not prepared by this method .



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

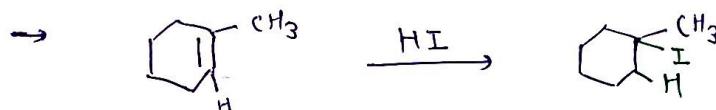
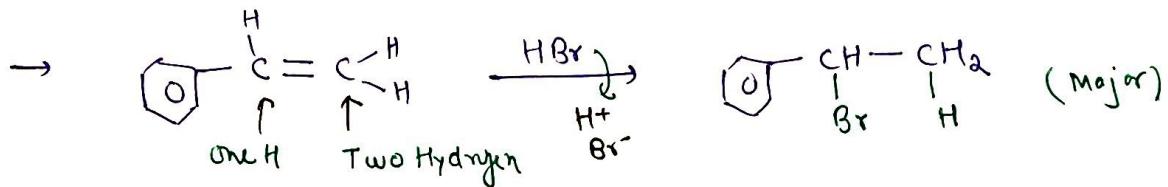


d.) From alkenes :- i) Addition of hydrogen halide (HCl, HBr, HI, HF)

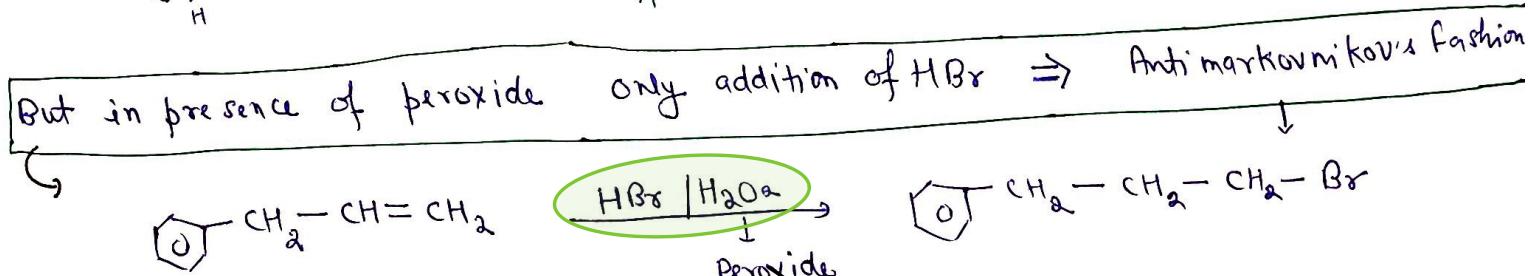


Add to that carbon
which has more no. of hydrogen. ← Markovnikov's

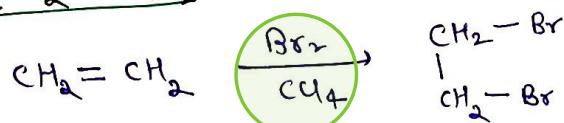
Major product
Minor product
Anti - Markovnikov's



Anti Markovnikov

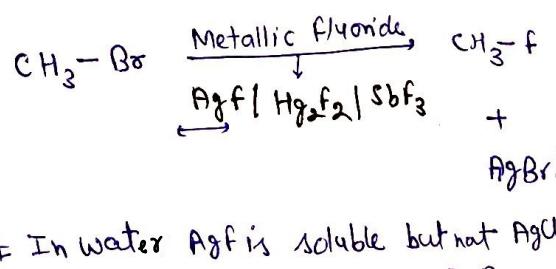
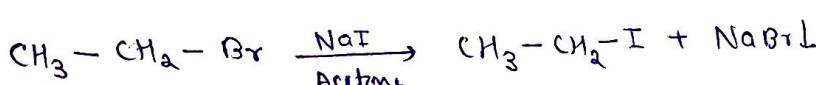
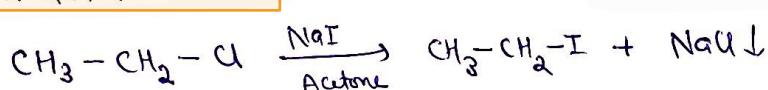


ii) Addition of halogens (Cl₂, Br₂) :-



Halogen Exchange

Swarts Reaction

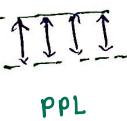
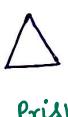
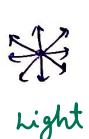


In Acetone : NaI is soluble but not NaCl/NaBr. # In water AgF is soluble but not AgCl/AgBr.

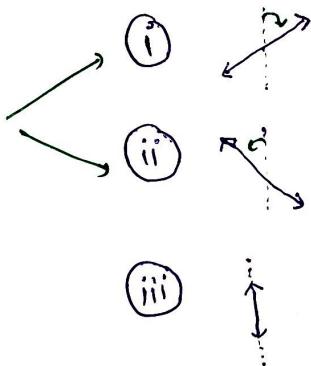


Optical active compound :-

"The compound which can rotate the plane polarized light"



Solution of Optical active compound



Rotation in right \rightarrow dextro-rotatory
direction

Rotation in left \rightarrow laevo-rotatory
direction

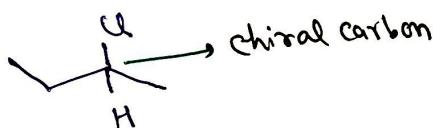
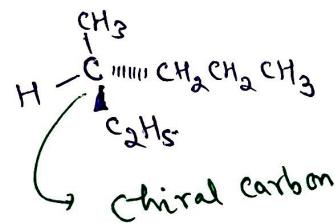
No Rotation \rightarrow optically inactive

Polarimeter Experiment

\rightarrow dextro-rotatory compound and laevo-rotatory compounds

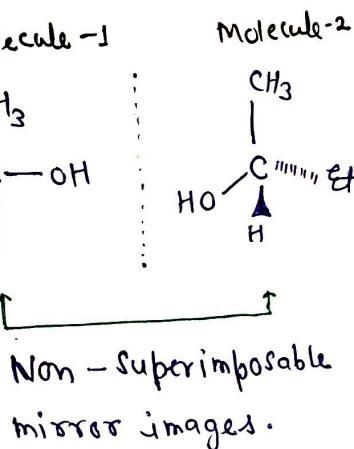
are optical isomers. This phenomenon is known as **optical isomerism**.

