Haloarenes

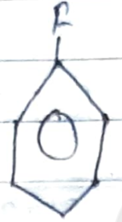
→ Haloarenes (arylhalides) are halogen derivatives of aromatic hydrocarbons (arenes) in which the halogen atom is directly attached to carbon of aromatic ring. they are represented by general formula: Ar-X.

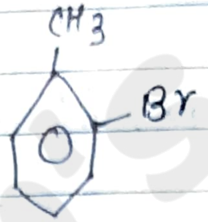
where

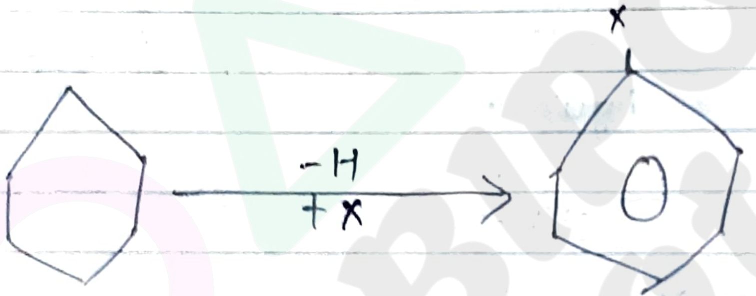
Ar = Aryl group

X = Cl, Br, I or F.

eg:-



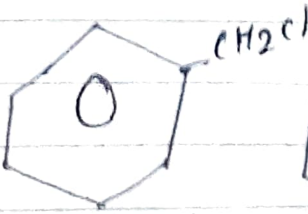




arene. aryl halide.

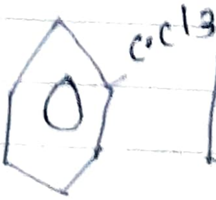
If the halogen atom is present in the side chain of aromatic ring, such compounds are not haloarenes or aryl halides. They are considered to be phenyl derivatives of haloalkanes.

eg:-

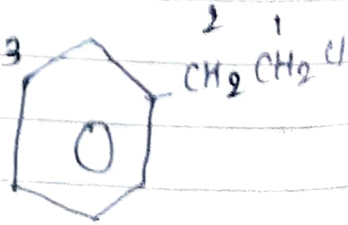


Benzyl chloride

Benzal chloride



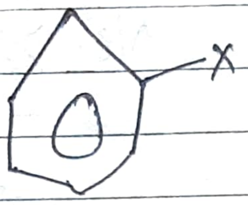
Benzo chloride



2phenyl-1-chloroethane

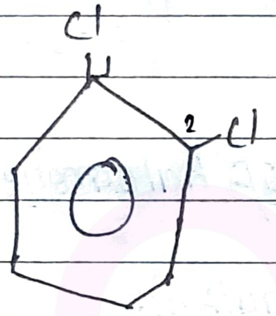
Nomen Clature:-
IUPAC

(I) In IUPAC system:- Haloarenes [If only one halogen atom is directly bonded (prefix) to aromatic ring]



halobenzene.

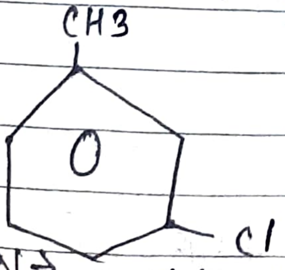
(II) If more than one same halogen atoms are present their position on the ring are indicated by number using lowest sum rule or appropriate prefixes on ortho, meta, para.



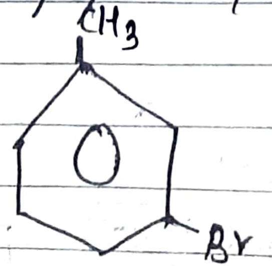
O-dichlorobenzene
1,2-dichloro benzene

1,3,5-trichloro benzene.

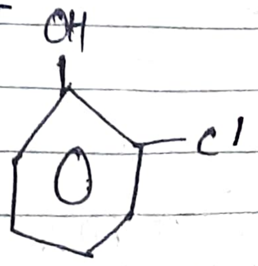
(III) If one of the groups present on the ring gives a special name to the molecules then the haloarenes is named as the haloderivative of special name:-



C/N → m-chloro~~form~~ ~~toulene~~ ~~fluorene~~
I/N → 3-chloro~~flu~~toulene



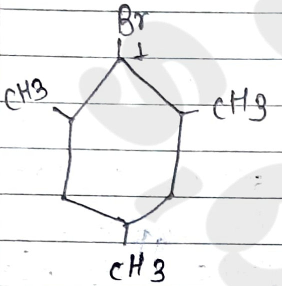
m-bromotoulene
3-bromotoulene



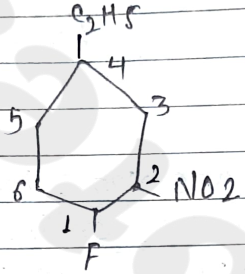
2-chloro-4-nitrophenol
O-chloro-p-nitro phenol

IV. If the groups are different and none of them gives special name to the molecule, the position of the group having highest priority get number 1.

Priority:- $COOH > -SO_3H > -CHO > -OH > NH_2 > X > NO_2 > R$ etc.



2,4,6-trimethyl bromo benzene

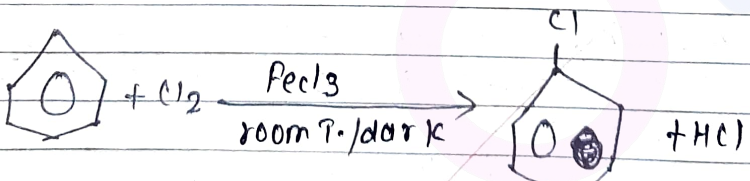


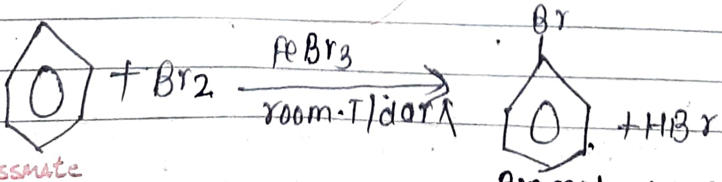
4-ethyl-1-fluoro-2-nitrobenzene.

General methods of preparation of haloarene →

1. From aromatic hydrocarbon (halogenation):- When benzene is treated with Cl_2 or Br_2 in presence of lewis acid like $FeBr_3$, $FeCl_3$, anhy. $AlCl_3$ etc, chloro or bromobenzene is formed.

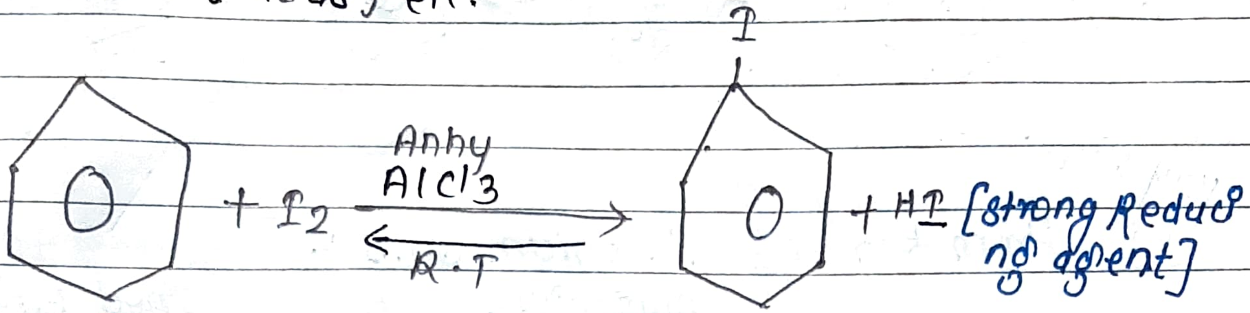
→ It is an electrophilic substitution reaction.





Bromobenzene.

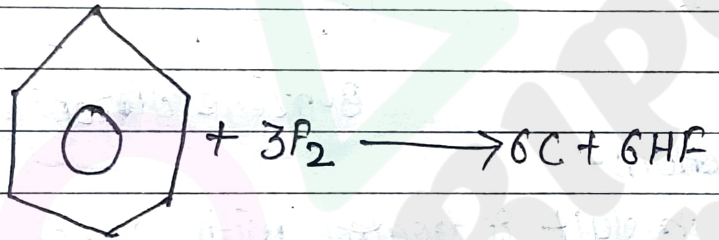
→ Iodination being reversible process it is carried out in the presence of strong oxidising agent like iodic acids, nitric acids, [nitric acids] etc.



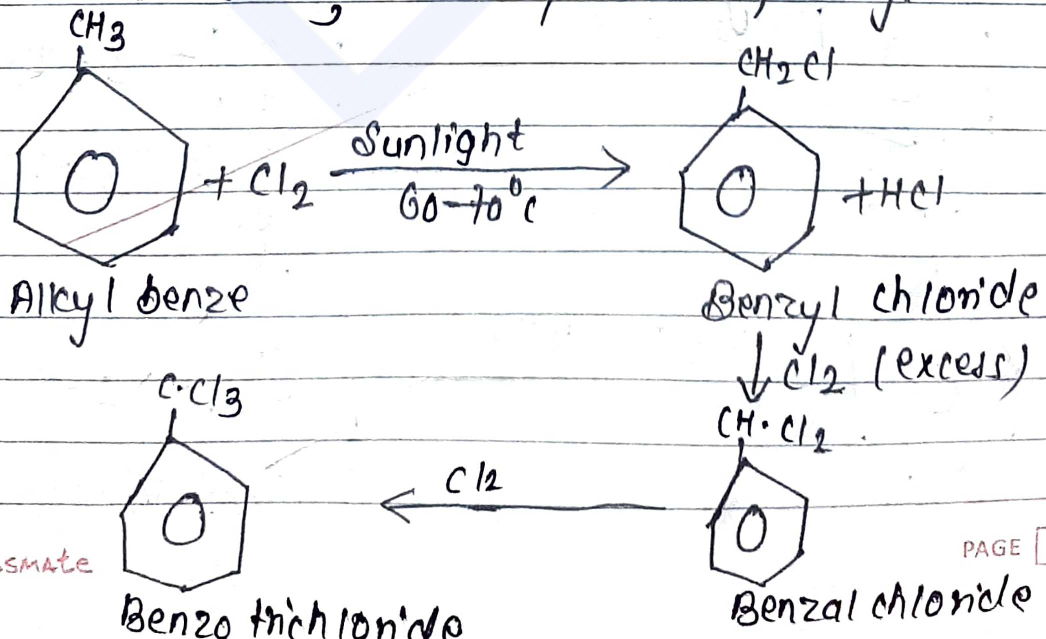
Iodobenzene.

$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$.

