The replacement of hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

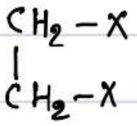
CLASSIFICATION

→ On the Basis of Number of Halogen Atoms :-

Monohaloalkane

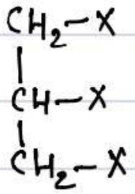
CH_3-CH_2-X

Dihaloalkane



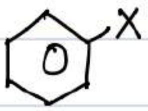
$$\begin{array}{l} CH_2-X \\ | \\ CH_2-X \end{array}$$

Trihaloalkane

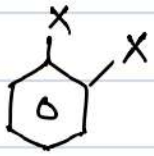


$$\begin{array}{l} CH_2-X \\ | \\ CH-X \\ | \\ CH_2-X \end{array}$$

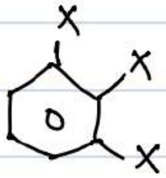
Monohaloarenes



Dihaloarenes



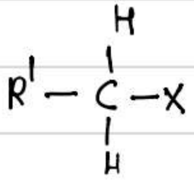
Trihaloarenes



→ Compound containing sp^3 C–X Bond :

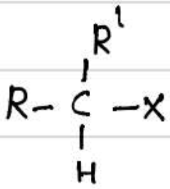
$(X = F, Cl, Br, I)$

(A) Alkyl halides :



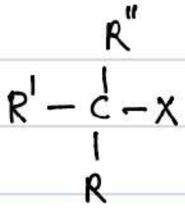
$R'-CH_2-X$

Primary (1°)



$R-CH(R')-X$

Secondary (2°)

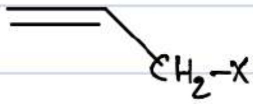


$R'-C(R'')(R)-X$

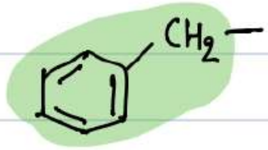
Tertiary (3°)

(B) Allylic halides:-

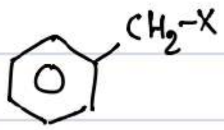
$R-\underbrace{CH=CH-CH_2-}_{\text{Allyl group}}$

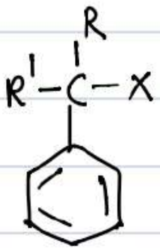


(C) Benzylic halides:-



Benzylic group

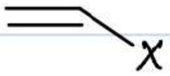


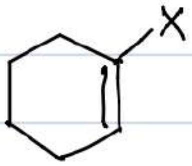


→ Compounds containing sp^2 C–X Bond :-

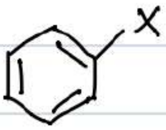
(A) Vinylic halides :-

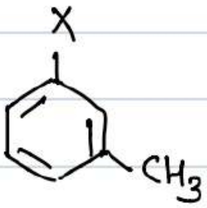
$\underbrace{R-HC=CH}_{\text{Vinylic group}}-$



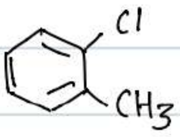
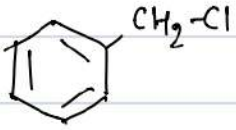


(B) Aryl halides :-

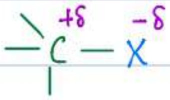




NOMENCLATURE

	Common name	IUPAC
$\overset{1}{C}H_2=\overset{2}{C}H\overset{3}{C}H_2Br$	Allyl bromide	3-Bromopropene
	O-Chlorotoluene	2-Chlorotoluene or 1-Chloro-2-methylbenzene
	Benzylchloride	Chlorophenylmethane

NATURE OF C-X BOND :-



The carbon-halogen bond of alkyl halide is polar since electronegativity difference is non zero between Carbon and halogen atom.

Carbon - halogen bond length — C-F < C-Cl < C-Br < C-I

Question:- Explain dipole moment of CH_3-F, CH_3-Cl, CH_3-Br and CH_3-I.

