_/_/__

PREPARATION OF HALO ALKANES

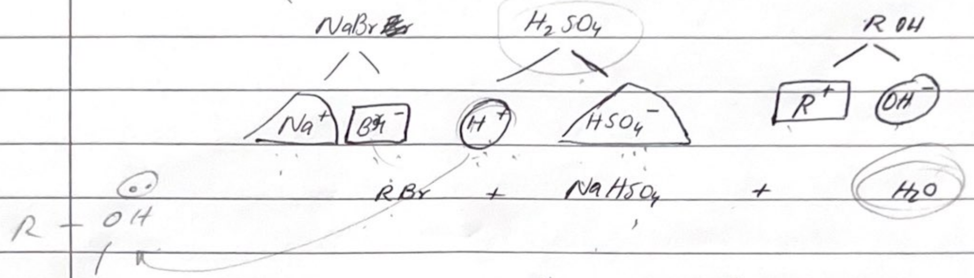
A] FROM ALCHOLS

① $R{-}\ddot{O}H \xrightarrow{HCl + \boxed{ZnCl_2}} R{-}Cl + H_2O$ Lewis acid

ZnCl2 Also called as LUCAS REAGENT

- $ZnCl_2$ ~~at~~ acts as lewis acid
- Lewis acid is ~~at~~ $e^{\ominus}$ deficient so can remove the lone pair $e^{\ominus}$s of OH making removal of OH from R easier
- Removed OH and seperated H^+ from HCl gives H_2O

② ~~Ba~~ $ROH \xrightarrow{NaBr + H_2SO_4} R{-}Br + NaHSO_4 + H_2O$

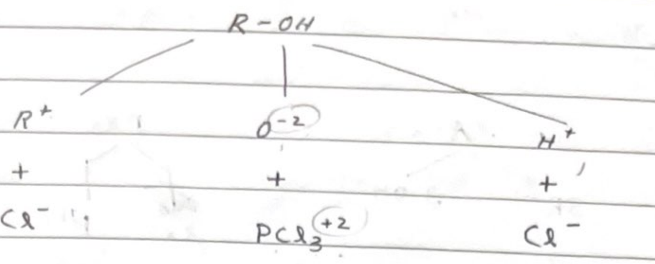


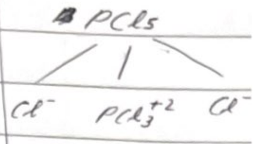
OH

- H_2SO_4 gives H^+ ions to ROH so ~~it gets becomed~~ ~~RH2O~~ ~~R=OH2~~ $R{-}\ddot{O}{-}H$ becomes $R{-}\overset{\oplus}{\ddot{O}}{-}H$ with H below (RH_2O). ~~OH~~
- OH is bad leaving group.
- But H_2O is good leaving group.
- So this way OH is removed then
- $Br^{\ominus}$ being neucleophile joins with $R^{\oplus}$.

③ $R{-}OH \xrightarrow{PCl_5} R{-}Cl + POCl_3 + HCl.$

- In ~~PCl5~~ PX_5 or PX_3, $X = (Br, I$ ~~F~~$)$ Dont exist ~~bea~~ because they are highly reactive and unstable. ~~so~~ So ~~the~~ once they are formed they mostly decompose ~~immediately~~ immediately So those cant be used





$\longrightarrow RCl + POCl_3 + HCl$

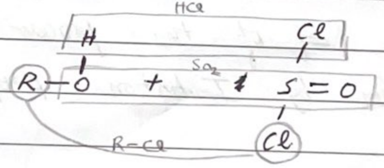
~~④ R – OH →~~

④ $R-OH \xrightarrow{\text{Red } P / X_2} R-X$

Real rxn: $3\ R-OH + \frac{3}{2} X_2 \xrightarrow{\text{Red P}} 3RX + H_3PO_3$

During rxn if red P is added with X_2, P easily removes OH and X gets ~~ther~~ inserted.

⑤ $R-OH \xrightarrow{SOCl_2} R-Cl + SO_2 + HCl$



- While comparing to PCl_5 experiment (③), this is prefered since ~~ther~~ the purity level of R-Cl is more since both HCl and SO_2 liberates from the reaction as gases leaving only R-Cl.

- $SOCl_2$ → Thionyl Chloride.

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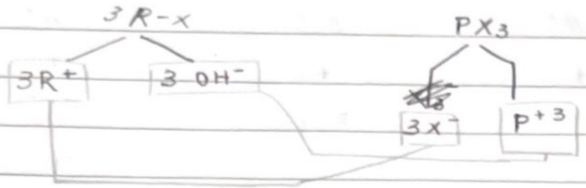
⑥ $3R-OH \xrightarrow{PX_3} 3R-X + H_3PO_3$ $[X = Cl, Br]$



B] FROM ALKANES

$$CH_4 \xrightarrow{Cl_2/h\nu} CH_3Cl \xrightarrow{Cl_2/h\nu} CH_2Cl_2$$

$$CH_2Cl_2 \xrightarrow{Cl_2/h\nu} CHCl_3 \xrightarrow{Cl_2/h\nu} CCl_4$$

$h\nu$ → sunlight

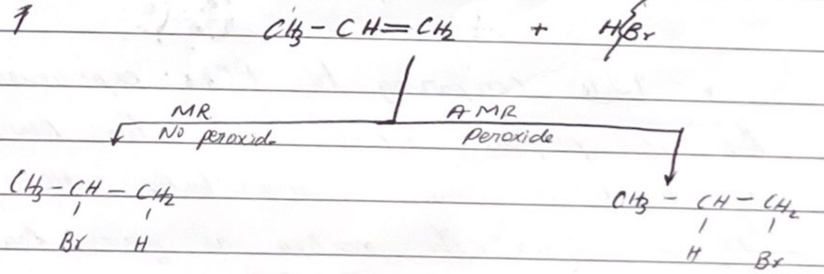
h → Planks constant $(6.626 \times 10^{-34}\ J)$

ν → Frequency of light wave

- Cl_2 undergoes homolytic cleavage forming free radical
- The stages ~~of~~ of this process from one stage to another by Initiation, propagation, termination

C] FROM ALKENES

1 $CH_3-CH=CH_2 + HBr$



$CH_3-CH(Br)-CH_2(H)$; $CH_3-CH(H)-CH_2(Br)$

- ~~since 2° $C^{\oplus}$~~ In absence of peroxide carbocations forms
- When pi bond breaks, the positive charce ~~q~~ can either go to 2° C or 1° C since 2° $C^{\oplus}$ > 1° $C^{\oplus}$ in stability, the ~~br~~ ~~halogen gets connected~~ 2° carbon get +ve charge