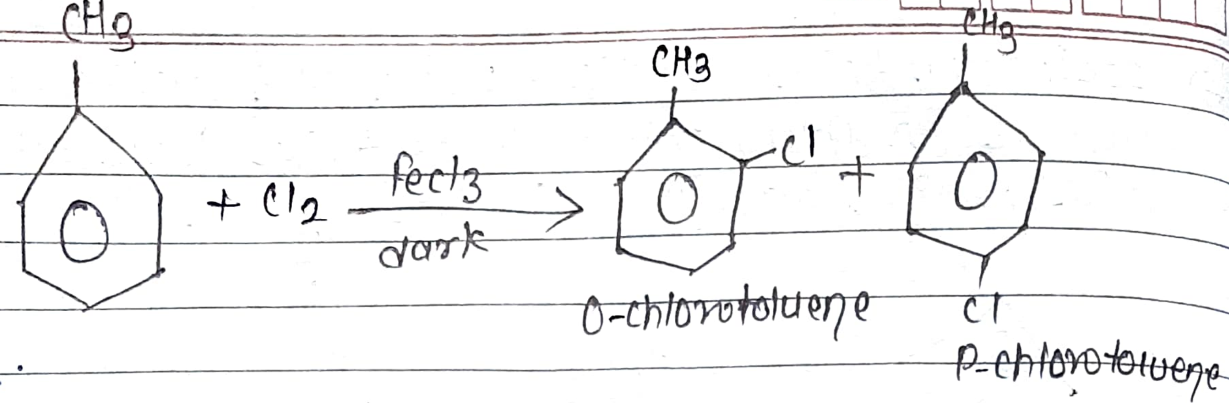
→ Flurobenzene cannot be obtained by this process because of high affinity of hydrogen atom (violent & uncontrolled).



→ If alkyl benzene is heated with halogen in presence of sunlight and in absence of halogen carries the substitution occurs at the side chain resulting in the presence of alkyl halide.



→

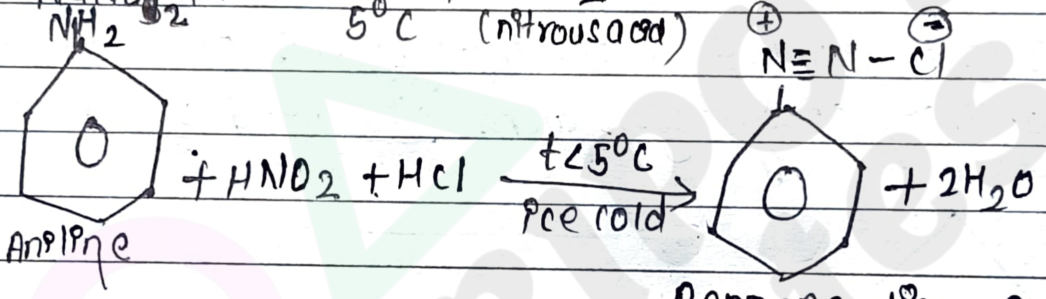


Very Imp.

(2) From benzene diazonium salts :-

Diazonium salts is obtained by the action of nitrous acid on aromatic primary amines at temperature below 5°C. This reaction is known as diazotisation reaction

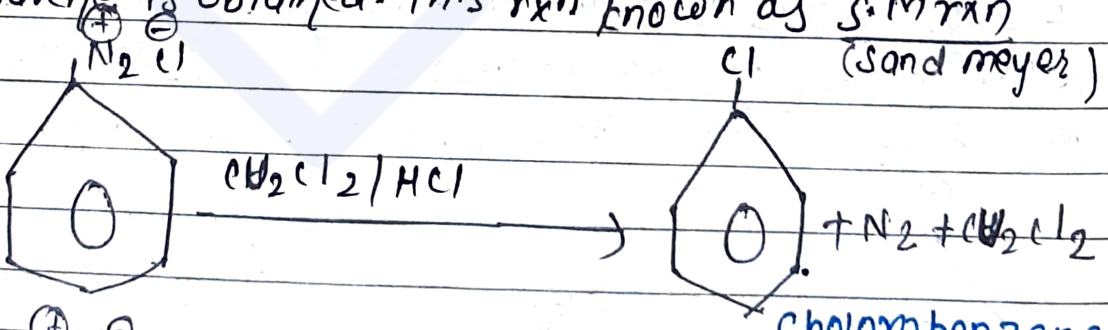
$NaNO_2 + HCl \xrightarrow[5^\circ C]{cold} HNO_2 + NaCl$ (nitrous acid)



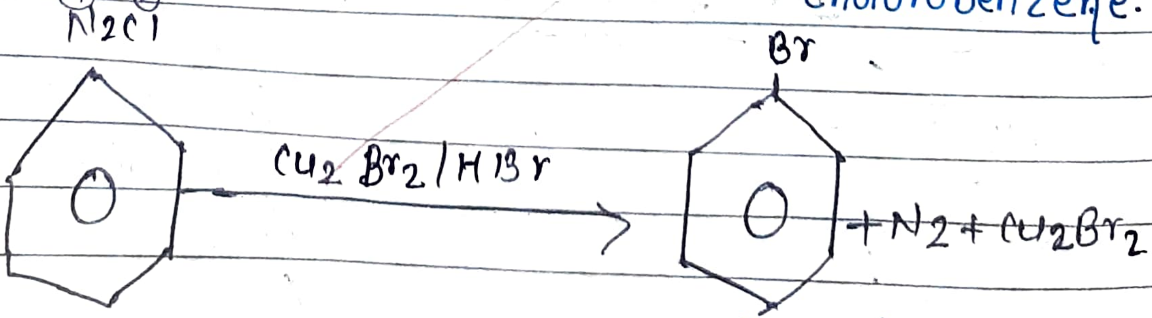
Benzene diazonium chloride.

* Sand Meyer Reaction:-

→ When diazonium salt is treated with cuprous halide in the presence of their corresponding halogen acid then haloarene is obtained. This rxn known as S.M rxn (Sand meyer)



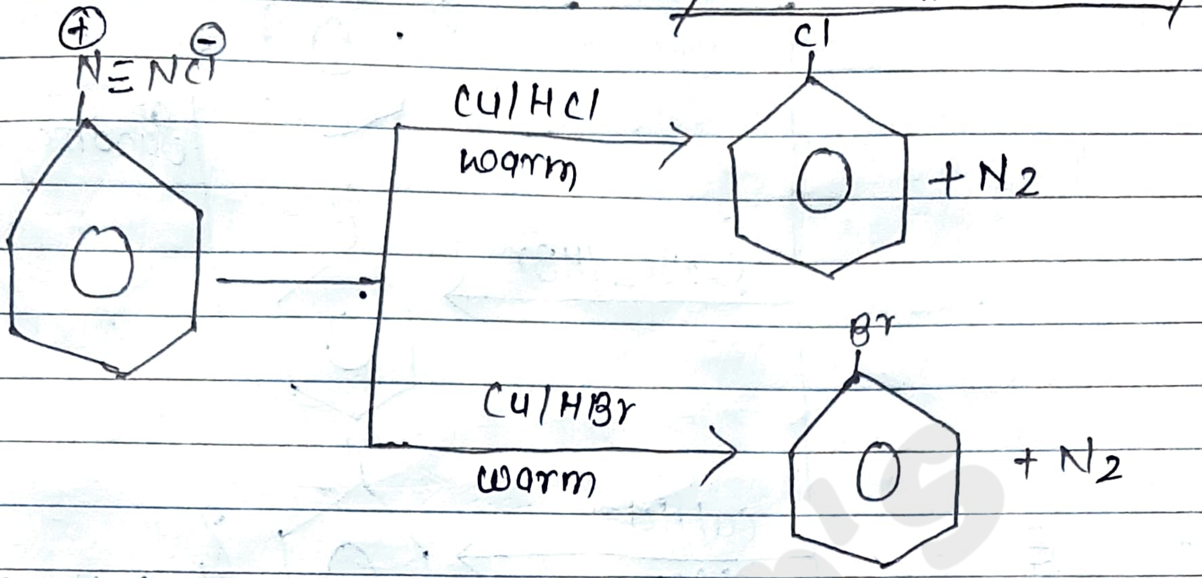
Cholorobenzene.



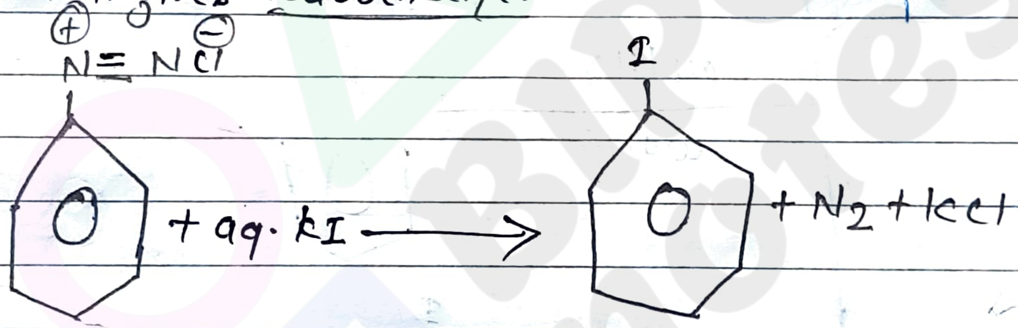
Bromobenzene

* Gattermann's reaction:-

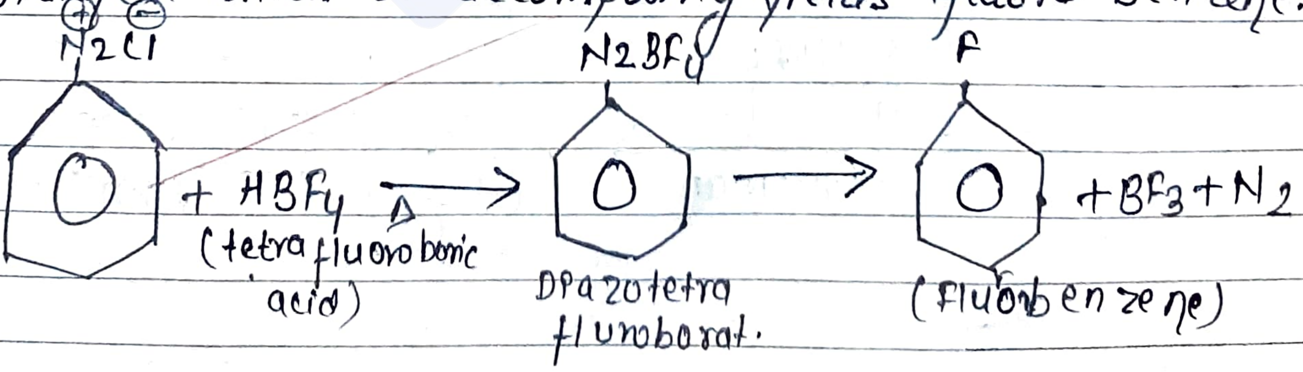
→ when diazonium salt is heated with copper powder in presence of halo-acid, haloarenes is obtained.
This reaction is known as Gattermann's reaction



→ when benzene diazonium chloride is treated with aqueous KI soln it gives iodobenzene.