Solution:-

	Dipole moment (Debye)
CH_3-Cl	1.860
CH_3-F	1.847
CH_3-Br	1.830
CH_3-I	1.636

Dipole moment $(\mu) = q \times d$

q = charge, increases with increase in ΔE.N.

d = bond length

$\therefore$ Result of both q and d, dipole moment of CH_3-Cl is maximum among the above compounds.

Foreign 2015, All India 2010, Delhi 2011, 2013

Ques:- Give reason -

The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

Solution:- In Chlorobenzene, the Cl-atom is linked to a sp^2-hybridised carbon atom whereas in cyclohexyl chloride, the Cl-atom is linked to a sp^3-hybridised carbon atom.

As sp^2-hybridised carbon has more s-character so, it is more electronegative, thus the density of electrons of C-Cl bond near the Cl-atom is less in chlorobenzene than in cyclohexyl chloride. Hence, the C-Cl bond of cyclohexyl chloride is more polar, i.e. it has higher dipole moment.

METHOD OF PREPRATION :–

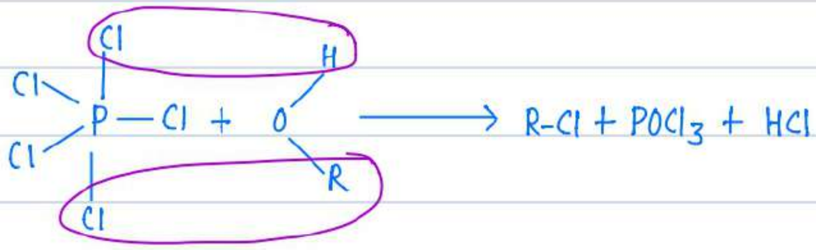
1. FROM ALCOHOLS :–

$$R{-}OH + HCl \xrightarrow{ZnCl_2} R{-}Cl + H_2O$$

Reactivity of alcohol :- $3° > 2° > 1°$

Reason :- stability of Carbocation

$$3R{-}OH + PX_3 \longrightarrow 3R{-}X + H_3PO_3 \quad (X = Cl, Br)$$



$$PCl_5 + R{-}OH \longrightarrow R{-}Cl + POCl_3 + HCl$$

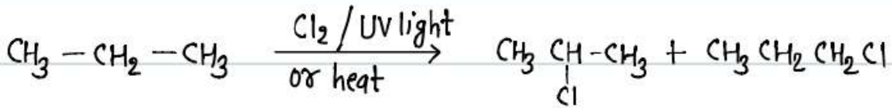
$$R{-}OH \xrightarrow[X_2 = Br_2, I_2]{red\ P/X_2} R{-}X$$

★★ $R{-}OH + SOCl_2 \longrightarrow R{-}Cl + SO_2\uparrow + HCl\uparrow$

→ Best method of prepration of alkyl halide because both side products are gaseous.

2. FROM HYDROCARBONS:-

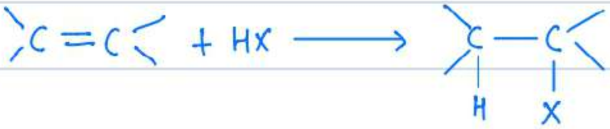
(A) From Alkane (Free Radical Halogenation):-



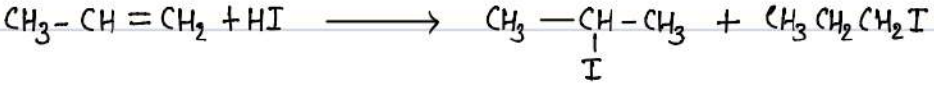
$$CH_3-CH_2-CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3\underset{\underset{Cl}{|}}{CH}-CH_3 + CH_3CH_2CH_2Cl$$

(B) From Alkene:-

I Addition of HX:-



$$>C=C< + HX \longrightarrow >\underset{\underset{H}{|}}{C}-\underset{\underset{X}{|}}{C}<$$