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



\rightarrow **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."



Non-superimposable mirror images.
 chiral molecule
 Optical active compound.

\rightarrow **Enantiomers** :- Stereoisomers with non-superimposable + mirror image character.

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

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

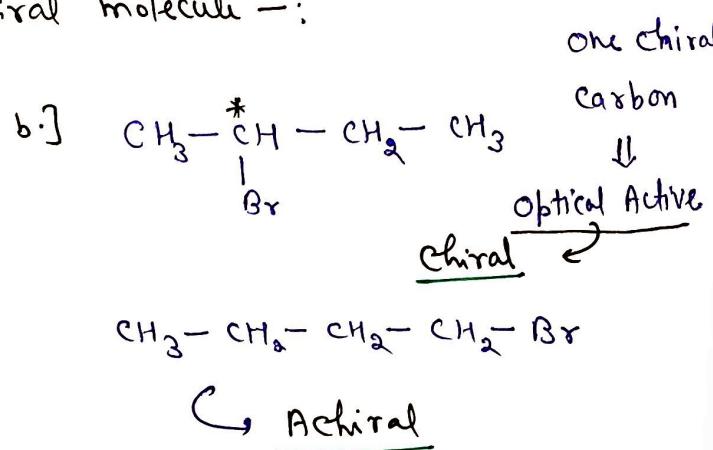
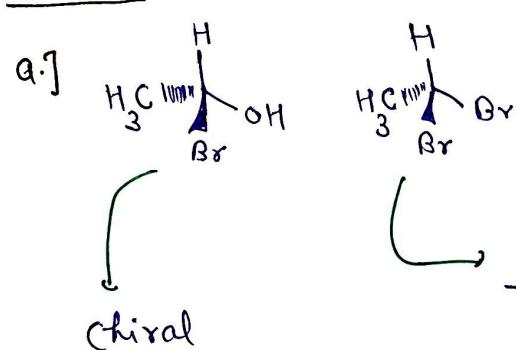
\rightarrow **Racemic mix** :- A mixture containing two enantiomers in equal proportions is known as racemic mixture.



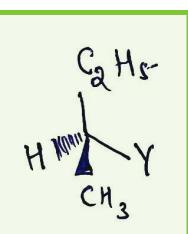
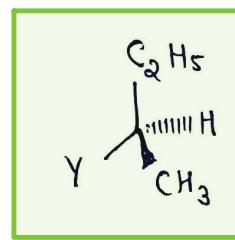
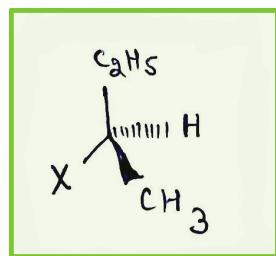
→ It is represented by dl or (\pm) .

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

Question :— Identify chiral and achiral molecule :-



Note :



Apni Kaksha

→ **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 80 - 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.

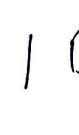
So. B.P. : Halogen Derivative compound > Parent hydrocarbon.



→ for a given halogen atom :- B.P. : $\text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{CH}_2\text{F}$

→ 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. : $\text{CH}_3\text{CH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{Br} > +\text{Br}$

→ Melting point : [CBSE 2019]  \gg  /  : Due to symmetry of para isomer that fits in crystal lattice better as ortho/para isomer.

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

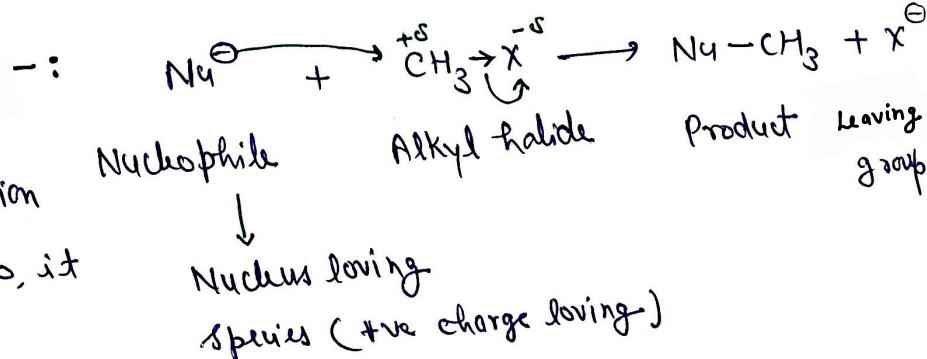
Nucleophilic substitution Reaction

Chemical Reactions of Haloalkanes

Elimination Reaction

Reaction with metals

Nucleophilic substitution Reaction

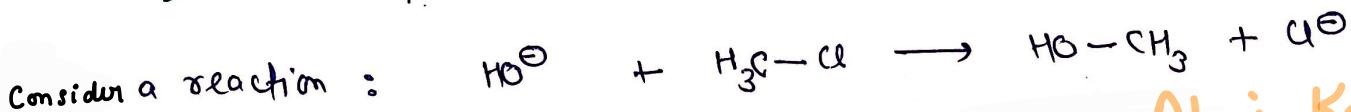


In this reaction, substitution reaction is initiated by a nucleophile so, it is called NSR.

→ Two different mechanisms can explain above reaction

i) Bimolecular Nucleophilic Substitution :-

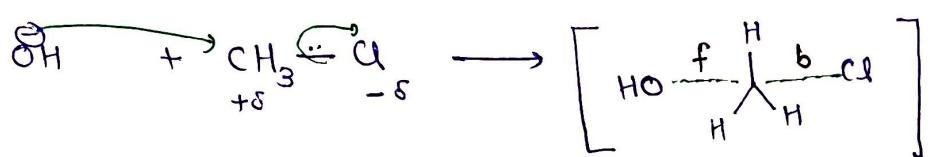
$\text{S}_{\text{N}}2$



Consider a reaction :

Aprni Kaksha

Mechanism :-

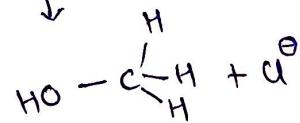


Transition state

→ It follows second order kinetics.