_/_/_

- And connects with $Br^{\ominus}$ then the 1° carbon gets -ve charge and connects with $H^{\oplus}$ (Markonikof's rule)
- Peroxide leads to formation of free radical. so the opposite happens (Anti Markonikof's rule)

PHYSICAL PROPERTIES:

~~Melt~~

i] Boiling point:

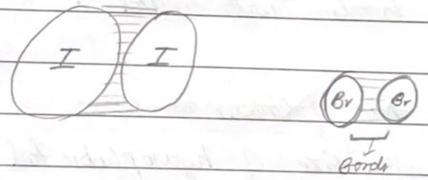
$RI > RBr > RCl > RF$

F
Cl
Br
I

$\downarrow$ size increases

ex: take Iodine and Bromine

due to size they will have surface area



size ∝ surface area that can contact ∝ no of bonds ∝ stability ∝ boiling point

ii] Density

Density of compound increases when mass of compound increases.

ρ (density) = m/v

$\rho \propto m$

SOLUBILITY : [UNIVERSAL RULE "Like Disolve In Like"]

- Despite partial ionic bond characte beween $\boxed{\overset{\delta+}{C}-\overset{\delta-}{X}}$ Haloalkanes are insoluble in water since they cannot form hydrogen bonding with water ~~from~~ (inorganic solvent)
- Even though if 1 H_2O Molecule breaks from the water and joins with halo alkanes it forms weak bond which is not preffered by any molecule ~~in this~~ as all the molecules want stability.
- There ~~are~~ is no enough energy required to break the already existing hydrogen bonds in water and pre-existing London dispersion forces between C-X
- C-x dissolve easily in organic solvents like benzene, ether or chloroform (CCl_3) by universal rule
- C-x ~~being po~~ having polar bond, ~~inter~~ wants to interact with H_2O but due to the hydrophobic tail of Alkyl ~~gro~~ group opposes formation of Hydrogen bonds with water.

~~No of Carbons in R~~

$$\boxed{\text{No of carbons in } -R} \propto \boxed{\text{size of hydrophobic tail}} \propto \boxed{\frac{1}{\text{solubility}}}$$

- In comparing ortho meta and para, para has highest mp due to its symmetry.

NOTE:

Comparing para and ~~meta~~ ortho for Halo arene, para has more e^- density ~~because who in~~ even though ortho will have same density as para, some of the electron density will be disturbed by halo atom [concider resonance diagram]

$\therefore$ ~~portho~~ para > ortho > meta

_/_/_

SUBSTITUTION RXN
→ ~~SN~~ S_N1 → Neucleophilic substitution (monomolecular)
→ ~~SN~~ S_N2 → " " (bimolecular)

S_N2 :

- Bond forming with neucliophile and bond breaking with leaving group does happen simontanously.
- ~~Com~~ Things involved :

LG
LEAVING GROUP
−X

Nu
NEUCLEOPHILE
Aq. −OH (usually)

~~C^+~~
~~CARBOCATION~~
~~forms after breaking bond with leaving group~~

- PROCESS: ~~leaving group LG~~

→ Neucleophile comes and interacts with Haloalkane (a compound with LG)

↓

→ An ~~Intermediate~~ TRANSISION state takes place where both LG and Nu is connected with the compound.

↓

→ ~~SN~~ More the Nu start to bond with compound, more the LG leaves the compound by breaking its bond with the compound

- Points To NOTE :

→ No Intermediate is formed.

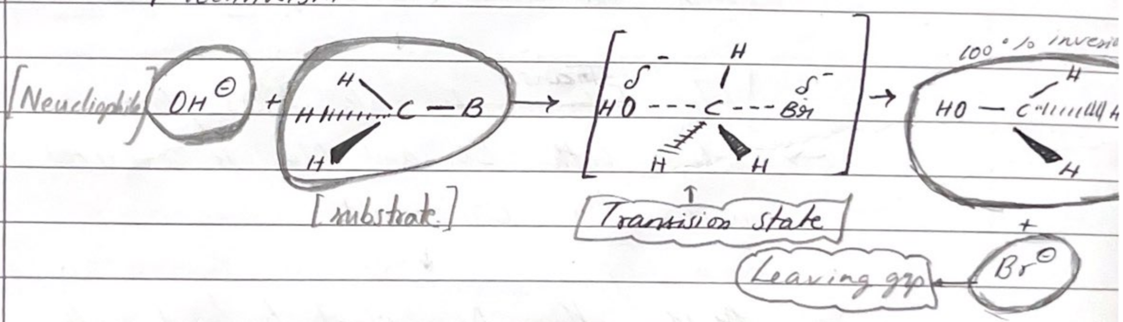
- ~~Both neucleophile con and leaving g~~
- Neucleophilic group being -vely charged and leaving group containing lone pair, causes the ~~opposition~~ repulsion ~~be~~ during interaction.
- So the Necliophilic group ~~attacks~~ attack exactly from the backside of the leaving group (180° away from LG).
- Rate $\propto$ ~~k~~ [Substrate]
  $\propto$ [Nucleophile]

$$\text{Rate} \propto [\text{Sub}][\text{Nu}]$$
$$\text{Rate} = k[\text{Sub}][\text{Nu}]$$

$k \longrightarrow$ rate constant

- Substrate is a specific ~~molecule~~ compound or substance on which the reaction acts ~~to~~ upon.
- Here Neucleophile is reagent. Reagent ~~is the~~ attacks the substance.

- MECHANISM



- <u>WALDEN</u> ~~EFFECT~~ <u>INVERSION</u>:
  → When Neucleophile attacks exactly from opposite side of the LG. ~~When~~ During transision state the ~~two~~ 3 hydrogens ~~obtain a linear~~ is pushed to a flat, planar position. To minimise ~~the~~ repulsion, after neucleophile joins, the three groups

snaps ~~over~~ over to the other side that causes 100% Inversion.
like a

→ Since the process looks like an umbrella turned inside out, It's also called umbrella effect.