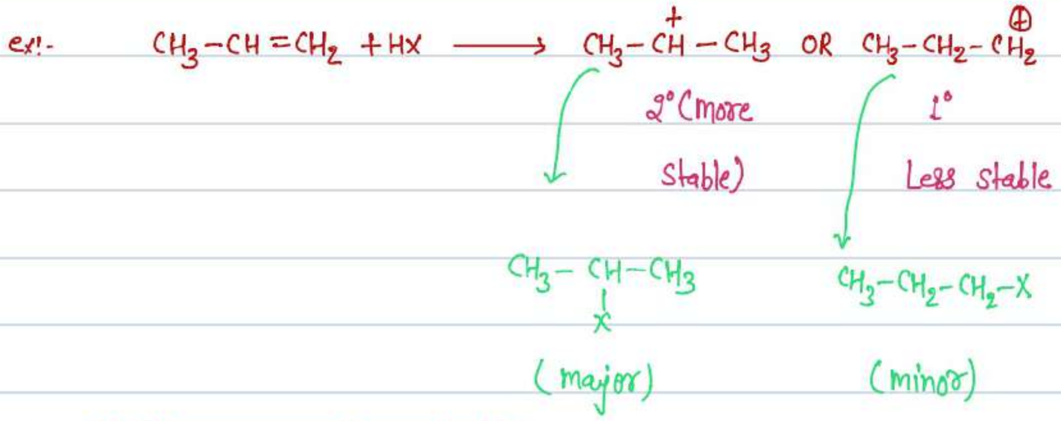
$$CH_3-CH=CH_2 + HI \longrightarrow CH_3-\underset{\underset{I}{|}}{CH}-CH_3 + CH_3CH_2CH_2I$$

Major Minor

(Markovnikov's rule)

SHORT Trick For Major product: Add halogen to the more stable Carbocation and H to less stable.

ex:- $CH_3-CH=CH_2 + HX \longrightarrow CH_3-\overset{+}{C}H-CH_3$ OR $CH_3-CH_2-\overset{\oplus}{C}H_2$



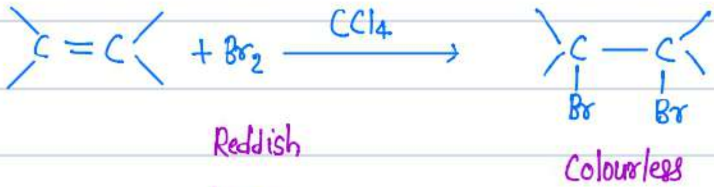
2° (more stable)

1° Less stable

$CH_3-\underset{X}{\underset{|}{C}H}-CH_3$ (major)

$CH_3-CH_2-CH_2-X$ (minor)

II Addition of Halogen (X_2) :-



Reddish brown

Colourless

★★ FINKELSTEIN REACTION :-

$$R-X + NaI \xrightarrow{\text{dry acetone}} R-I + NaX$$

$(X = Cl, Br)$

★ SWARTS REACTION :-

$$CH_3-Br + AgF \longrightarrow CH_3F + AgBr$$

PHYSICAL PROPERTIES

Ques: Give reason – Foreign 2012, 2015, Delhi 2013, All india 2010.

Alkyl halides, though polar, are immiscible with water. why?

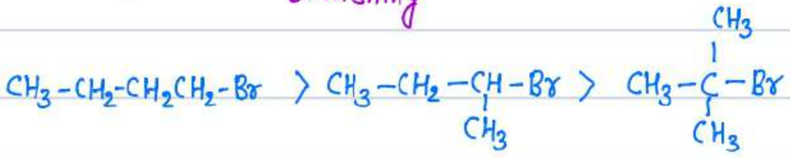
Solution: Alkyl halides are polar molecules and so held together by dipole-dipole interactions. Similarly, strong H-bonds exist between the water molecules. The new force of attraction between the alkyl halides and water molecules is weaker than the forces of attraction already existing between alkyl halide-alkyl halide and water-water molecules. Hence, alkyl halides (though polar) are immiscible (or insoluble in) with water.