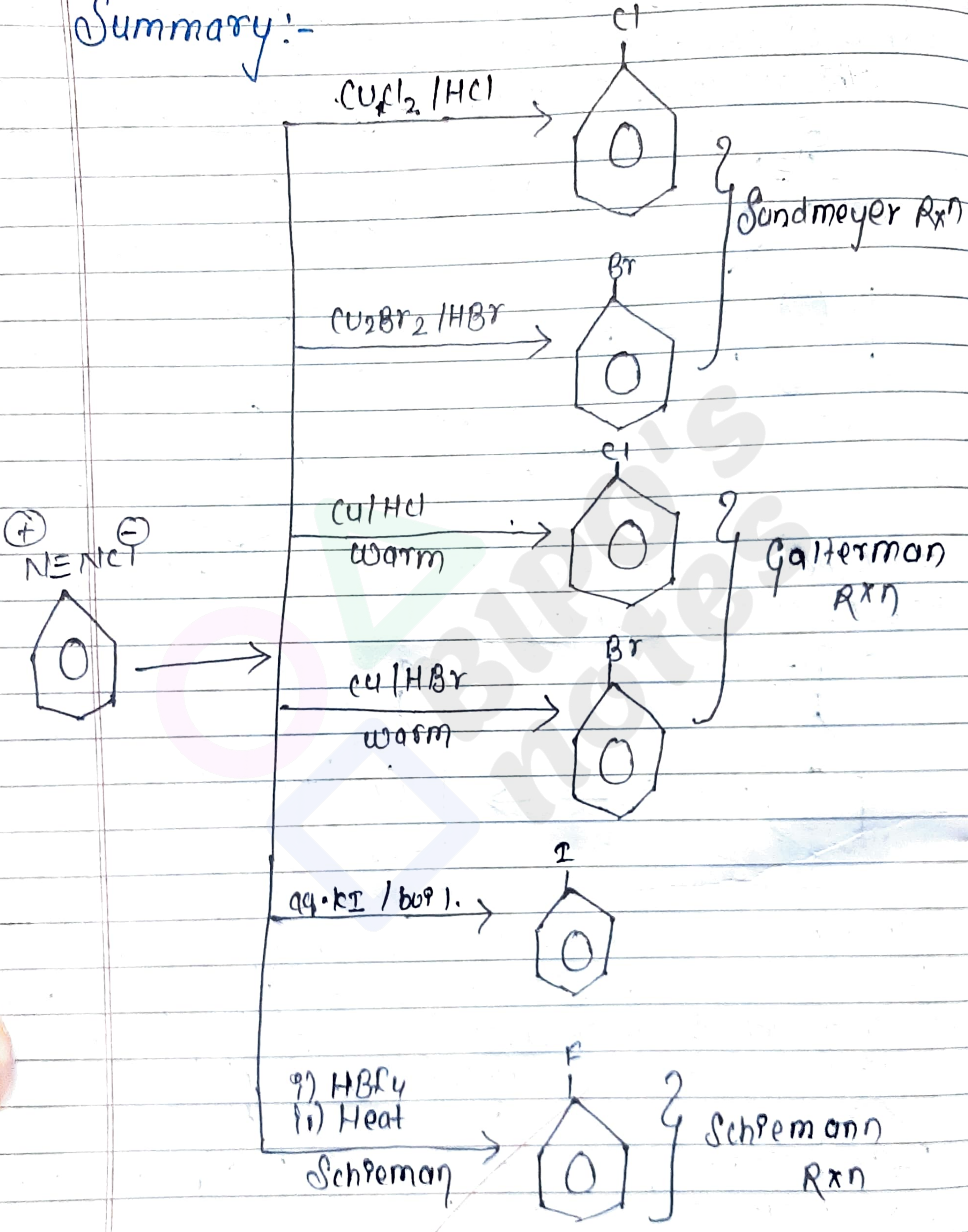


→ when benzene diazonium chloride is heated with ~~fluorine~~ fluoroboric acid, then diazonium tetra fluoroborate is obtained which on decomposing yields fluoro benzene.



Note :- This reaction is known as Schimann Rxn.

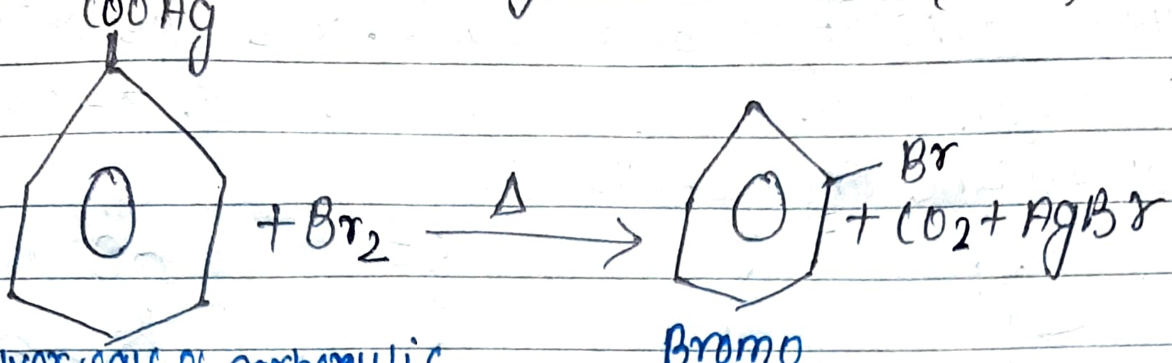
Summary:-



⊕ ⊖
N≡NCl
CuCl2 / HCl
Cl
Cu2Br2 / HBr
Br
Sandmeyer Rxn
Cu / HCl
warm
Cl
Cu / HBr
warm
Br
Gatterman Rxn
aq. KI / boil.
I
i) HBF4
ii) Heat
Schieman
F
Schiemann Rxn

③ From silver salt of aromatic acids:→

~~wh~~ when silver salt of aromatic acids is heated with halogens halobenzene is formed.

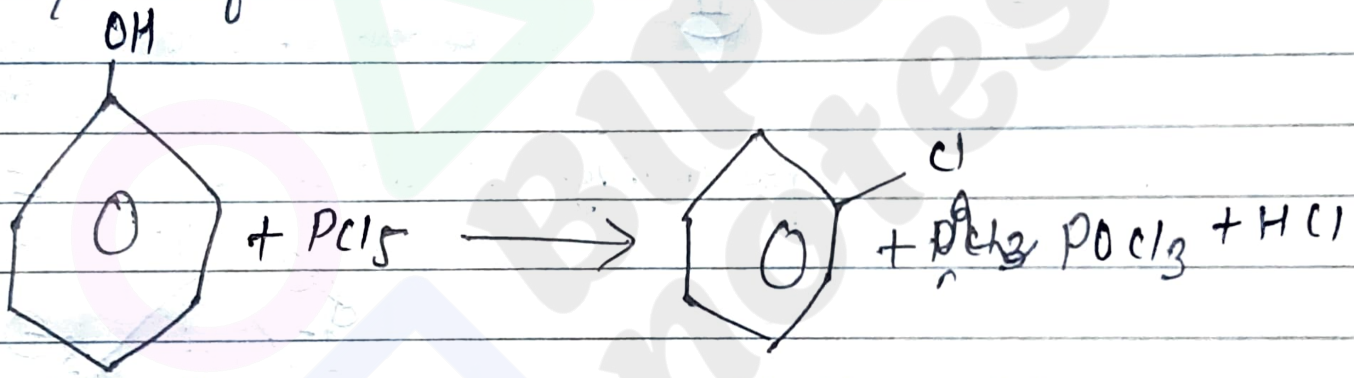


silver salt of carbonylic acid.

Bromo benzene

④ From phenol:-

when ~~SR~~ phenol is treated with PCl_5, chloro benzene is formed.



Phenol

chlorobenzeene

CHEMICAL PROPERTIES

1. Nucleophilic substitution.
2. Electrophilic substitution.
3. Reduction.
4. Reaction with metals.
5. Others.

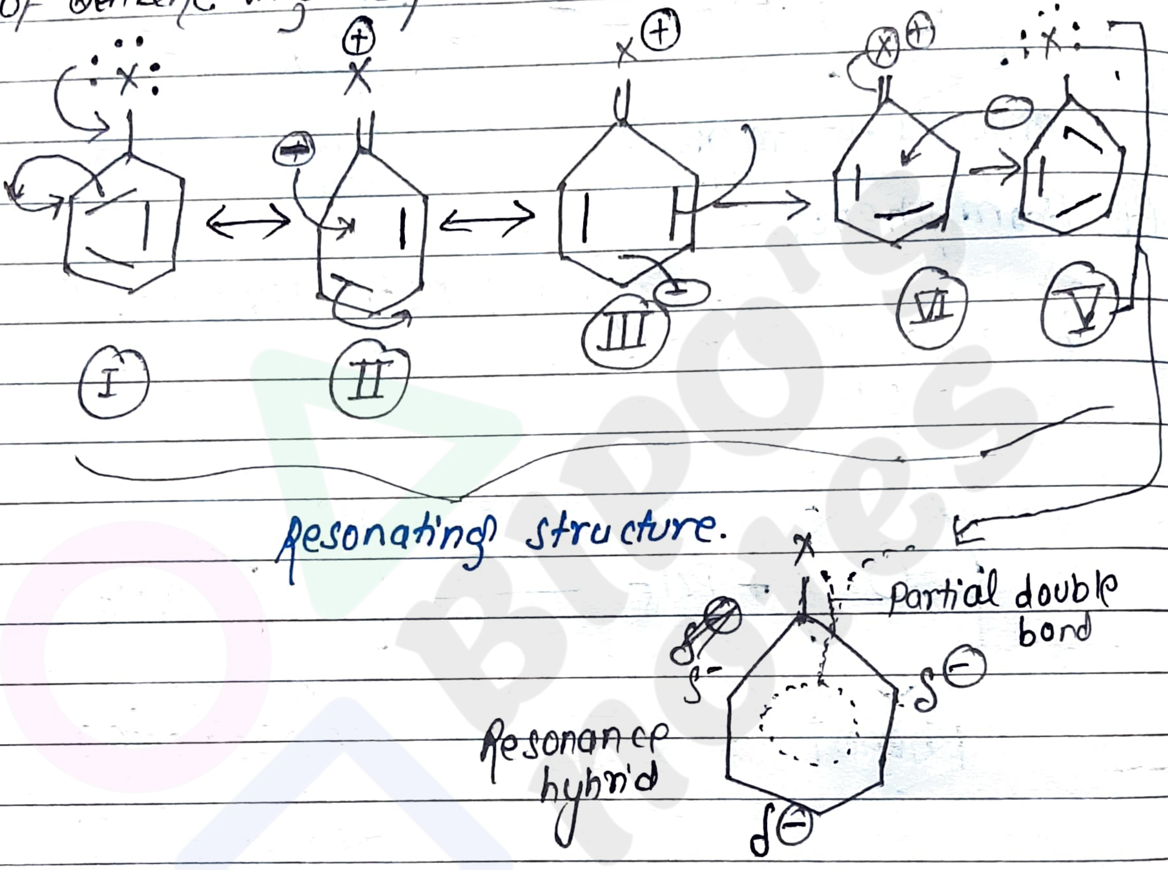
Haloalkane → fast substitution rxn.
Haloarenes → slow substitution rxn.