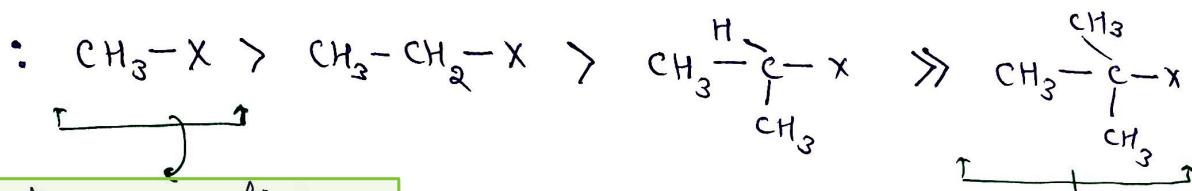
$$\text{Rate} = k [\text{OH}^-] [\text{CH}_3\text{Cl}]$$

$$\text{Rate} \propto [\text{Na}^+] [\text{substrate}]$$



→ It is a single step (concerted) reaction.

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

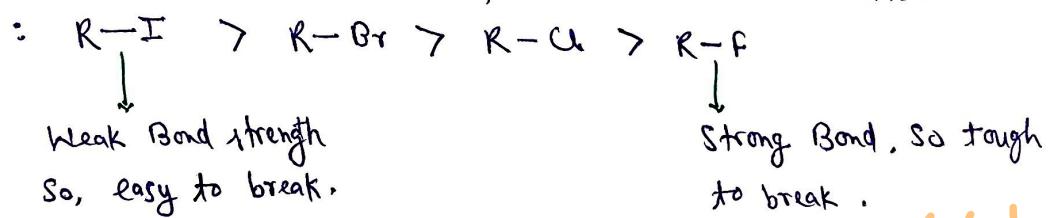


Most reactive : Less hindrance

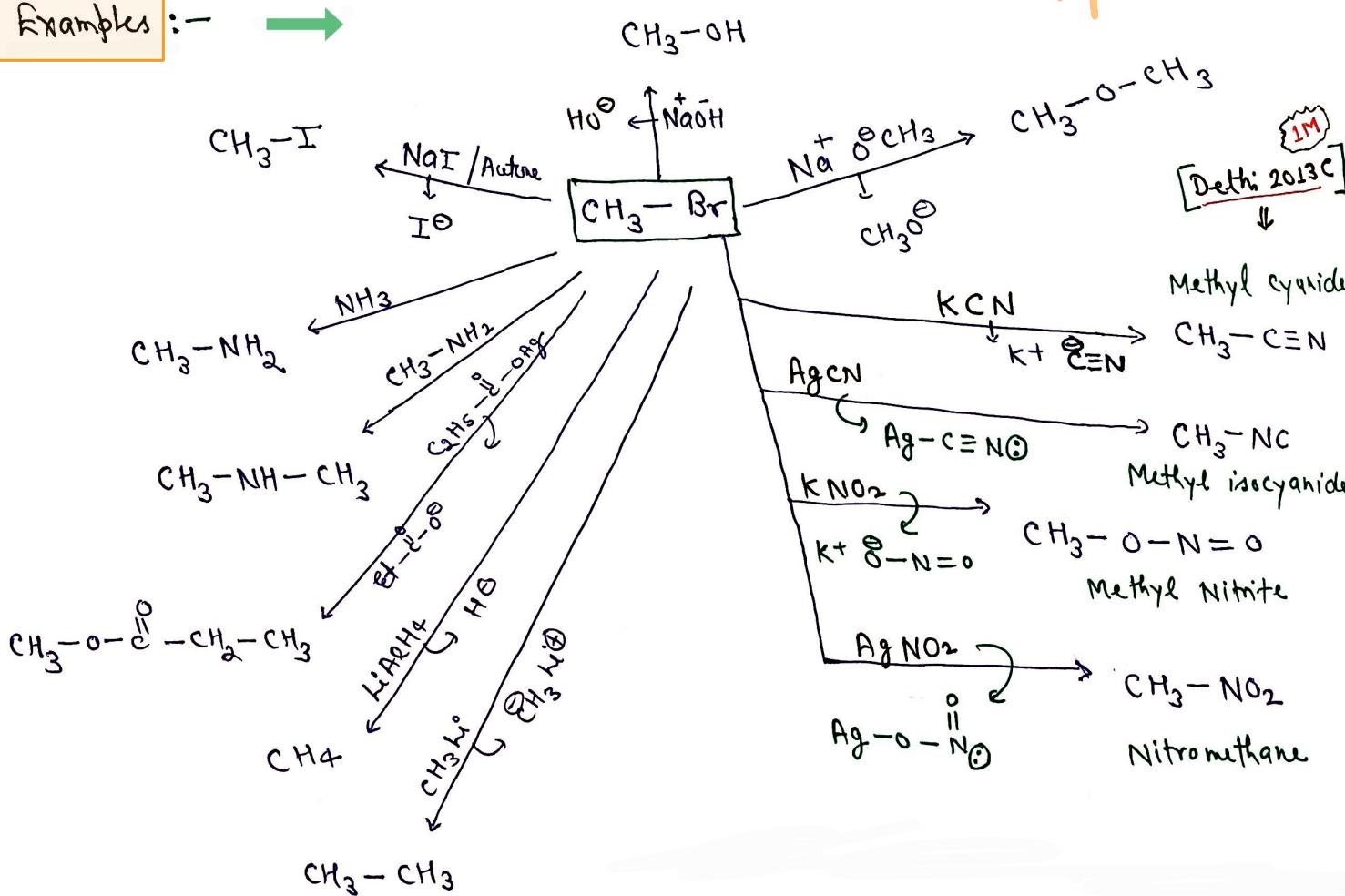
Least reactive because

bulky groups hinder the approaching of nucleophile towards carbon.