- CONDITIONS:

→ Strong neucleophile to be used:

KOH, NAOH, CN^-, I^-

→ Good leaving group

$I^- > Br^- > Cl^- > F^-$

→ Less steric ~~hid~~ hinderance

$CH_3 > 1° > 2° > 3°$

→ Polar Aprotic Solvent (Non Polar)(Organic solvent)

Acetone, DMSO

S_N1 :

- Process → First the leaving group leaves itself resulting in the formation of ~~ca~~ an intermediate called carbocation

Nu	LG	$\overset{\mid}{C}^{\oplus}$
Neucleophile	leaving group	Carbo cation
preferably OH^-	$-X$	The Intermediate

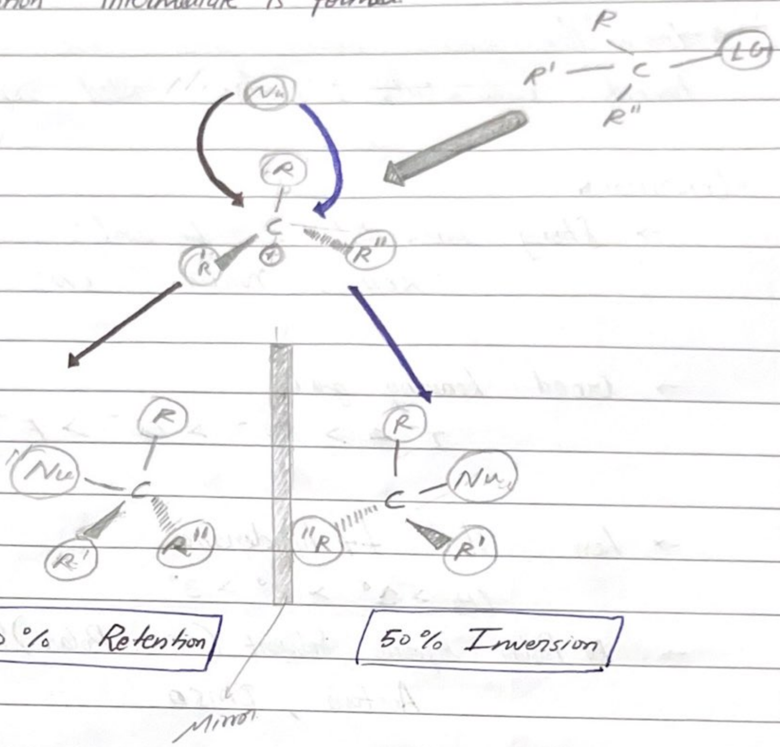
→ This process is $\boxed{\text{slow process}}$ as breaking a bond by itself requires lot of energy. and $\boxed{\text{reversible.}}$

→ After this process ~~a~~ ~~reacti~~ if a neucleophile comes near the carbo cation, these both react immediately since opposite charges attract [$\overset{\mid}{C}^{\oplus}$ and $Nu^{\ominus}$] and it is a $\boxed{\text{fast process}}$

NOTE :

→ Carbocation intermediate is formed.

→



→ 50% Retention + 50% Inversion = 100% Raecemisation
(due to umbrella effect)

→ SN' reaction leads to the formation of raesemisation.

- CONDITIONS :

→ Weak Neucleophile can also be used.

→ ~~Go~~ Good Leaving group

$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$

→ Since stability is required for the carbocation in the moment absence of the leaving group,

$3^{\circ} > 2^{\circ} > 1^{\circ} > CH_3$

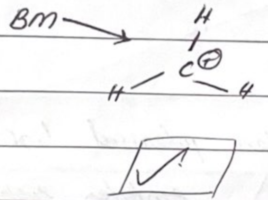
→ Polar Protic Solvent:

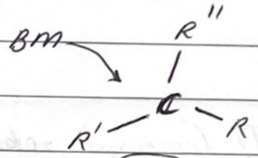
H_2O

Steric Hinderance

- The Process of slowing down a chemical reaction due to the bulky molecules surrounding the atom which is attaked.
- This occur when large and bulky substituents occupy space like for 3° Alkyl, the three alkyl groups connected with leaving group is just carrying so much hinderance

$\boxed{BM}$ → Bulk molecule.





☒ Due to steric ~~hinder~~ hinderance

FACTORS AFFECTING NEUCLEOPHILICITY:

- −vely charged neucleophile is better than its conjucate base
  ex: $OH^\ominus > H_2O$
  (conjucate acid → add 1 Hydrogen (proton))
- $CH_3^\ominus > NH_2^\ominus > OH^\ominus > F^\ominus$
- Solvation capacity:
  - In Protic Solvent
    $I^\ominus > Br^\ominus > Cl^\ominus > I$
  - In Aprotic Solvent
    $F^\ominus > Cl^\ominus > Br^\ominus > I$
- $\boxed{\text{Size of } e^\ominus \text{ cloud}}$ ∝ ~~plor~~ $\boxed{\text{polarizeable}}$ ∝ $\boxed{\text{effectivity of neucleophile}}$

NEUCLEOPHILICITY: Measure of how fast a neucleophile is abled to attack an electrophilic ~~ect~~ center.

Chloro Benzene
Chloro hexane } → Which is best in SN' RxN?

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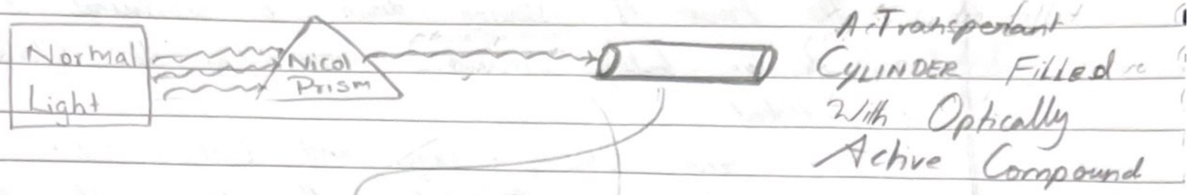
STEREOCHEMICAL ASPECTS OF SN rxn :

I OPTICAL ACTUVITY



- When passed throug Optically Active Compound, the light tilts
- Angle of tilting of polarised light is measured by polarimeter

If Compound rotates plane of plane polarised light

rotates left side or anticlockwise	rotates right side or clockwise
l-form (or) laevo-rotatory	d -form(or) dextrorotatory
Indicated by −ve sign	Indicated by +ve Sign

such (+) and (−) isomers are called Optical Isomers and this phenomenon is termed as Optical Isomerism.

II ASSYMETRY :

If the mirror image does not ~~upon~~ overlap completely on ~~each other~~ the original compound it is said to be ~~assymetric co~~ a compound with assymetric carbon (or) stereo center.