Boiling point :- R-I > R-Br > R-Cl > R-F

Reason :– Increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

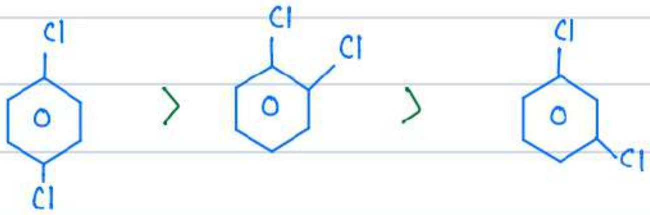
For Isomeric haloalkanes :-

$$\text{Boiling point} \propto \frac{1}{\text{Branching}}$$



$$CH_3-CH_2-CH_2CH_2-Br > CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-Br > CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-Br$$

Melting points of dihalobenzene :-



323K　　256K　　249K

CHEMICAL PROPERTIES

Haloalkanes shows three type of reactions –

- → Nucleophilic substitution
- → Elimination reactions
- → Reaction with metals

Nucleophilic Substitution :

- → S_N1
- → S_N2

See detail in ppt.

Ques:- Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief (main) product. Explain

Solution: KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C–C bond is more stable than C-N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

IMPORTANT DEFINITIONS ABOUT OPTICAL ISOMERISM

CHIRAL (ASYMETRIC) CARBON ATOM :— The carbon atom which is attached to four different atoms / groups is called asymmetric or chiral carbon atom

ENANTIOMERS :— Enantiomers are the non-superimposable mirror image of each other.

Substances which rotate the plane polarized light towards right are called dextrorotatory (+) and those which rotate the plane polarized light towards left are called laevorotatory (−).

RETENTION OF CONFIGURATION :– If the product formed in a reaction has same stereochemistry as that of reactant, this process is called retention of configuration.

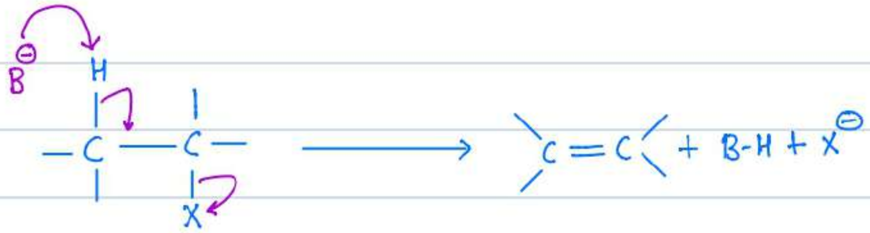
INVERSION OF CONFIGURATION :– If the product formed in a reaction has a stereochemistry opposite to that of reactant, it leads to inversion of configuration.

RACEMIC MIXTURE :– It is a mixture containing two enantiomers in equal proportion. Racemic mixture is optically inactive and have zero optical rotation.

If in a reaction, 50% inversion and 50% retention occurs, the process is called racemisation.

ELIMINATION REACTION :—

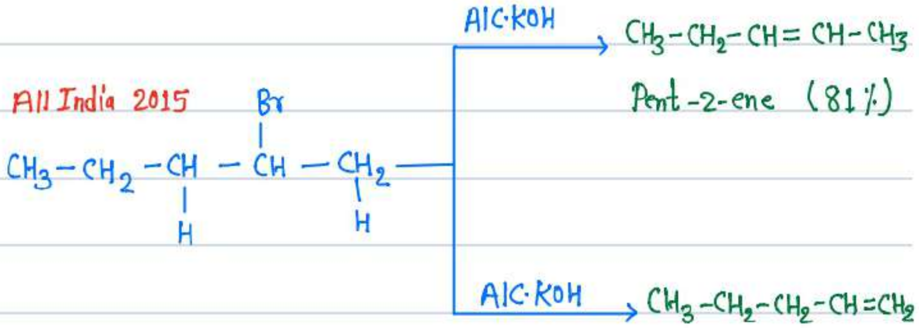
(β - Elimination OR Dehydrohalogenation)



$B^- =$ alc·KOH, $NaNH_2$ etc.

★★ Major product will be decided by Saytzeff rule. Alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms, will be major product.