→ Order of reactivity with different halogen atoms



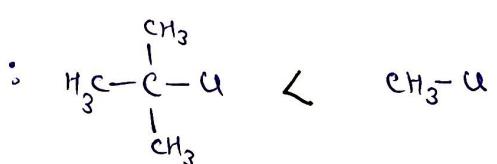
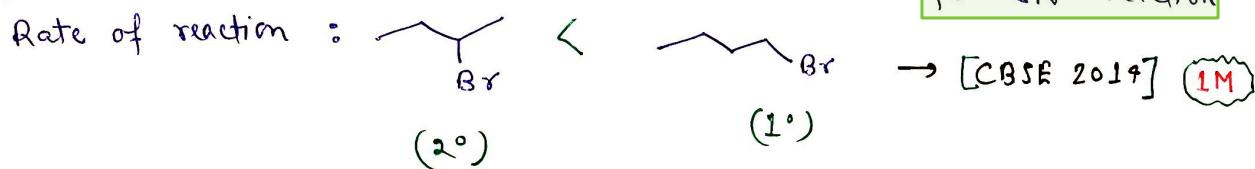
Examples :-





Substrate having less crowding is more effective than more crowding substrate

Example :-



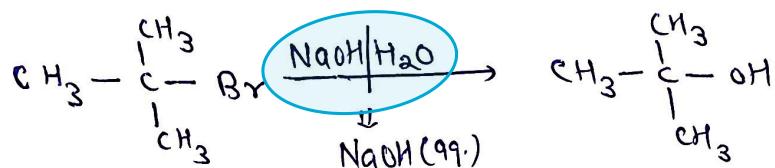
Delhi 2014
CBSE 2014
CBSE 2010

1M

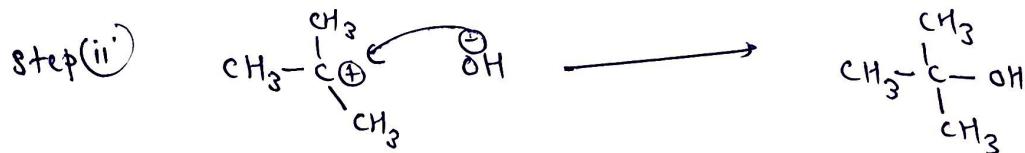
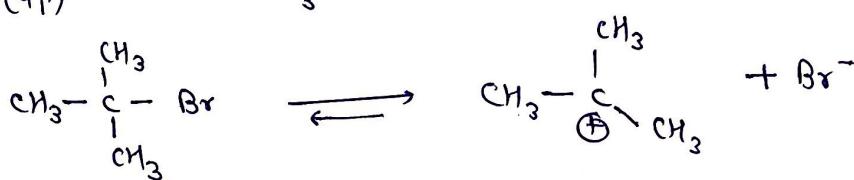


Unimolecular Substitution nucleophilic reaction

: SN¹



Mechanism :- Step (i)



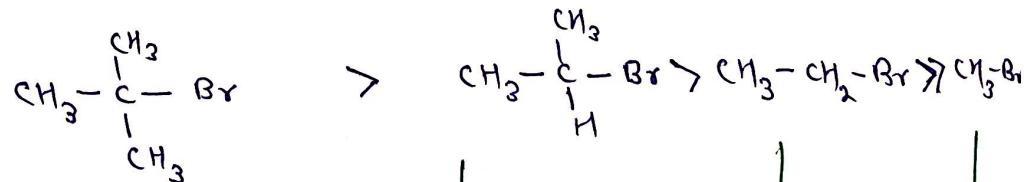
Aparna
Kaksha :-

→ Above reaction follows first order kinetics.

Rate ∝ [Alkyl halide]

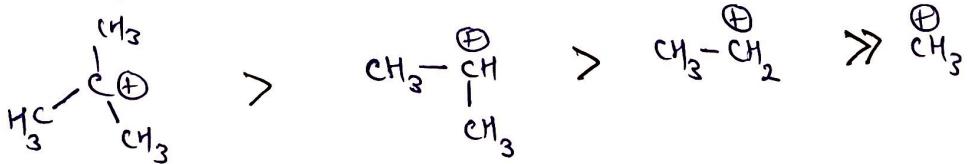
- It is a two step reaction and carbocation reaction intermediate is formed.
- Step (i) is slow and reversible & Rate of reaction depends on slowest step.