DATE ☐☐ ☐☐ ☐☐☐☐

Imp

1. Nucleophilic substitution Reaction ⇒

Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction due to stabilisation by resonance. The lone pair electro of halogen atom is in conjugation with π-electrons of benzene ring as follows:-

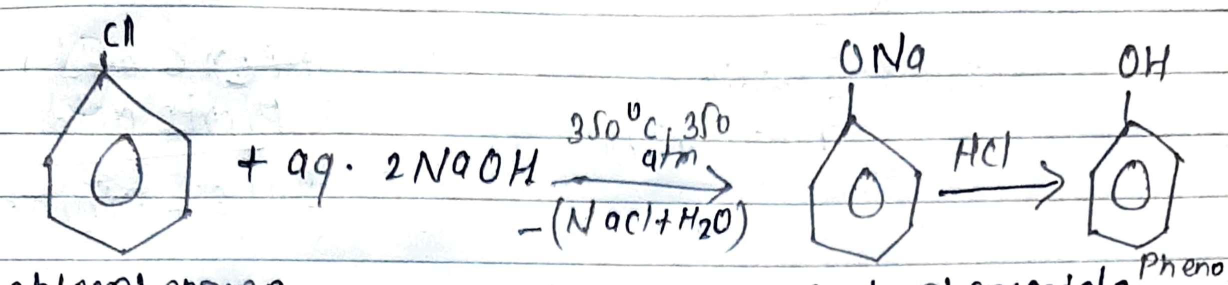


The contributing structure II, III & IV include that the C–X bond of haloarenes has partial doubles bond character. As a result the ~~C-X~~ C–X bond of haloarene is shorter and stronger as compared to that of haloalkane. Hence the clevage of C–X bond of halo alkane. Hence the clevage of C–X bond of haloarenes becomes difficult which make it less reactive than haloalkanes.

Hence, the haloarenes undergoes nucleophilic substitution reaction only under drastic condition.

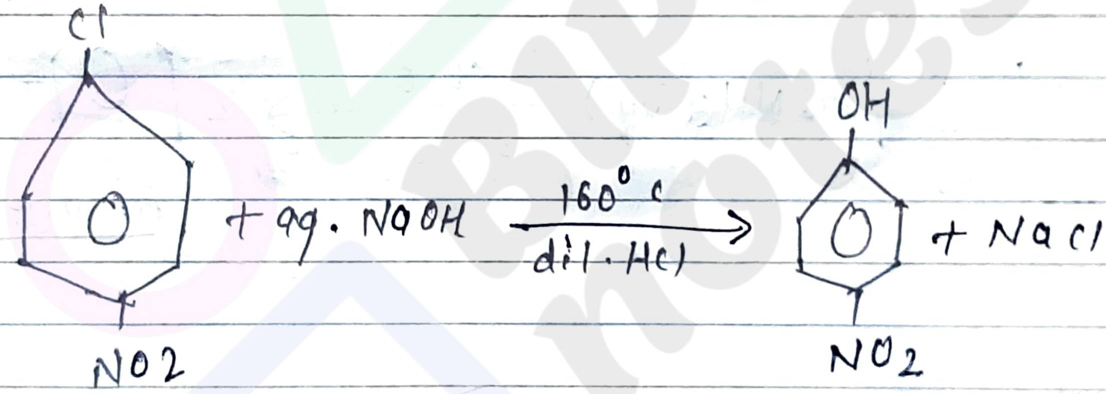
a) Reaction with NaOH →

When chlorobenzene is heated with aq. NaOH at 350°C under a pressure of 350 atm, sodium ~~phen~~ phenoxide is formed ~~wit~~ which on acidification gives phenol.



chlorobenzene. sod. phenoxide

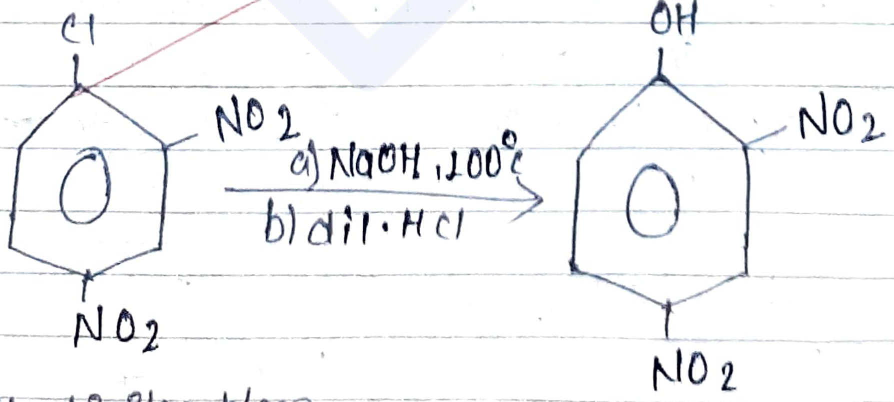
The reactivity of haloarenes towards nucleophilic substitution reaction increase if some electron withdrawing group like $\leftarrow NO_2$ $\leftarrow \overset{O}{\overset{\|}{C}}-OH$, $\leftarrow C\equiv N$ etc present at ortho or para position relative to the halogen atom.



p-nitrochlorobenzene

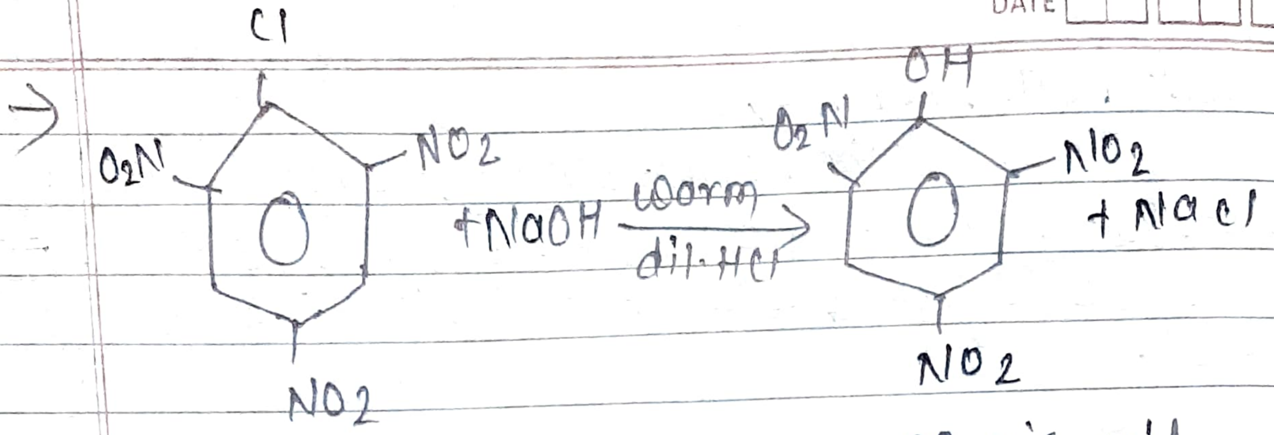
p-nitrophenol

→



2-4-dinitrochloro benzene

2,4-dinitrophenol.

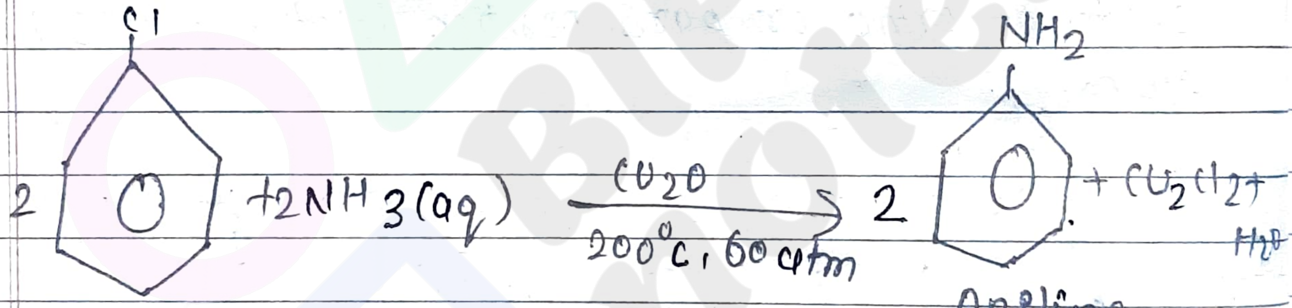


2,4,6 - trinitro chlorobenzene

~~Picric acid~~
Picric acid

2,4,6 - trinitrophenol.

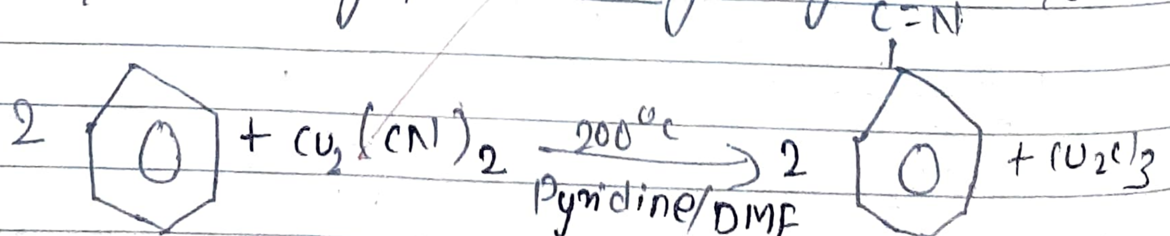
b) Reaction with aq. NH_3 → when cholorobenzene is heated with aqueous ammonia at 200°c under 60 atm pressure in the presence of cuprous oxide as catalyst gives aniline.



Aniline

V. Imp.

c) Reaction with cuprous cyanide → when ~~the~~ chlorobenzene is heated with cuprous cyanide, in the presence of pyridine or dimethyl formamide gives cyanobenzene.