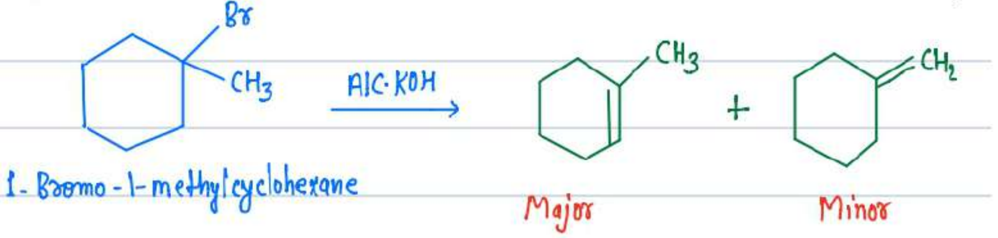
Ex:- All India 2015



Pent-1-ene (19%)

CBSE 2018

Ex:-



REACTION WITH METALS:- Compounds containing carbon - metal bonds are known as organo-metallic compounds.

Ex:- RMgX — Grignard Reagent

$$R\text{-}X + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{RMgX}$$

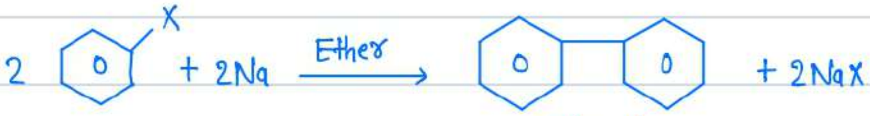
Grignard reagents are highly reactive. Grignard reagent react with water, alcohols, amines and formed hydrocarbon.

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

WURTZ REACTION:- When alkyl halide react with Sodium in dry ether, reaction known as wurtz reaction.

$$2RX + 2Na \xrightarrow{\text{dry ether}} R\text{-}R + 2NaX$$

When R = Aryl ⟶ Fitting Reaction



Diphenyl

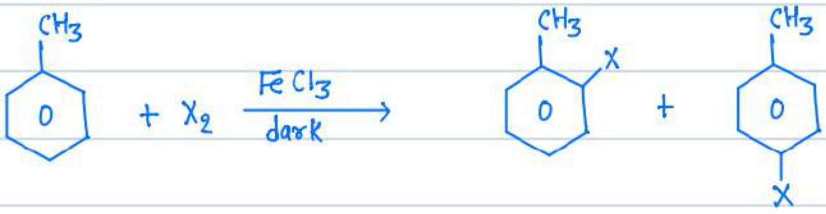
When One R is alkyl and one is aryl ⟶ Wurtz-Fitting Reaction

Toluene

HALOARENES / ARYL HALIDES

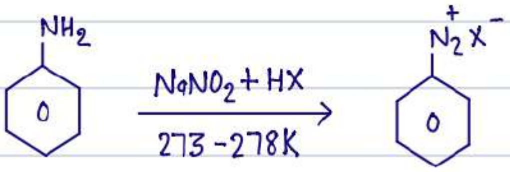
PREPRATION :-

ELECTROPHILIC SUBSTITUTION :-

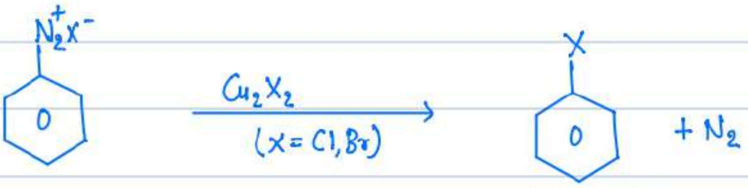


O-Halotoluene P-Halotoluene

SANDMEYER'S REACTION :-



Benzene diazonium halide



Aryl Halide

Sandmeyer reaction

REACTIONS OF HALOARENES

Question:- Aryl halides are extremely less reactive towards nucleophilic substitution. Why?

OR

Aryl halides and vinyl halides are less reactive towards SN1 and SN2 reaction. Why?

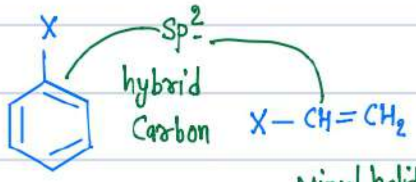
OR

Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why?

Solution:- 1. Resonance effect — In haloarenes or vinyl halides, the electron pairs on halogen atom are in conjugation with π-electrons of the ring or alkyl group.