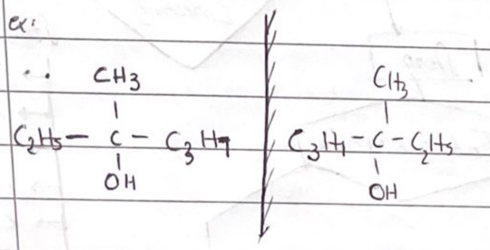
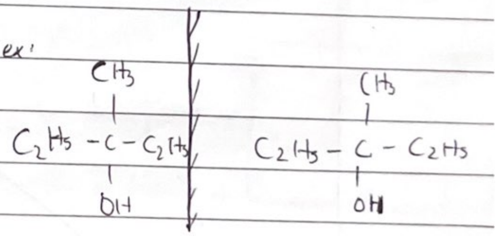
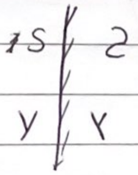
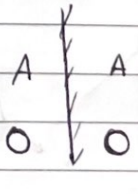
III ASSYMERIC MOLECULE

- Lacks ~~an~~ symmetric property.
- Assymetric property and non - superimposability (~~ops~~ overlap

is responsible for Optical activity in organic compounds

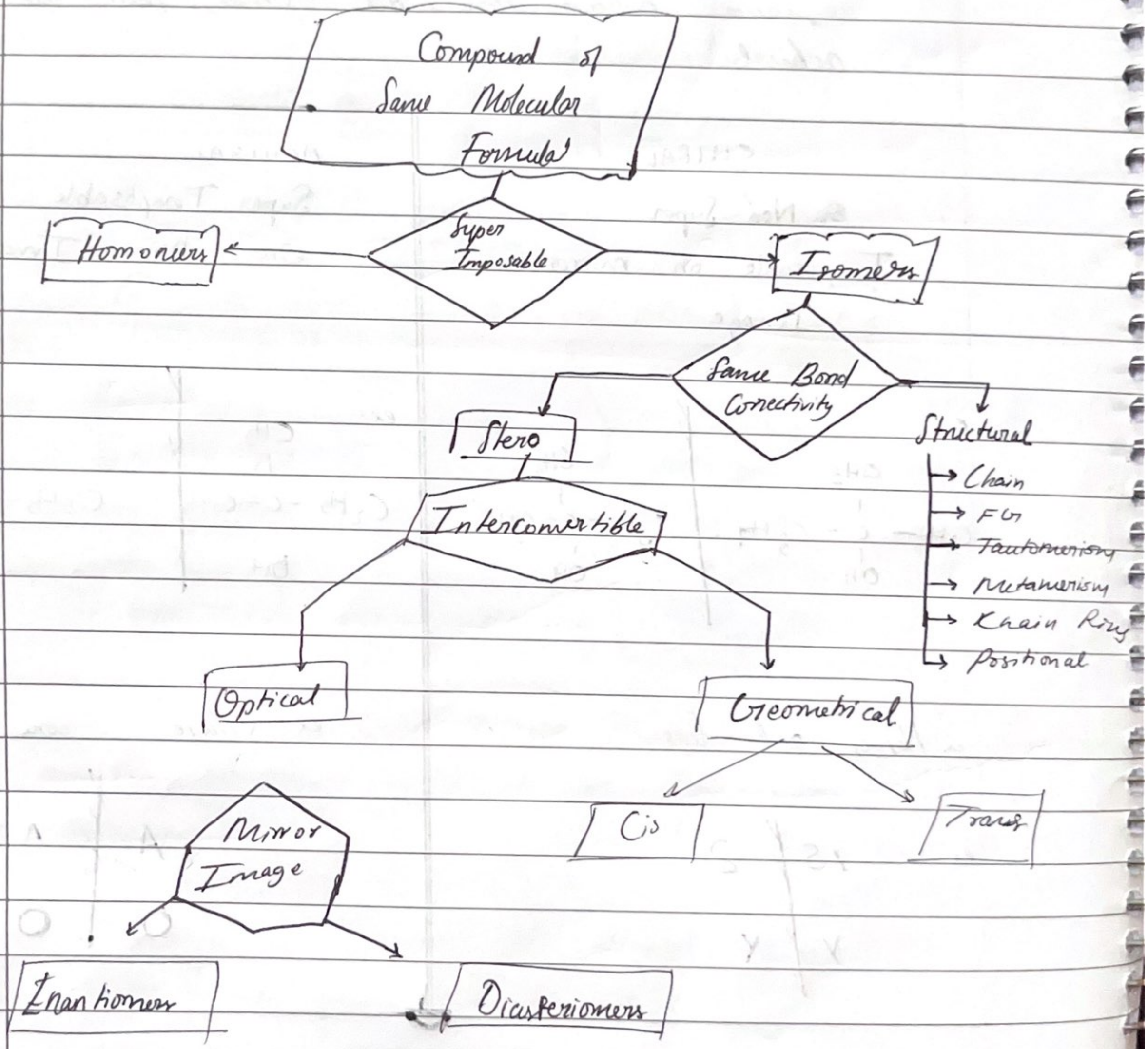
IV CHIRALITY :

- If a carbon atom is connected to 4 different groups, then it is said to be chiral carbon
- The compound containing chiral compound ~~is~~ is said to be ~~chiby~~ chiral compound.
- Optically Active.
- If atleast 2 groups connected to ~~a compound~~ same carbon atom, are same, then its called achiral.

CHIRAL	ACHIRAL
~~Su~~ Non Super Imposable on mirror Image	Super Imposable On Mirror Image.
ex: 	ex: 
ex: Hands and legs	ex: Phere, cone, cube
ex: 	

V ENANTIOMERS

- Non Super Imposable
- Mirror Images
- Another name: Optical Anti-Podes
- They ~~have~~ ~~same~~ physical and chemical properties do not vary they vary only by only Optical Rotations.
- Optically active (or) Chiral.

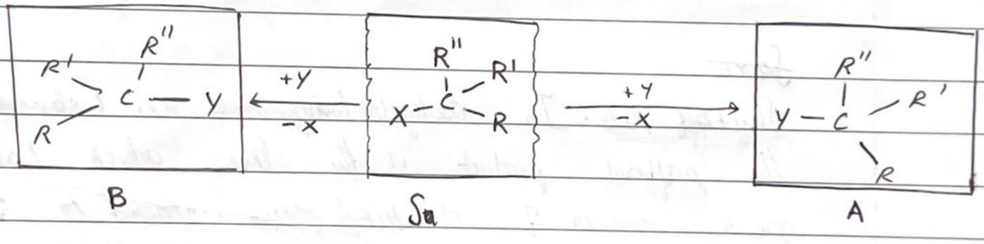


- If one enantiomer is dextro rotatory then the other will be leavorotatory
- For a mixture,

d-form enantiomer : l-form enantiomer
1 : 1
50% : 30%

Here, Half on right rotation and half on left rotation will cancel out each other's rotation ~~other~~ resulting in ~~ze~~ zero optical rotation. This is called as racemic mixture or raecemic modification.