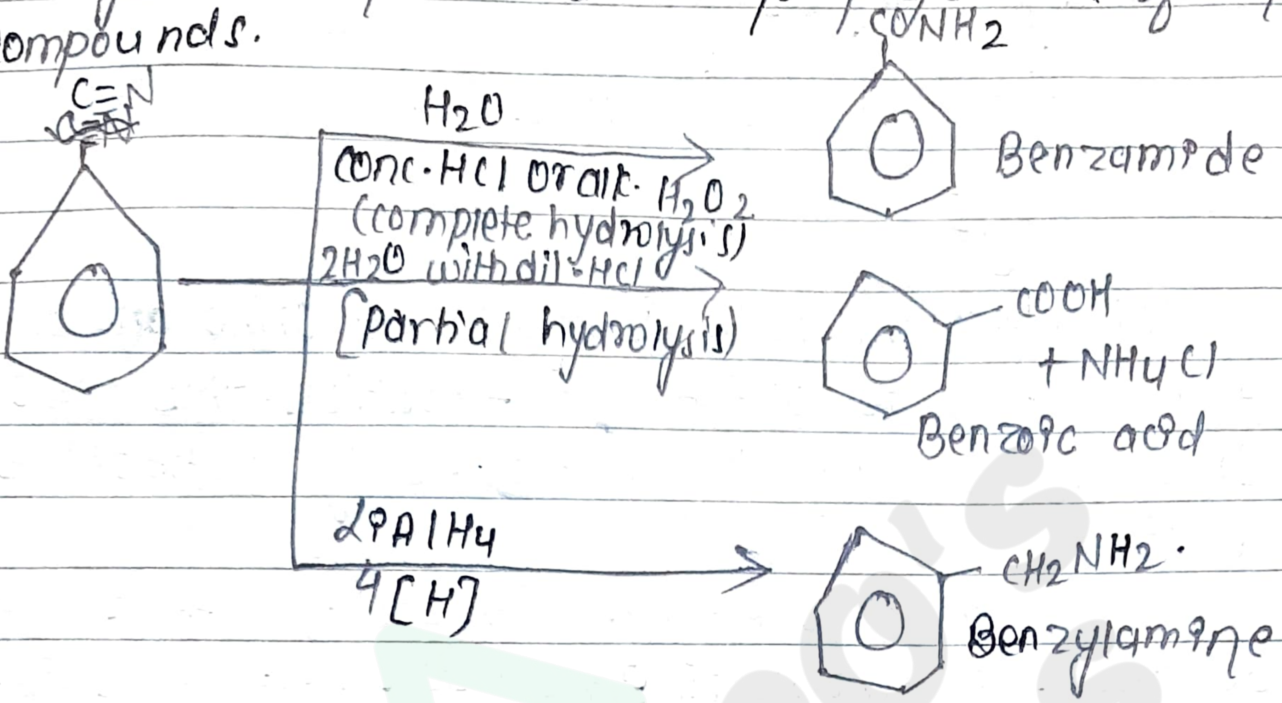


cyanobenzene

V. Imp.

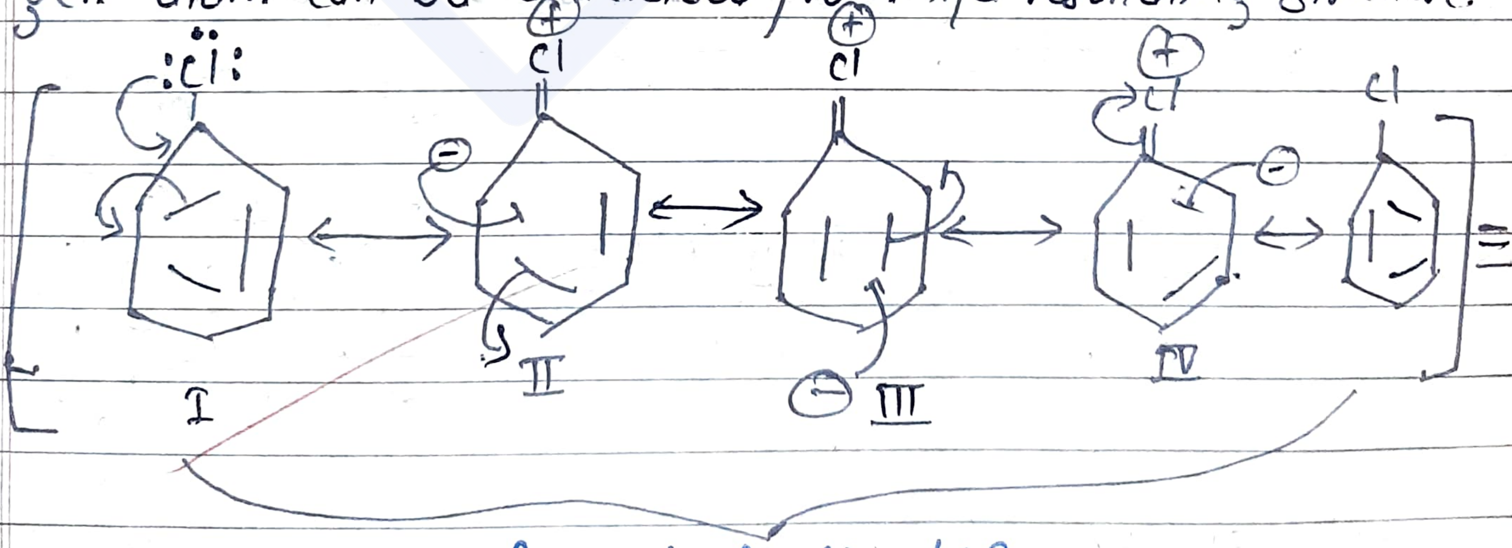
Note:

→ the cyanobenzene can be used for preparation of other useful compounds.

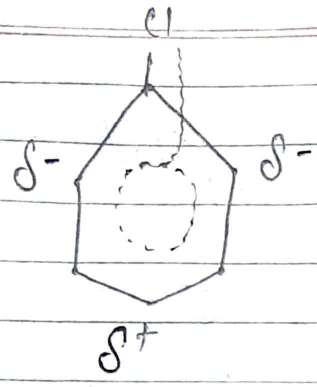


[2] Electrophilic substitution reaction → Haloarenes undergo electrophilic substitution reaction at the benzene ring. The halogen atom of haloarenes is ortho and para-director towards electrophilic substitution reaction.

The ortho and para directing nature of halogen atom can be understood from the resonating structure.



Resonating structure.

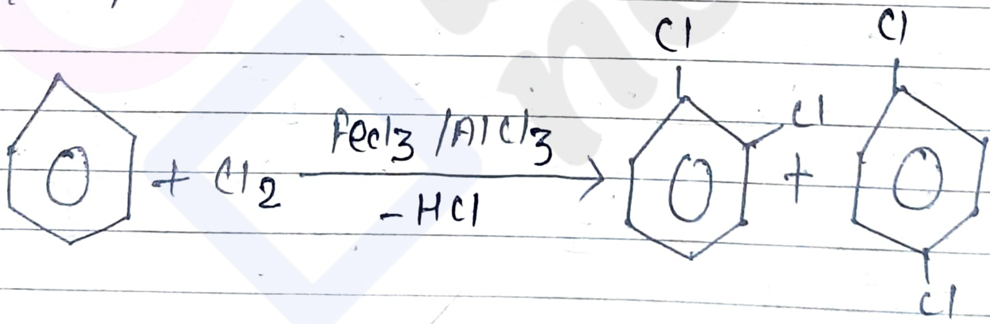


Resonance hybrid.

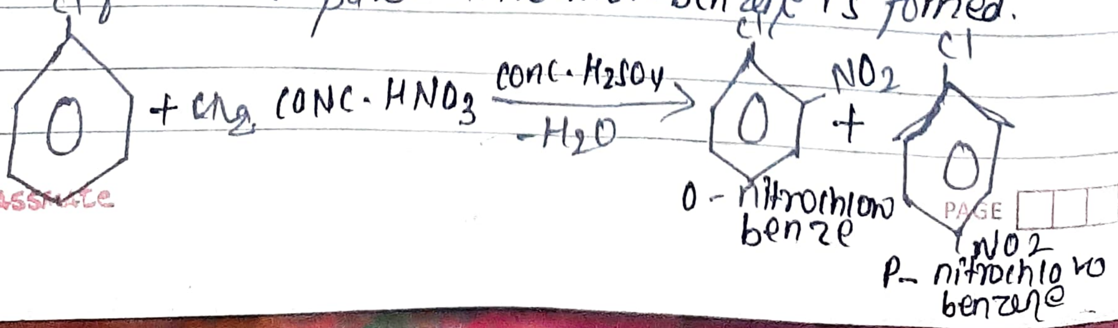
→ The electron density is higher at ortho and para pos tion compare to that of meta - position. thus these positi on are more likely to be attacked by electrophile pro ducts.

Further the electron withdrawing effects of haloge deactivates the benzene ring towards electrophilic substituti on reaction. Hence the electrophilic substitution reaction occurs slowly and under drastic conditions as compared to benzene.

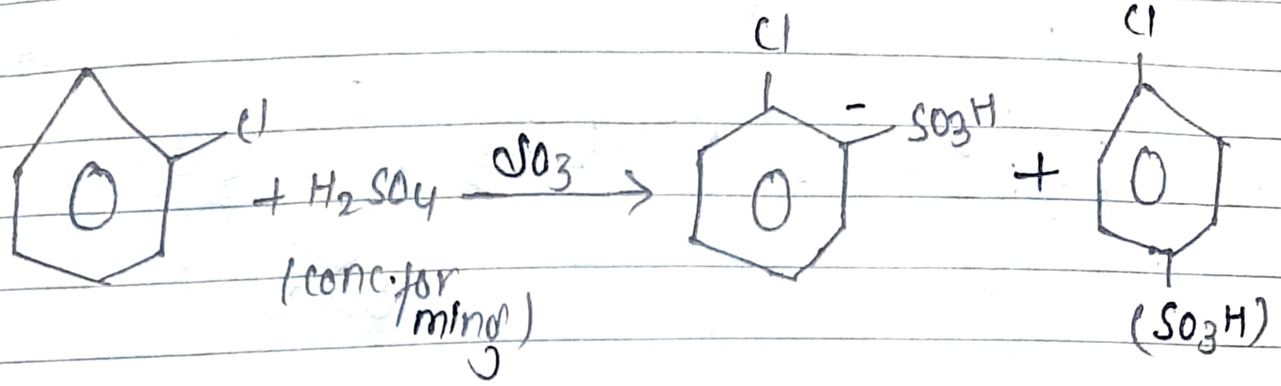
(a) Halogenation :→ when chlorobenzene reacts with chlorine in the presence of ferric halide or aluminium halide as catalyst mixture of ortho and para dichlorobenzene is formed.



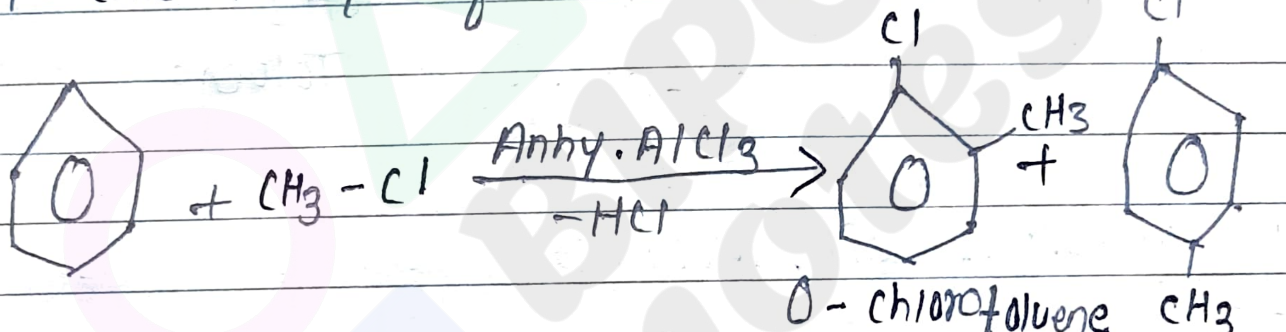
b) Nitration ⟶ when chlorobenzene reacts with chlorine in the presence of conc. HNO_3 and conc. ~~HNO~~ H_2SO_4 mixture of ortho & para- nitrochlorobenzene is formed.