Order of reactivity



During reaction → ↓

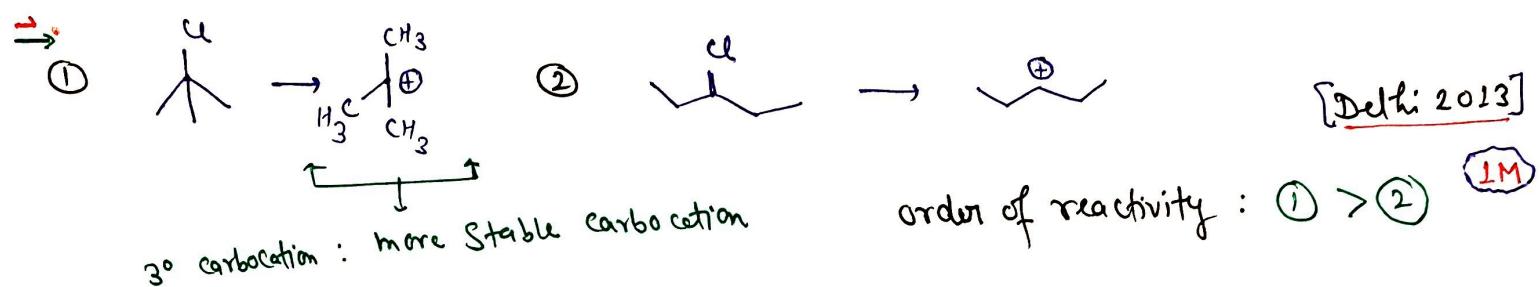
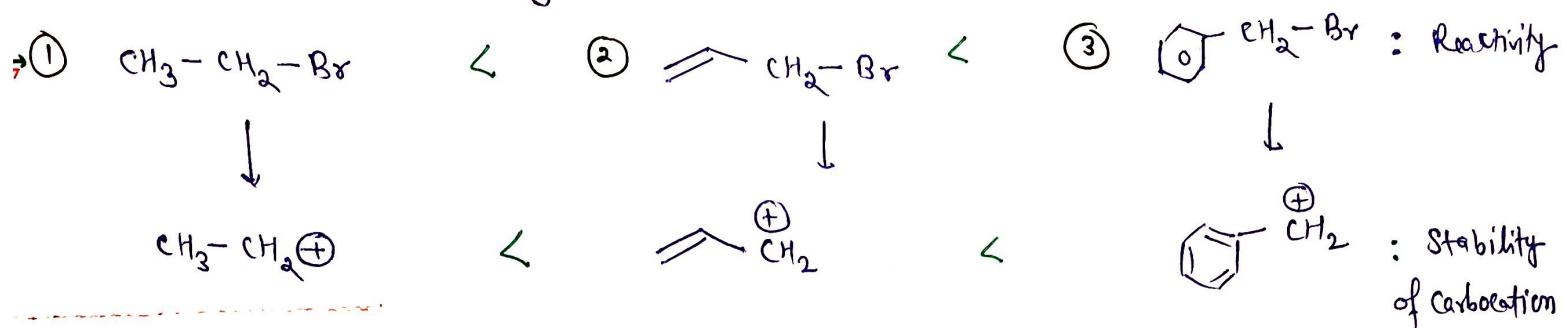
Stability of : > > >>



- If carbocation intermediate is stable then that substrate gives fast SN¹ reaction.

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

→ find the order of reactivity for S_N1 reaction ?



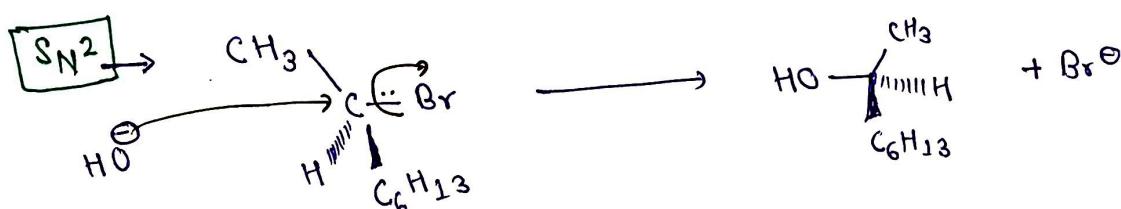
Stereochemistry of S_N1 vs S_N2 :-



S_N2 reaction gives inverted product.

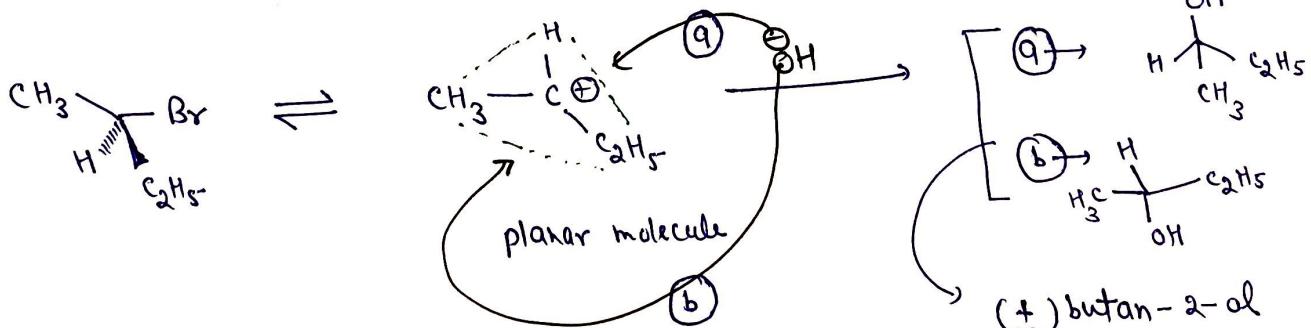
But S_N1 reaction gives racemic mixture (It goes through racemisation)

Example :-



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

S_N1 :-



Order of reactivity for S_N1 : Tert. Halide > sec. Halide > 1° Halide > CH₃-X Racemic mixture

for S_N2 : CH₃-X > 1° Halide > sec. Halide > tert. Halide

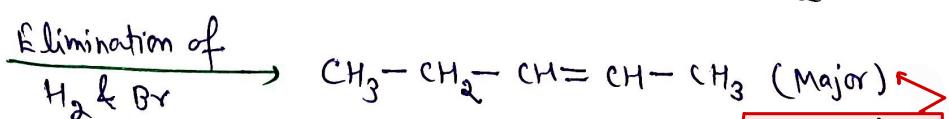
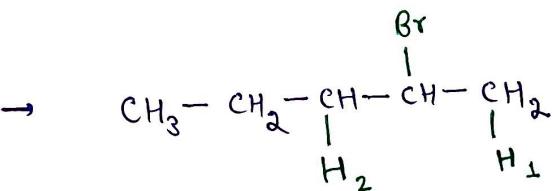
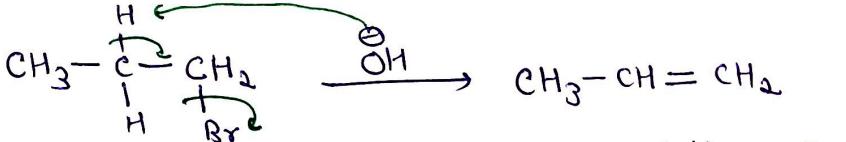
→ S_N1 : (CH₃)₃CBr > CH₃-CH(Br)-CH₂-CH₃ > CH₃-CH₂-CH₂-CH₂-Br