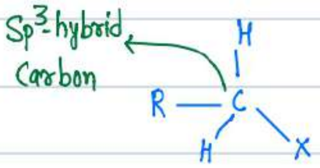
2. Difference in hybridisation of carbon atom in C-X bond :-

The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C-X bond more tightly than sp^3-hybridised carbon in haloalkane with less s-character. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes or vinylhalides are less reactive than haloalkanes towards nucleophilic substitution reaction.



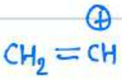
Aryl halide

Vinyl halide



3. Instability of phenyl cation or vinyl cation — No resonance stablization

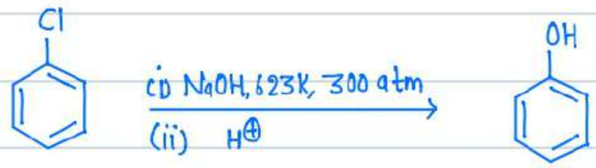
Phenyl Cation



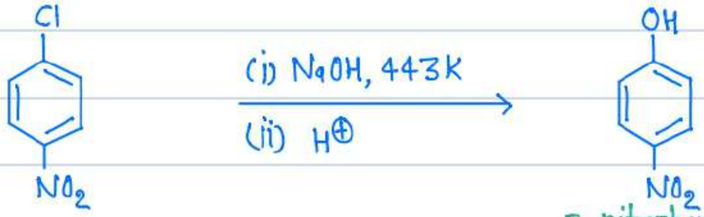
$CH_2=\overset{\oplus}{C}H$

Vinyl cation

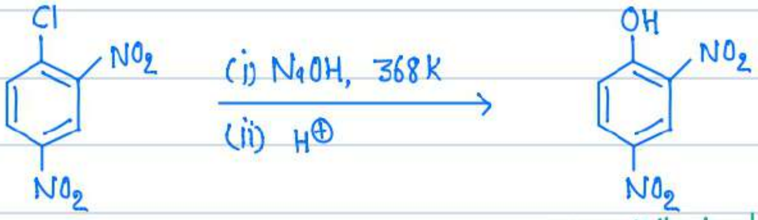
★★ Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution



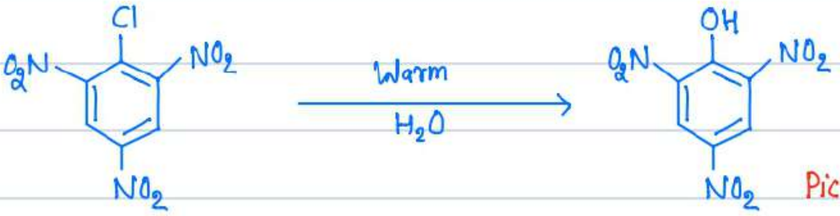
★★ The presence of an electron withdrawing group ($-NO_2$) at ortho, and para-positions increases the reactivity of haloarenes.



p-nitrophenol or
4-nitrophenol



2,4-dinitrophenol



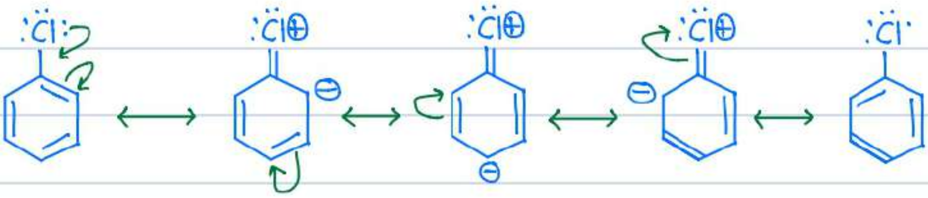
Picric Acid
OR
2,4,6-Trinitrophenol

ELECTROPHILIC SUBSTITUTION REACTION:-

Ques:- Although chlorine is an electron withdrawing group, yet it is ortho-, para- directing in electrophilic aromatic substitution reactions. Why?