(C) **Sulphonation →** when chlorobenzene reacts with conc. and fuming H_2SO_4, mixture of O & P - chlorobenzene sulphonic acid is formed.



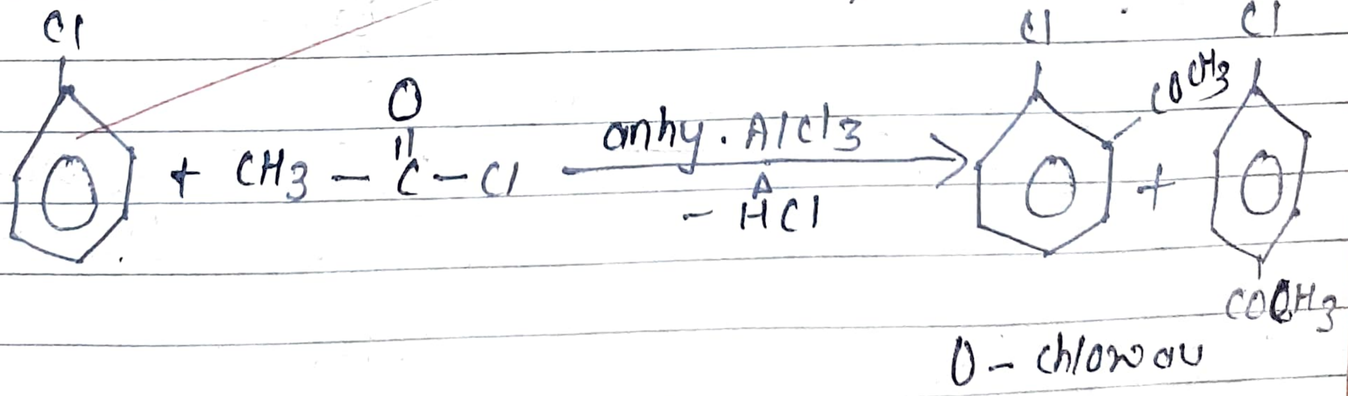
(D) **Friedal craft alkylation →** when chloro benzene reacts with alkylhalide in the presence of anhydrous $AlCl_3$ mixture of O & P - chlorotoluene is formed.



O - chlorotoluene

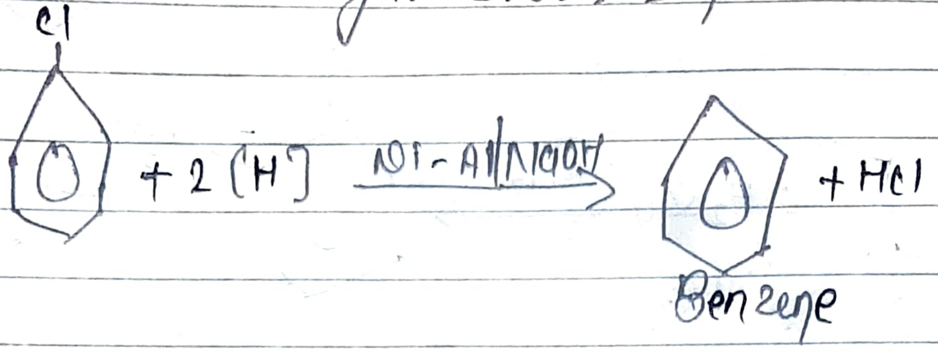
P - chloro toluene

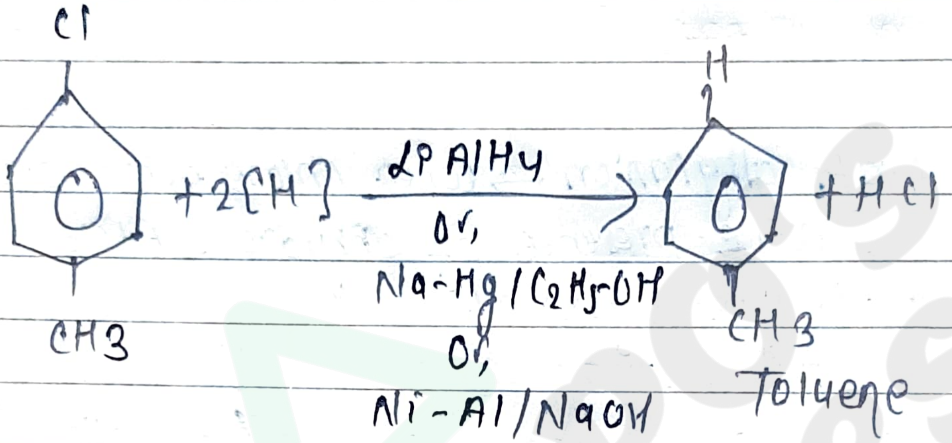
(E) **Friedal craft acylation →** when chlorobenzene reacts with acid - chloride in the presence of anhy. $AlCl_3$ mixture of ortho & para - chloro acetophenon is formed.



O - chloro ac

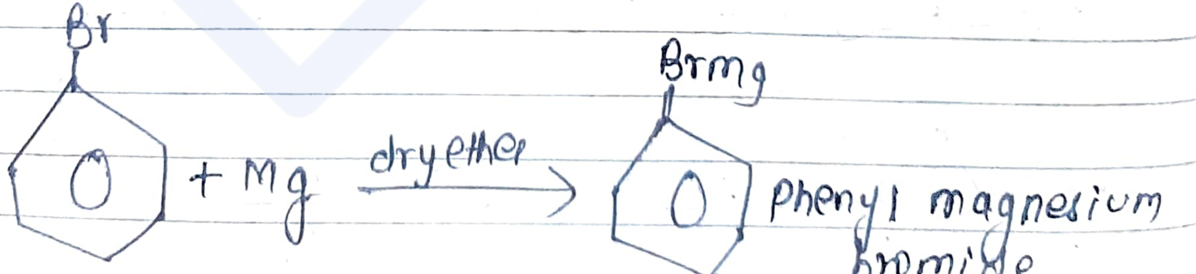
(3) **Reduction reaction** → when chloro benzene are reduced by Nickel - aluminium alloy in the presence of alkali parent aromatic hydro carbon is formed.

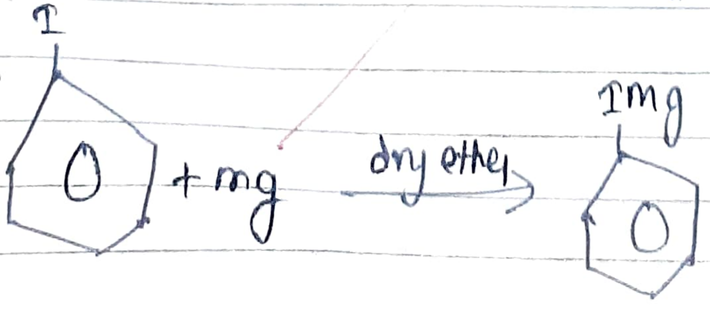




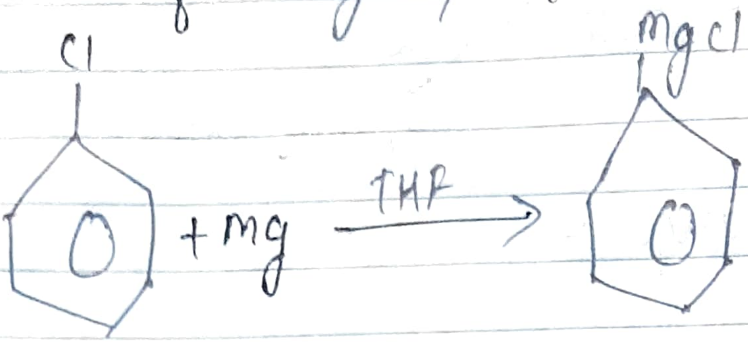
(4) **Reactions with Metals** →

~~Imp~~
(a) **Reaction with Magnesium** → when bromo benzene and iodo benzenes reacts with magnesium in presence of dry ether aryl magnesium hallide is formed.

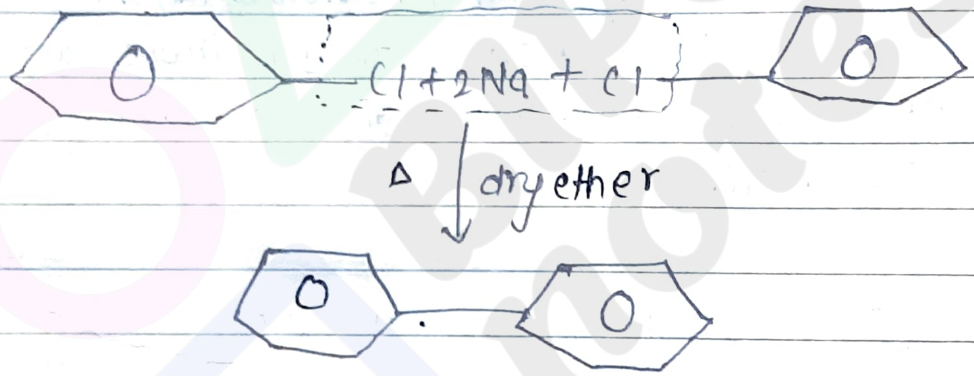




→ chlorobenzene forms grignards reagent with magnesium in the presence of tetrahydro furone (THF)

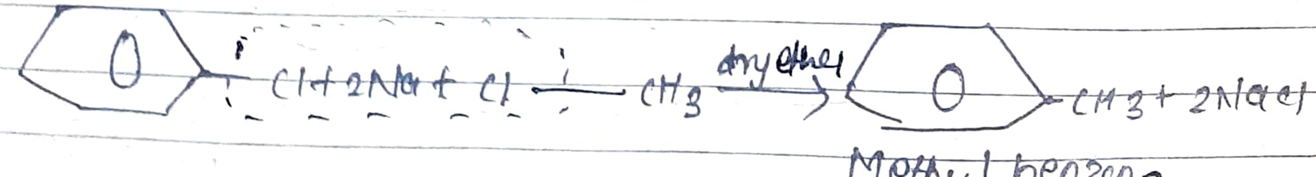


(b) Reaction with sodium (Wurtz reaction or fitting rxn) → when haloarene is heated with Na-metal in the presence of dry ether, the halogen atom of haloarenes is replaced by aryl group.

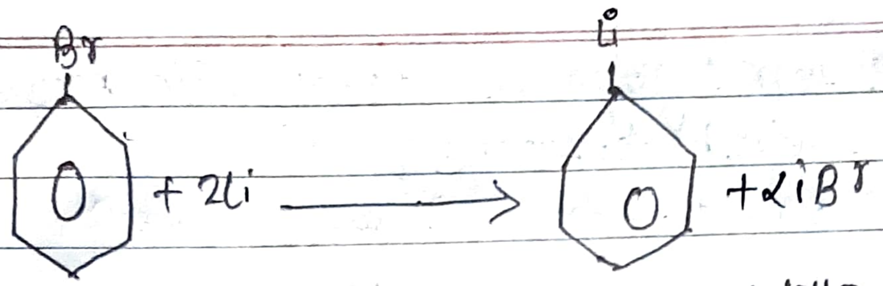


di-phenyl / phenyl benzeene.