- The process of converting enantiomer → raecemic mixture is called raecemisation.
- Raecemic ~~A~~ mixture is optically inactive since net rotation is zero



A → Renkention : It has same general configuration of groups around the stereo centre ~~before~~ as 's'

B → Inversion : It has the mirror image of general configuration of groups around the stereo centre of 's'.

Note that A is mirror image of B.

50% of A + 50% of B = Racemic mixture.

__/__/____

In SN^2 → Inversion

In SN^1 → Racemisation

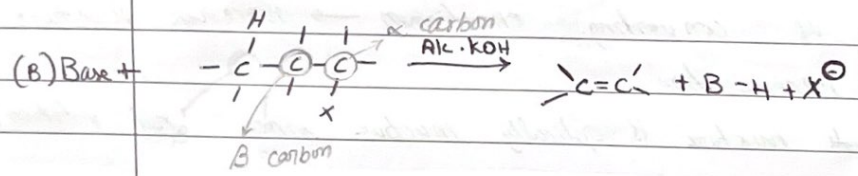
ELIMINATION REACTION :

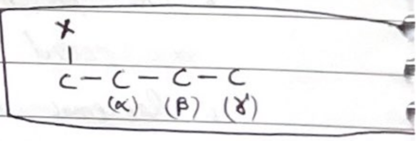
- Things Involved
  - BASE - B
  - LG - Leaving Group
  - -X, hallide

IMP NOTE

~~Aq Ag OH~~

- Aq OH leads it to behave as Neucleophile
- Alc OH leads it to behave as Base.





~~SaYE~~

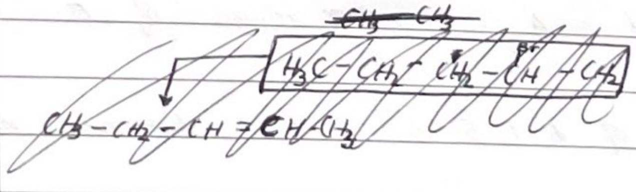
Saytzeff Rule: In dehydrohalogenation rxn (elemination rxn) The preffered product is the alkene which has the greater number of of Alkyl groups attached to the doubly bonded carbon ~~att~~ atom

Means

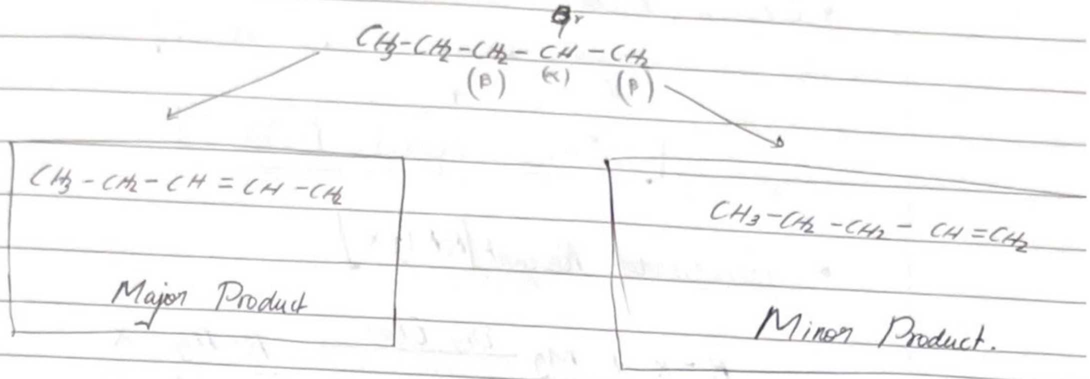
The side of higest number of carbon ~~at~~ connected to the β carbo ~~β-Carbon α-Carbon~~ is the side where the double bond will be formed.

- X from α-Carbon is removed and H from β-Carbon is removed.

ex:



Ex:



$CH_3-CH_2-\underset{(\beta)}{CH_2}-\overset{Br}{\underset{(\alpha)}{CH}}-\underset{(\beta)}{CH_3}$

$CH_3-CH_2-CH=CH-CH_3$

Major Product

$CH_3-CH_2-CH_2-CH=CH_2$

Minor Product.

ELIMINATION RXN VS SUBSTITUTION RXN

- A substrate ~~can eit~~ (Alkyl Halide) can either undergo substitution or Elimination.
- The choosing of type of reaction depend upon :
  - → Nature of H-X
  - → Strength of base/Nucleophile
  - → Size of base / Nucleophile
  - → Reaction conditions
- Bulkier Neucleophile prefers to act as base
- " " " " react with a proton rather than a tetravalent compound that ~~creates~~ ~~to~~ rises the issue of steric hinderance.

- 1° H-X prefers S_N2 rxn
- 2° H-X prefers S_N2 (or) Elimination rxn
- 3° H-X prefers S_N1 (or) Elimation rxn (depends on stability of $C^{\oplus}$)

_/_/__

REACTION WITH METALS

- Organo-Metalic compounds :

$$\boxed{\text{Organic } \cancel{\text{metal}} \text{ Cl, Br or I}}$$

$$+$$

$$\boxed{\text{Some Specific Metals}}$$

- Grignard Reagent [RMgX]

$$\underset{\delta^+}{R} - \underset{\delta^-}{X} + Mg \xrightarrow{\text{Dry Ether}} \underset{\delta^-}{R} - \underset{\delta^+}{Mg} - \underset{\delta^-}{X}$$

→ Highly reactive so we have to avoid even traces of water so only the reaction takes place in dry ether.