S_N2 : (CH₃)₃CBr > CH₃-CH(Br)-CH₂-CH₃ > CH₃-CH₂-CH₂-CH₂-Br

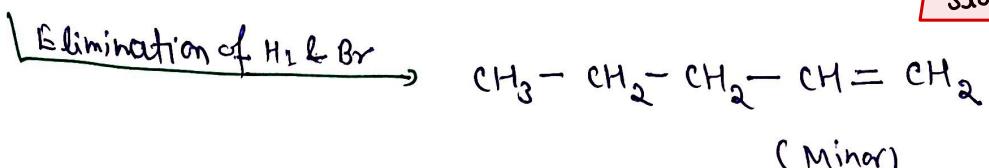
Elimination Reaction :-

Dehydrohalogenation Reaction

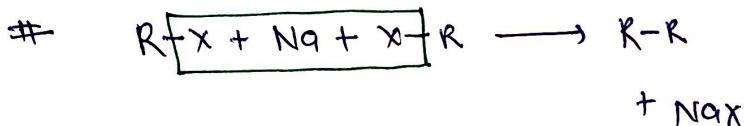
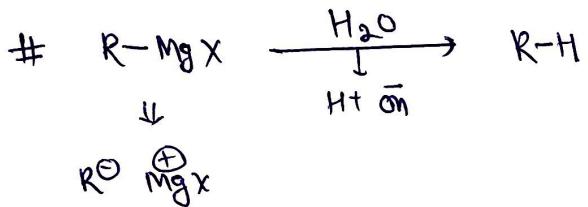
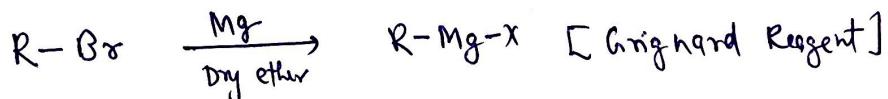
Haloalkane with β -hydrogen atom $\xrightarrow[\text{CalcOHic}]{\text{KOH}}$ Alkene



Stable Alkene



Reaction with metals :-



Reactions of haloarenes

Nucleophilic Substitution

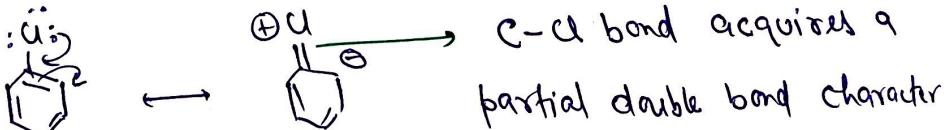
Aryl halides are extremely less reactive toward

[Delhi 2013] 2M

NSR due to following reasons :-

i) Resonance effect :-

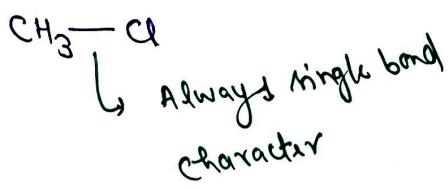
[Delhi 2013] 1M



C-Cl bond acquires a partial double bond character

due to resonance as a result

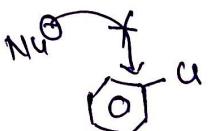
bond breaking in haloarene is difficult than haloalkane. Therefore haloarenes are less reactive than haloalkane towards NSR.



ii) Instability of phenyl cation :-

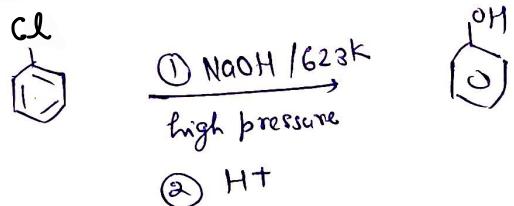
Haloarenes can not follow S_{N}^1 path because

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

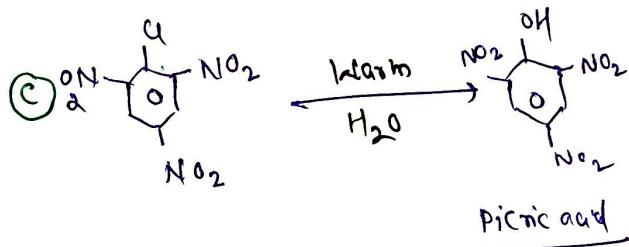
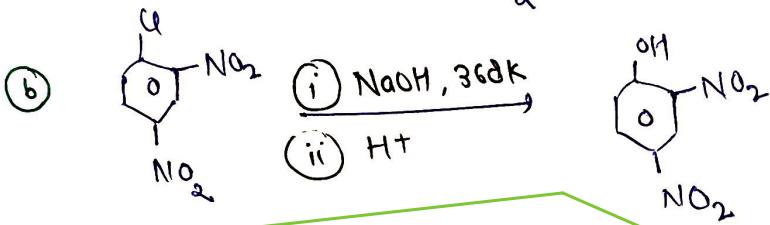
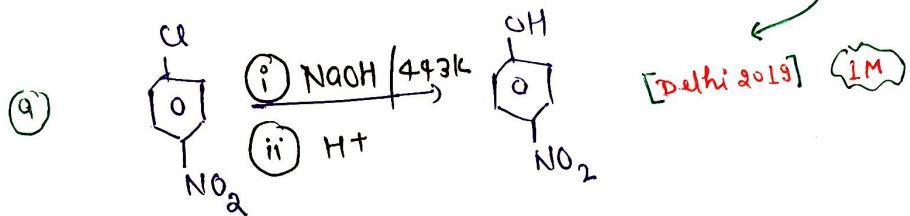


Because of possible repulsion, it is less likely for electron rich nucleophile to approach electron rich aren.