(c) Wurtz fitting reaction → when haloarene is heated with haloalkanes and sodium in presence of dry ether the halogen atom of haloarene is replaced by alkyl group.



Methyl benzene
(Toulene)



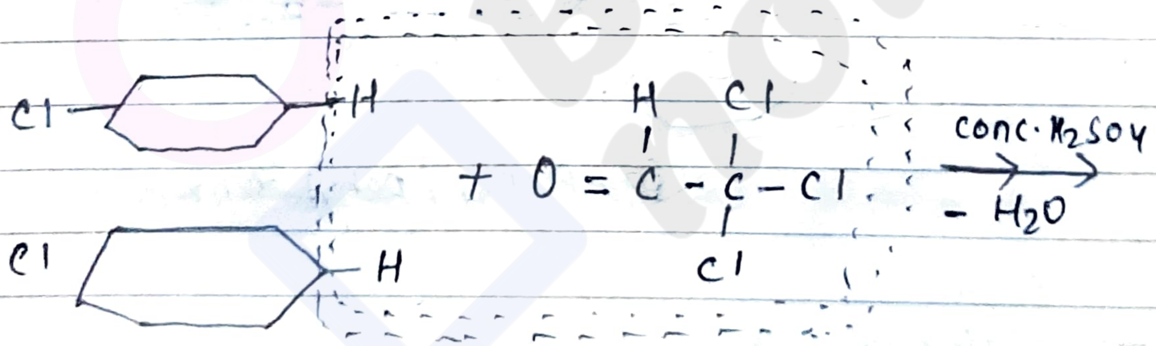
Phenyl lithium.

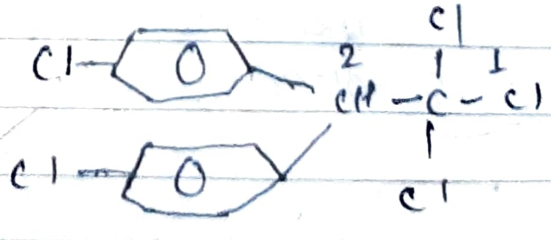
* Uses of haloarenes:-

Haloarenes are used in the prepartion of other aromatic compounds like phenol, aniline, ~~DDT~~ DDT etc.

Some commercially important halo compounds.

1. DDT:- (Dichloro-diphenyl trichloroethane) → when chlorobenzene is treated with chloral in presence of Conc. H_2SO_4, dichlorodiphenyl trichloro ethane is formed.





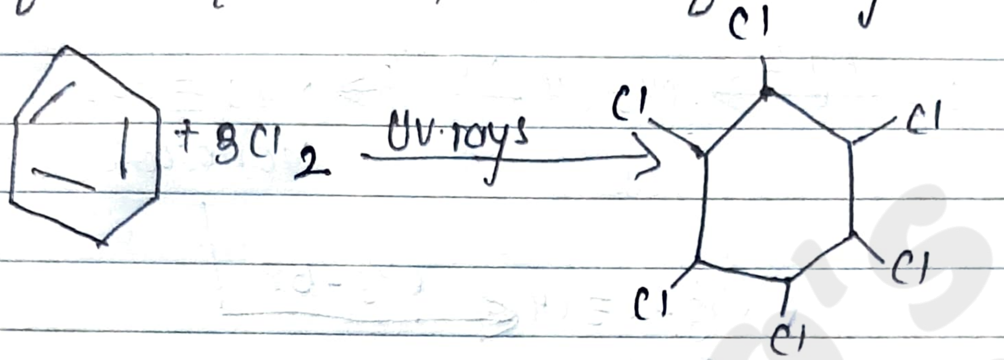
2,2 - bi(p - chlorodiphenyl trichloro methane (~~DDT~~ DDT)

→ It is used as insecticides mainly to kill mosquito.

→ It is non biodegradable.

→ It's residue accumulate in the environment a long time and are toxic to human beings.

2. BHC (Benzene hexachloride) → It is obtained by the chlorination of benzene in the presence of UV rays.



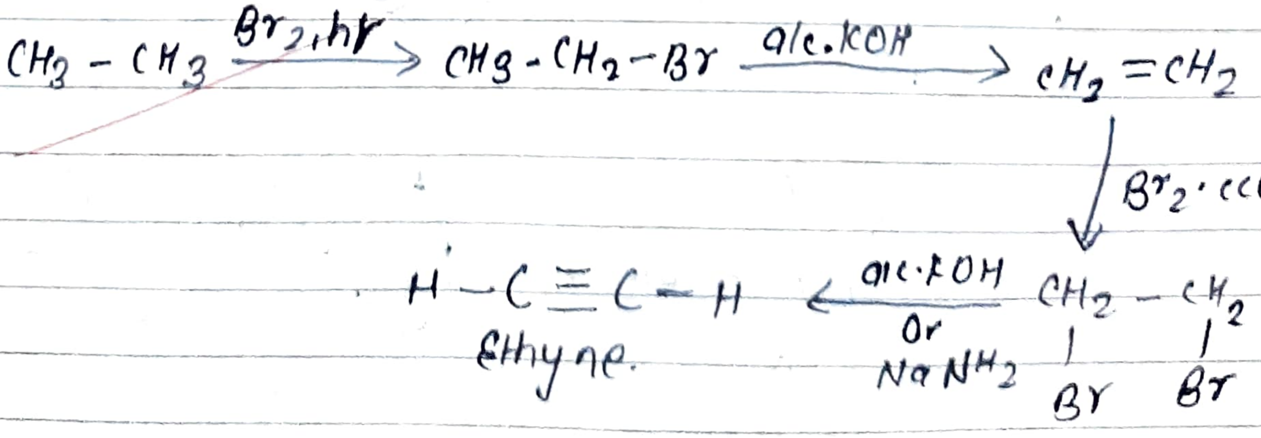
$C_6H_6Cl_6$, Lindane, 666

1,2,3,4,5,6 - hexachloro cyclohexane.

→ It is used as pesticides in the agriculture to kill termite, white ants, leaf flowers.

Q. Convert the following.

1. Ethane to ethyne →



$$CH_3-CH_3 \xrightarrow{Br_2, h\nu} CH_3-CH_2-Br \xrightarrow{alc.KOH} CH_2=CH_2$$

$$\downarrow Br_2 \cdot CCl_4$$

$$\underset{\text{Ethyne}}{H-C\equiv C-H} \xleftarrow[\text{Or } NaNH_2]{alc.KOH} \underset{Br}{CH_2}-\underset{Br}{CH_2}$$

2. Ethane to propanoic acid →

$CH_3-CH_3 \xrightarrow{Cl_2, h\nu} CH_3-CH_2-Cl \xrightarrow{alc. KCN} CH_3-CH_2-CN \xrightarrow{H_2O/H^{\oplus}} CH_3-CH_2-COOH$

3. Tri-iodomethane to propyne →

$CHI_3 \xrightarrow{Ag, \Delta} CH\equiv CH \xrightarrow{NaNH_2} NaC\equiv C-H$

Monosodium acetylide

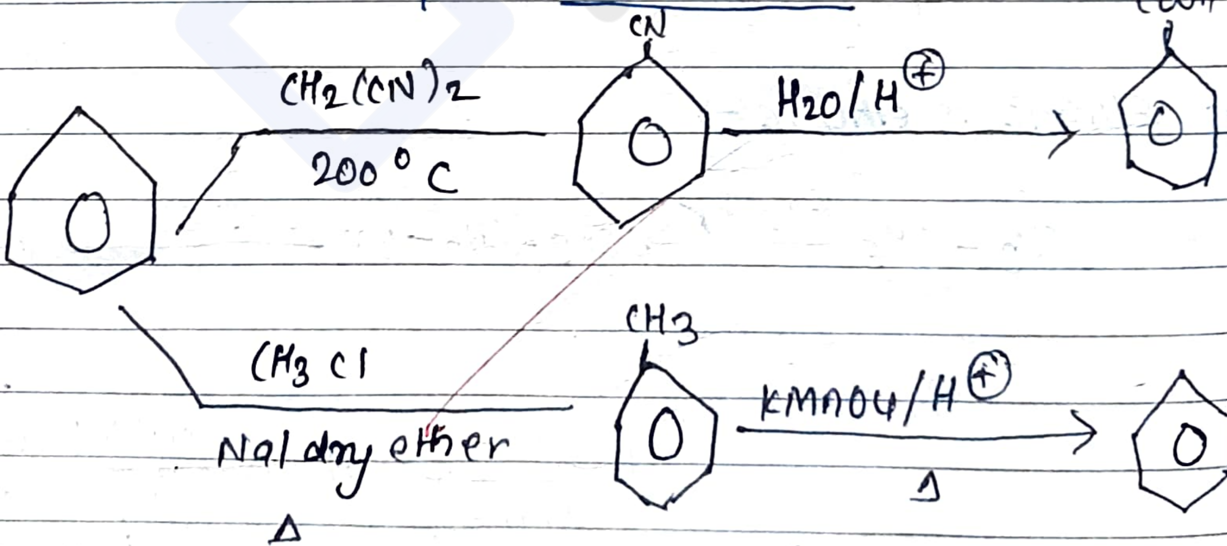
$\xrightarrow{CH_3-Br} CH_3-C\equiv CH$

Propyne

4. convert bromoethane to amine ethane →

$CH_2-Br \xrightarrow{KCN} CH_3-CN \xrightarrow{Na/C_2H_5OH} CH_3-CH_2-NH_2$

5. Convert chlorobenzene to benzoic acid →



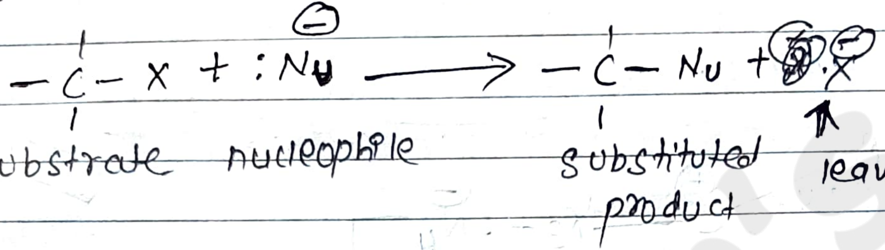
Benzoic Acid.

Back → Rear

Carbocation are planar in nature.

* Nucleophilic substitution reaction in haloalkane

A nucleophilic substitution reaction is a chemical reaction which involves the displacement of leaving group by a nucleophilic. In this process the leaving group i.e halogen atom departs with bonding pair of electrons and the electrons for the formation of new bond is furnished by a nucleophile.



$$-\overset{|}{\underset{|}{C}}-X + :Nu^{\ominus} \longrightarrow -\overset{|}{\underset{|}{C}}-Nu + X^{\ominus}$$

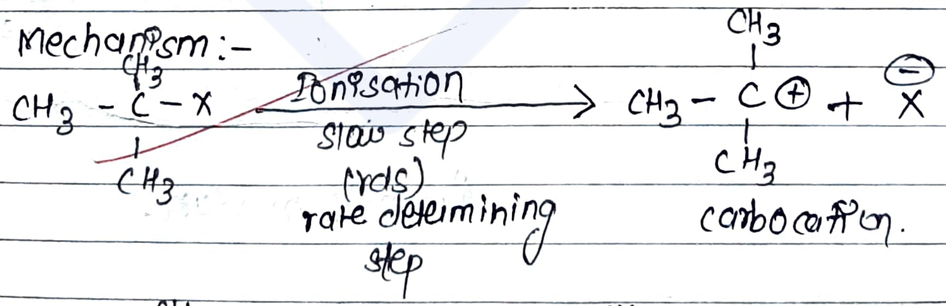
Ⓐ SN1 or substitution nucleophilic unimolecular →.