~~→ Method to convert Halides to Alkyl halides~~

→ Method to convert A-Halides to Hydrocarbons ;

~~RG~~ $RMgX + H_2O \longrightarrow RH + \underset{+2}{Mg}(\underset{-1}{OH})\underset{-1}{X}$

- Wurtz Reaction

$$R - \boxed{X + 2Na + X} - R'$$

$$\Big\downarrow {\scriptstyle \text{Dry ether}}$$

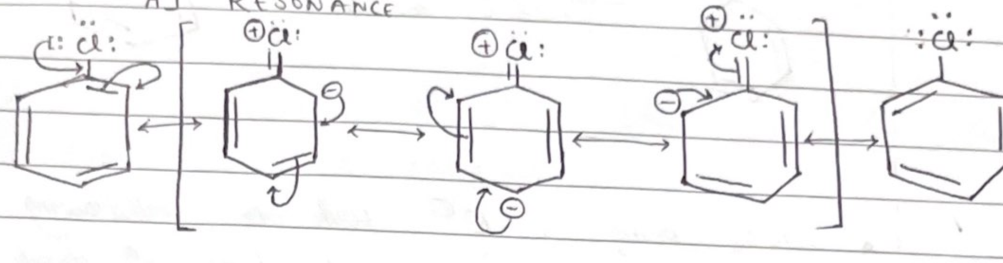
$$2NaX + R - R'$$

~~Reactions 0~~

REACTIONS OF HALO ARENES:

Very Less reactive to SN reactions due to :

A] RESONANCE



Since C-Cl bond aquires partial double bond character due to resonance, bond cleavage in halo arene is dificult than in ~~cyclo~~ halo alkane.

B] In halo arenes the Ẋ atom is connected to sp^2 hybridized carbon and has greater s% character.

S-character ∝ strength of holding atoms

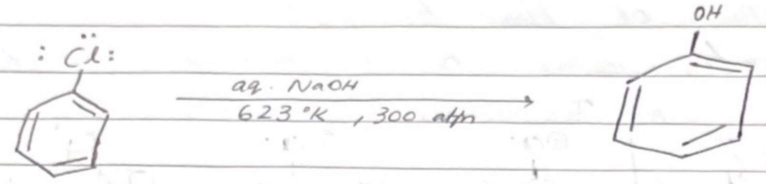
Cl-C bond is more tightly holded due to high s% character.

Compared to sp^3 Hz, sp^2 Hz has high bond strength ~~than~~. Since It requires more energy to breake stronger bond Halo Arenes are less reactive.

C] The phenyl cation formed due to self ionisation is inable to exhibit resonance ~~and~~ ∴ ~~SN~~ S_N1 rxn is ruled out.

D] Halo arene is ~~elec~~ $e^{\ominus}$ rich and when a -vely charged neucleophile approaches it there would be a repulsion which reduces reactivity

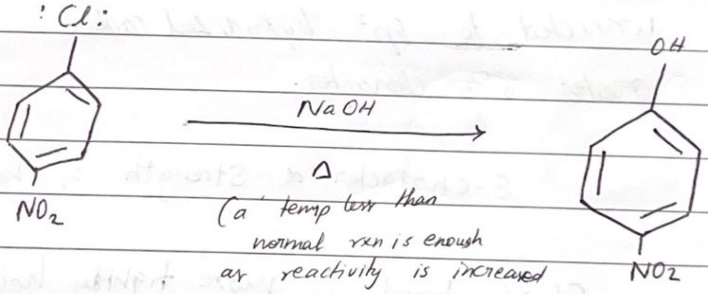
REPLACEMENT ~~OF~~ OF $-X$ BY $-OH$:



- $-NO_2$, being a e⊖ ~~with dr~~ withdrawing group ~~occupi~~ (e⊖ loving) goes to high e⊖ density places by preferences :

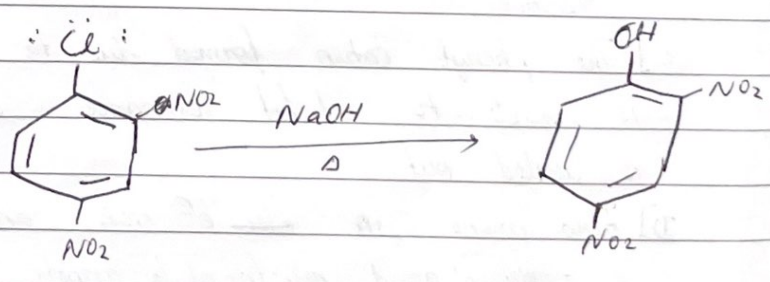
  para > ortho ~~> met~~

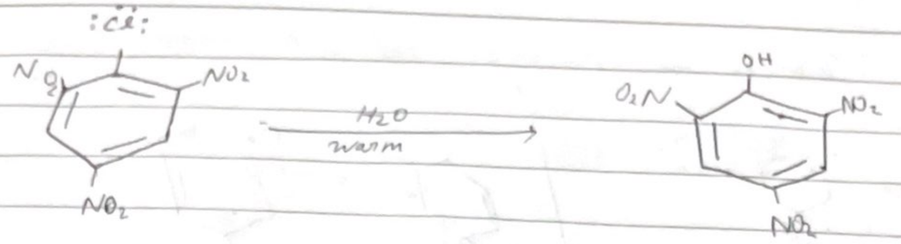
- EWG at ortho and para positions ↑ses reactivity of Haloarenes