→ Replacement by hydroxyl group :-



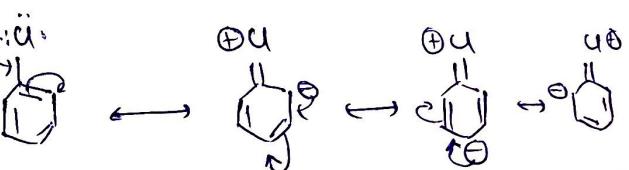
The presence of an electron withdrawing group ($-NO_2$ | $-CN$) at ortho and para positions increases the reactivity of halo-arenes.



i) Electrophilic Substitution Reaction :-

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

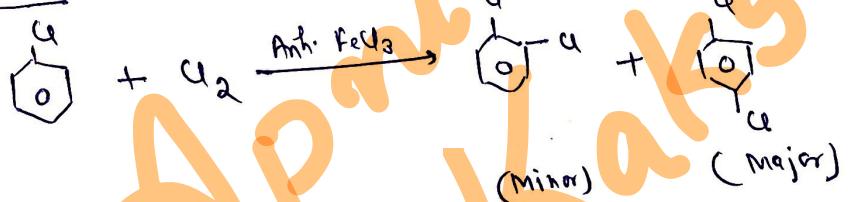
3M



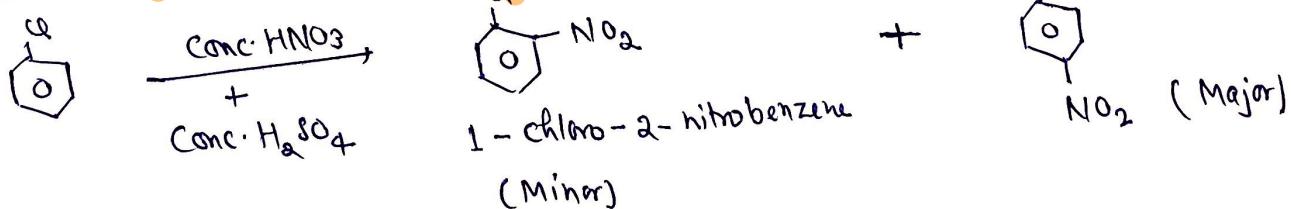
Due to resonance, the electron density increases more at ortho and para position.

→ [CBSE 2015] 1M

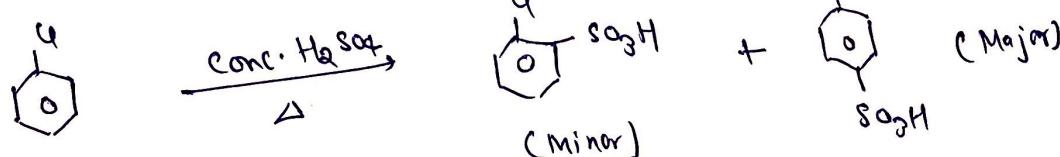
i) Halogenation :-



ii) Nitration :-



iii) Sulphonation :-



iv

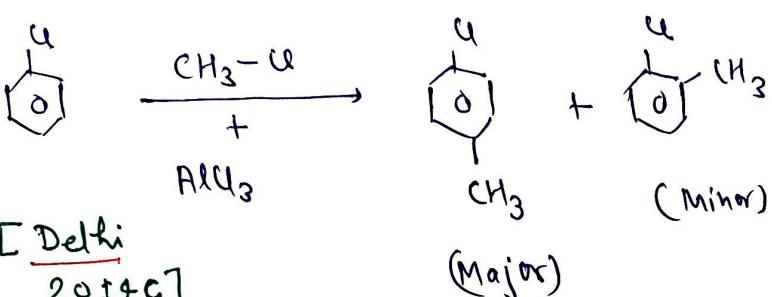
Friedel - craft's Reaction

[Delhi 2010]

1M

Alkylation

Addition of alkyl group on benzene

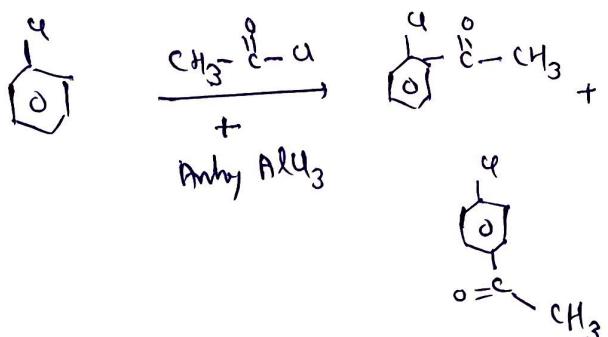


[Delhi 2014C]