- SN1 reaction depends on concentration of alkyl halide (substrate) and is independent up on concⁿ of nucleophilic i.e

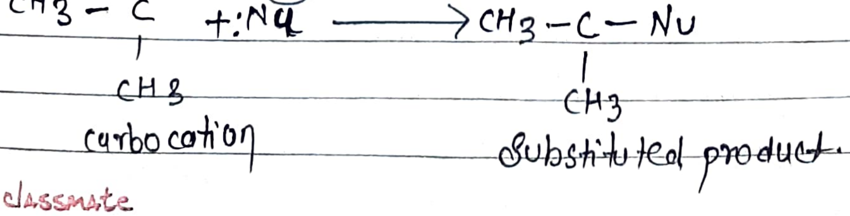
$$\text{Rate} \propto \underset{\text{haloalkane}}{[R-X]}$$

- The reaction occurs in two steps. In the first step carbocation is formed. In second step nucleophile attacks the carbocation to give substituted product.

Mechanism:-

I. 

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-X \xrightarrow[\text{slow step (rds) rate determining step}]{\text{Ionisation}} CH_3-\overset{CH_3}{\underset{CH_3}{C}}^{\oplus} + X^{\ominus}$$

II. 

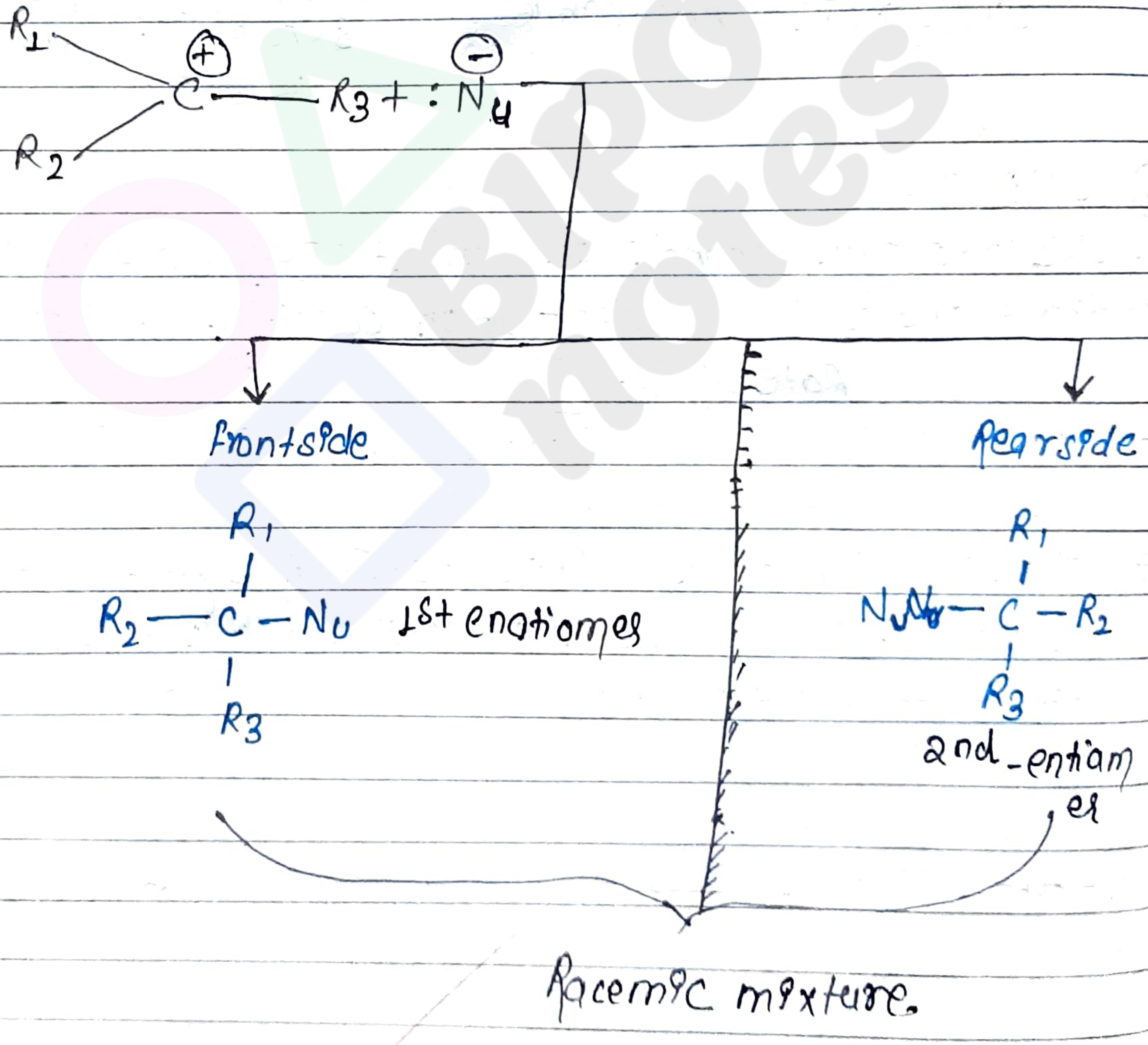
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}} + :Nu^{\ominus} \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Nu$$

- Racemic mixture is obtained in SN1 reaction due to attack at front and rear side.
- All tertiary alkyl halide undergoes SN1 mechanism.
- The rate of reaction is directly proportional to the stability of carbocation.

Hence, the order of reactivity is:-

$\boxed{3^\circ > 2^\circ > 1^\circ \text{ haloalkanes.}}$

Mechanism:-

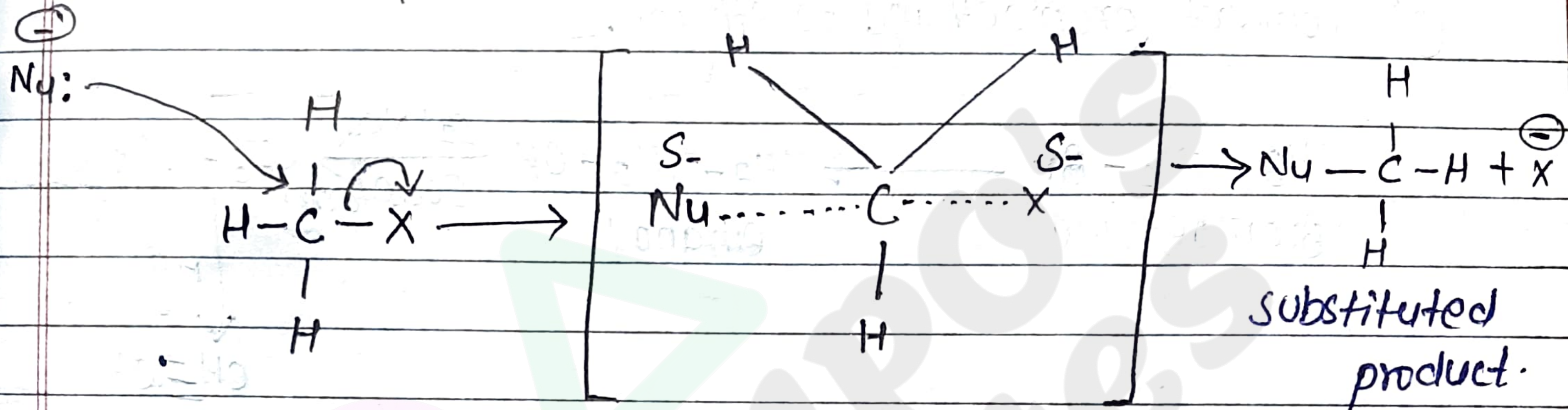


② SN2 reaction or substitution nucleophilic bimolecular:-

- the rate of SN_2 reaction depends on concentration of both substrate (alkyl halide) and nucleophile i.e

$$Rate \propto [R-X][:\overset{\ominus}{Nu}]$$

- The reaction occurs in single step. SN_2 reaction occurs through transition step. as shown below:-



Transition state
(Pentavalent)

- the rate of reaction is inversely proportional to the bulkier group attached to the carbon atom.

Hence, the order of reactivity follows the order;

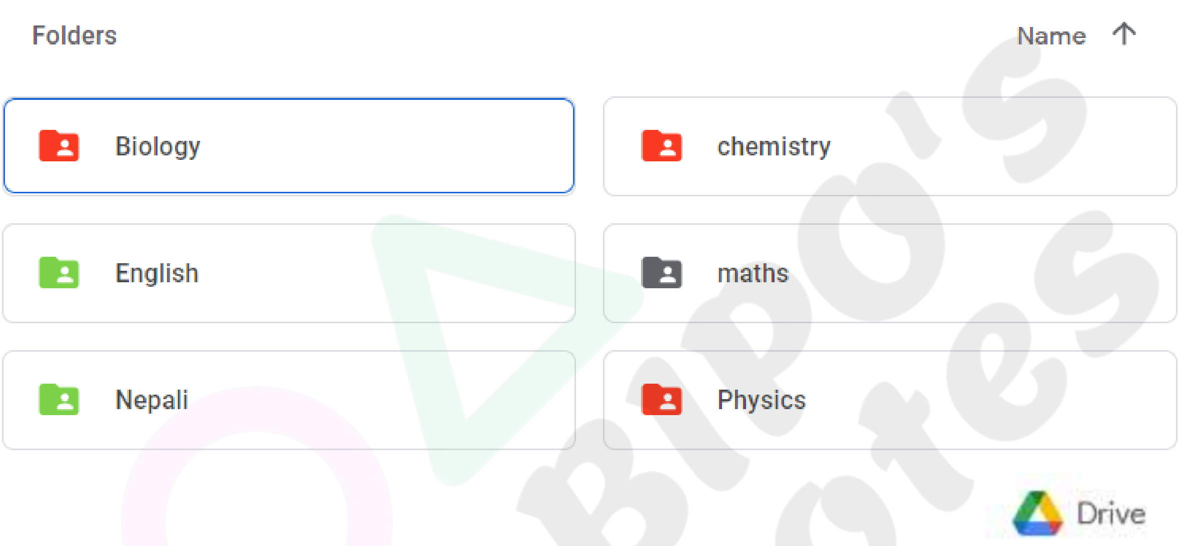
$1^\circ > 2^\circ > 3^\circ$ haloalkanes.

- The SN_2 reaction are always accompanied by inversion of configuration. This inversion of configuration is commonly known as '<u>walden inversion</u>'.

Bipin Khatri

(Bipo)

Class 12 complete notes and paper collection.



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