(a temp less than normal rxn is enough as reactivity is increased

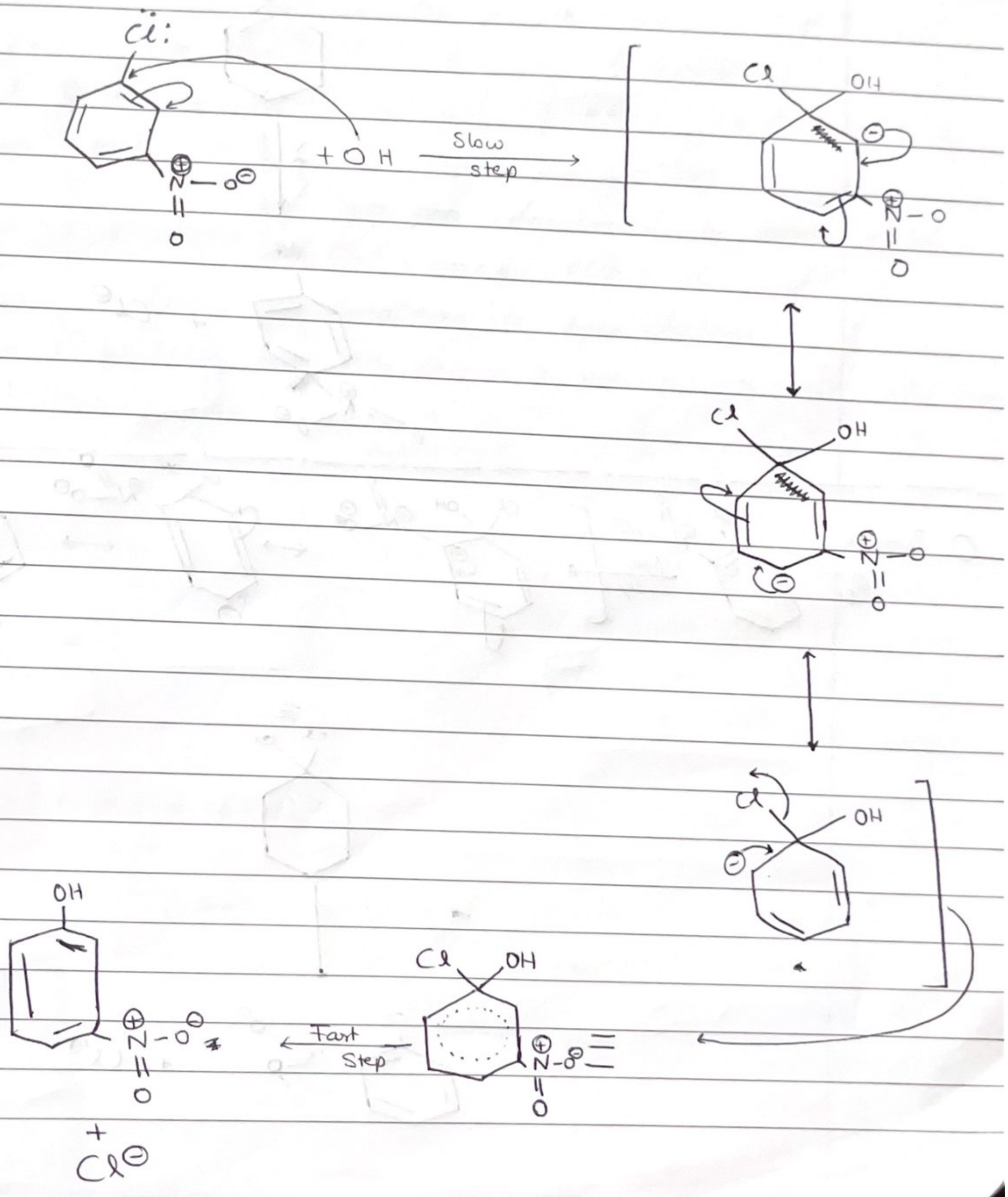
$$\frac{1}{\text{Heat required}} \propto \text{No of EWG at ortho/para positions} \propto \text{Reactivity of Halo Arene}$$





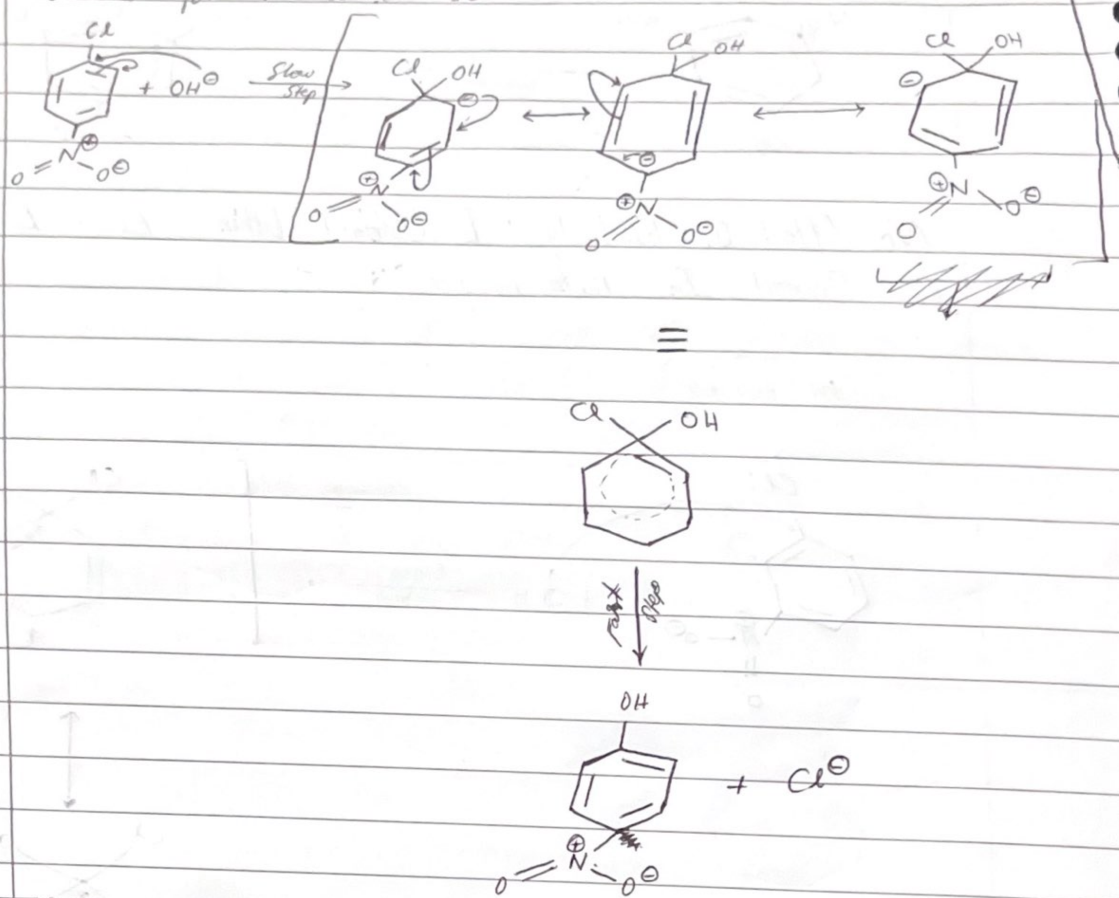
No Effect On Reactivity Is Observed When EWG Like NO_2 Is Present In meta position :