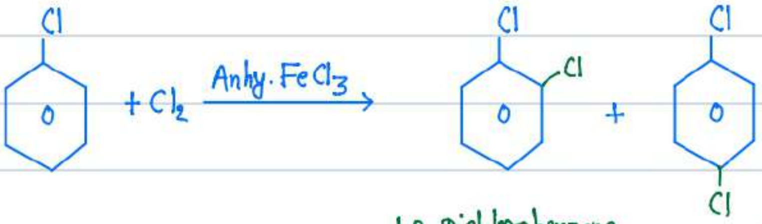
Solution:- Chlorine withdraws electrons through inductive effect and releases electrons through resonance.

In chlorobenzene, one of the lone pair on chlorine atom Conjugates with the ring.



Since, electron density is maximum at o- and p- positions due to +R- effect, therefore an electrophile can easily attack at such positions.

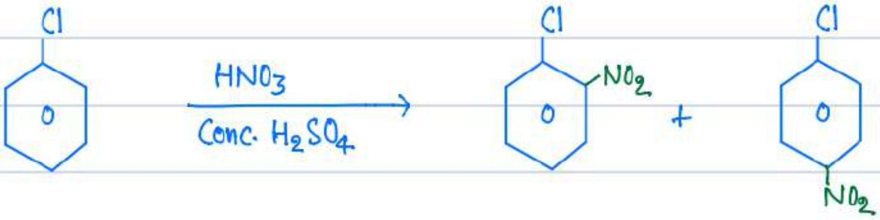
HALOGENATION :–



1,2-Dichlorobenzene (Minor)

1,4-Dichlorobenzene (Major)

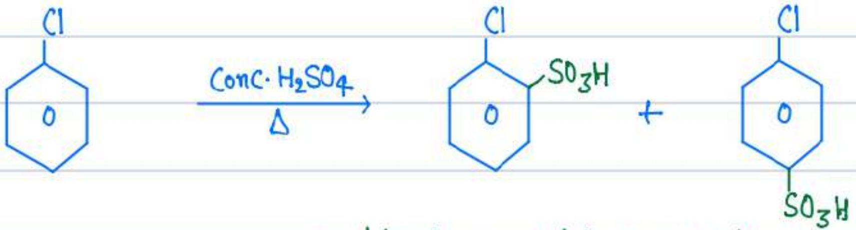
NITRATION :–



1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitro benzene (Major)

SULPHONATION :–

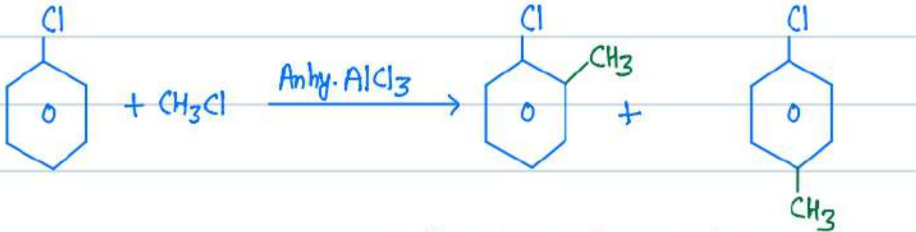


2-Chlorobenzene sulphonic acid (Minor)

4-Chlorobenzenesulphonic acid (Major)

FRIEDEL - CRAFTS REACTION :—

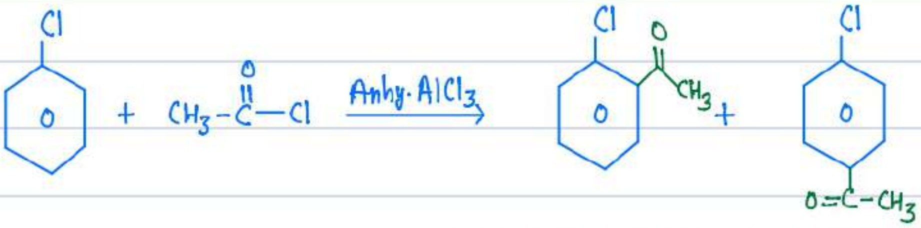
ALKYLATION :—



1-Chloro-2-methyl benzene (Minor)

1-chloro-4-methyl benzene (Major)

ACYLATION :—



2-chloroacetophenone (Minor)

4-Chloroacetophenone (Major)