1M

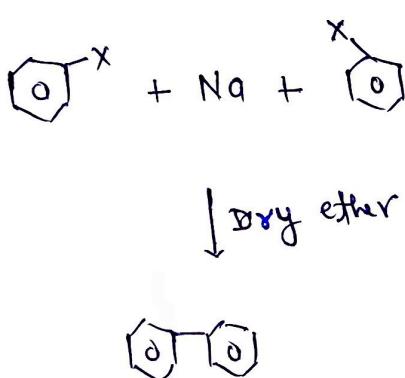
Acylation

Addition of acetyl group on benzene

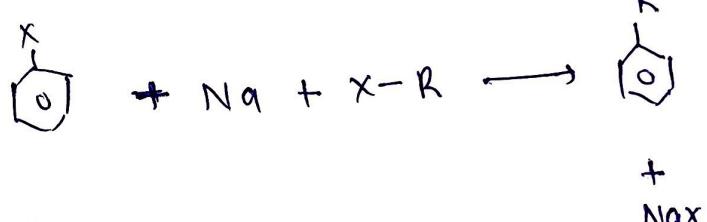


Reaction with metal :-

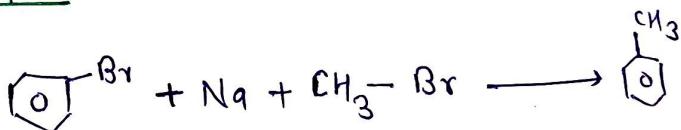
Fittig Reaction



Wurtz - Fittig Reaction



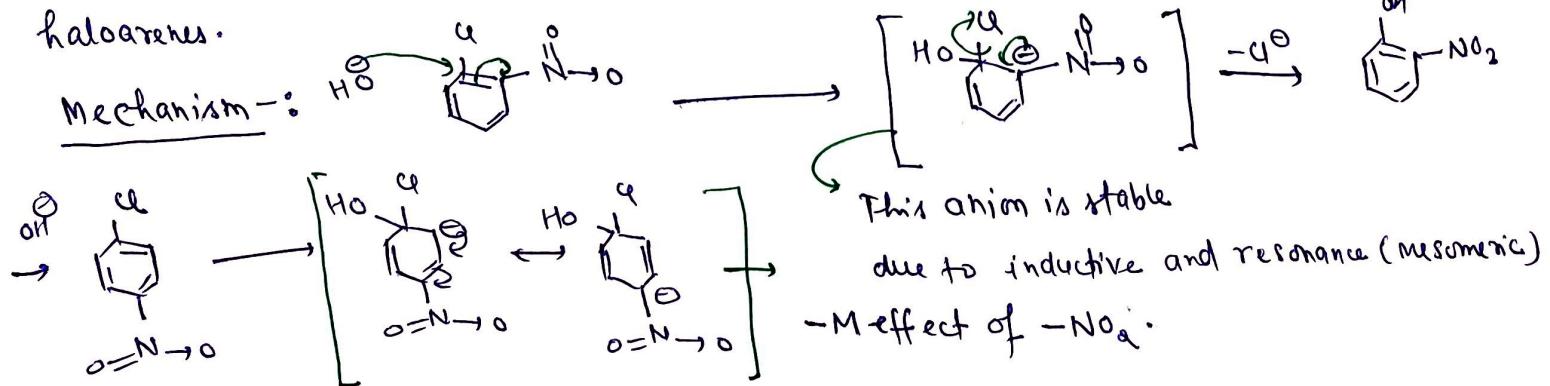
Example:-



Question :— The presence of nitro group at ortho - para positions increase the reactivity of haloarenes towards N.S.R, Why ? [CBSE 2019] 1M

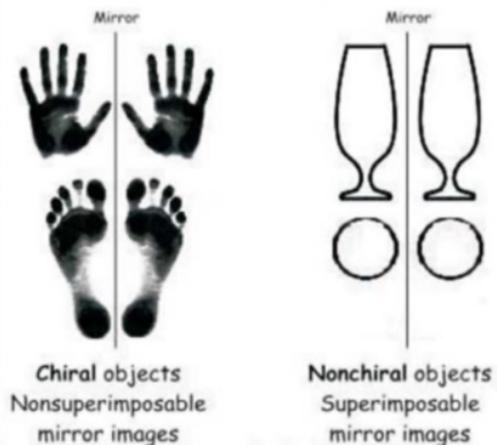
Answer :— Because $-\text{NO}_2$ group at ortho and para positions withdraw electron density from the benzene ring and thus facilitates the nucleophilic attack on haloarenes.

Mechanism :-



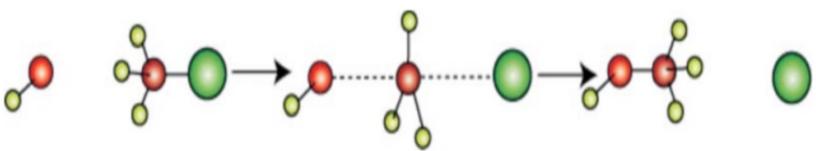
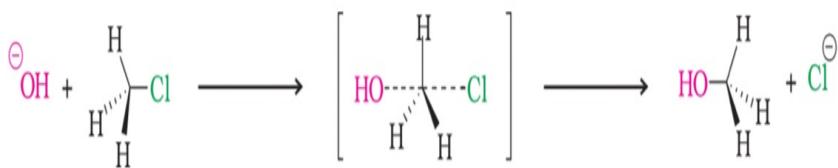
CHIRALITY

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

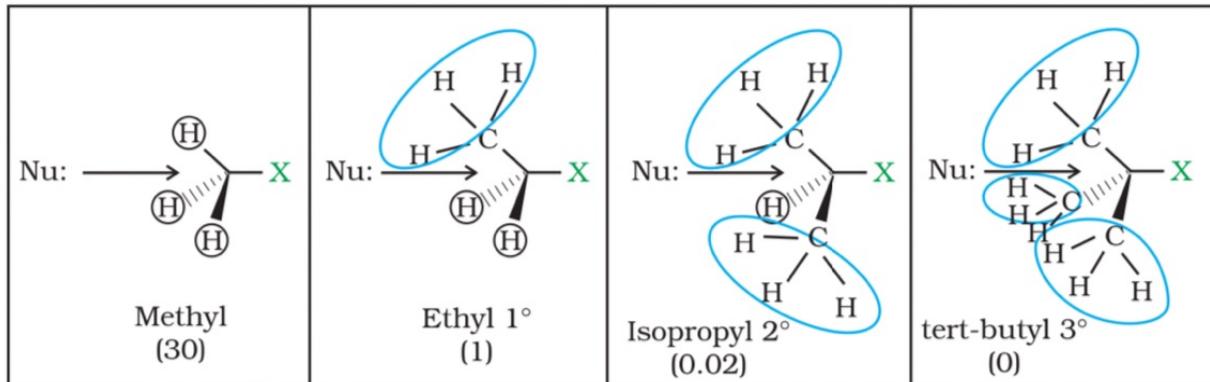


Some common examples of chiral and achiral objects

S_N^2 Reaction



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



Steric effects in S_N^2 reaction. The relative rate of S_N^2 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_N^1 and S_N^2) 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_N^2 reaction, a secondary halide- S_N^2 or elimination depending upon the strength of base/nucleophile and a tertiary halide- S_N^1 or elimination depending upon the stability of carbocation or the more substituted alkene.