M- isomer

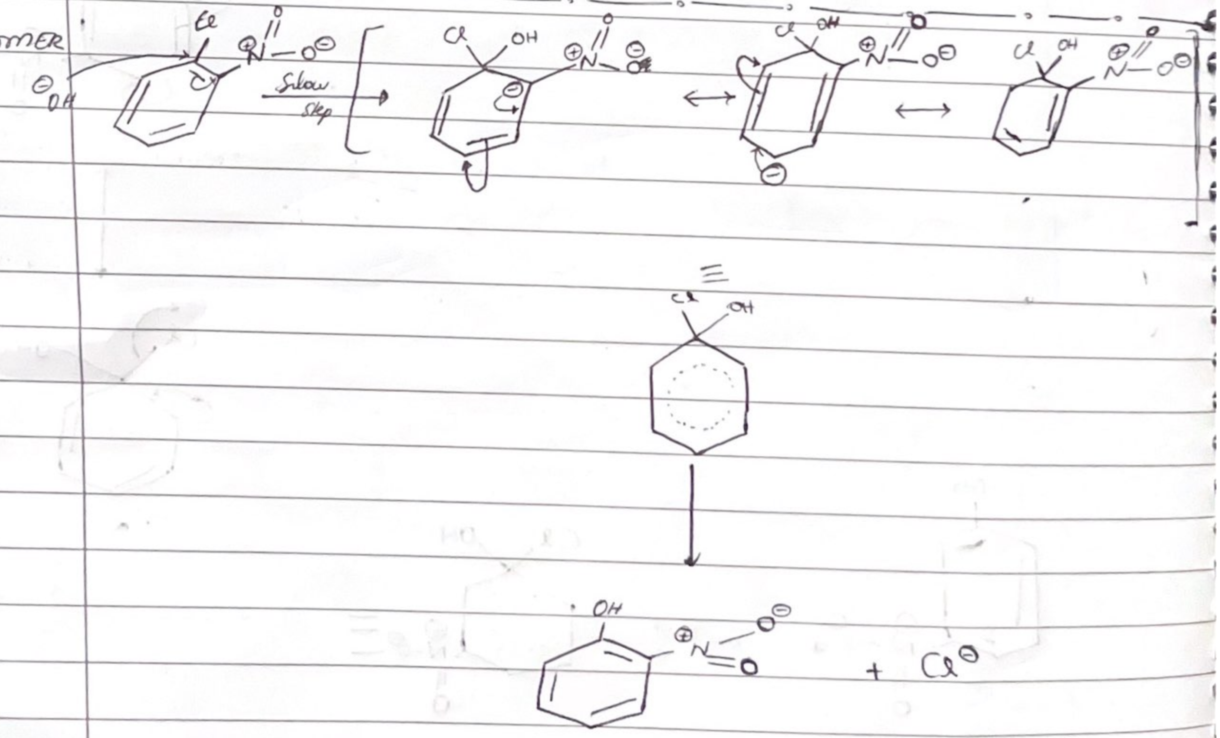


Whereas for P-isomer and O-isomer.

P-Isomer

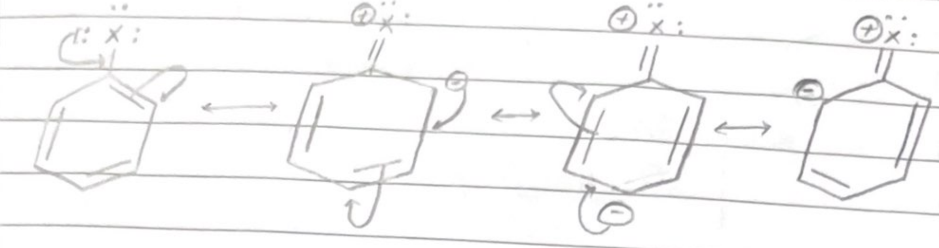


O-Isomer



ELECTROPHILIC SUBSTITUTION RXN

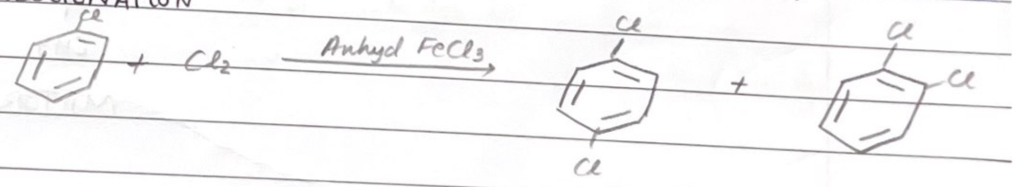
Even though ~~ortho and~~ being slightly deactivating in ~~at~~ ortho and para position, substitution rxn



- Notice that electron density increases in ortho and para ~~ton~~ than at meta due to resonance.
- Halogen produces $\boxed{-I}$ effect and has ability to with draw $e^{\ominus}$ from benzene ring
- There fore ~~rig~~ ring gets deactivated to some extent.
- electrophilic substitution rxn occor slow and require more drastic ~~on~~ conditions to ~~hap~~ happen.

- Some $e^{\ominus}$ are drawn from ortho ~~post~~ as its near so para - major, ortho - minor

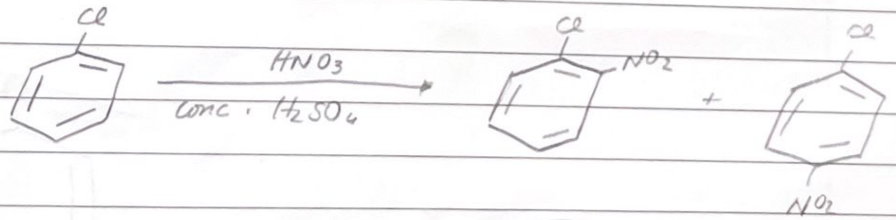
1] HALOGENATION



[1,4 - Dichlorobenzene] [Major]

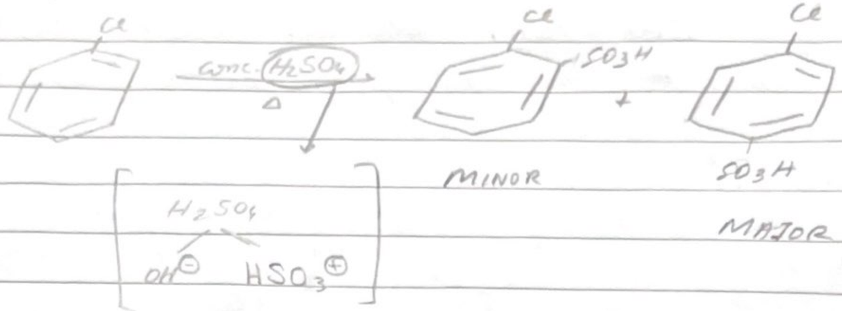
[1,2 Dichloro benzene] [Minor]

II] NITRATION [NO_2 -] → NITRO

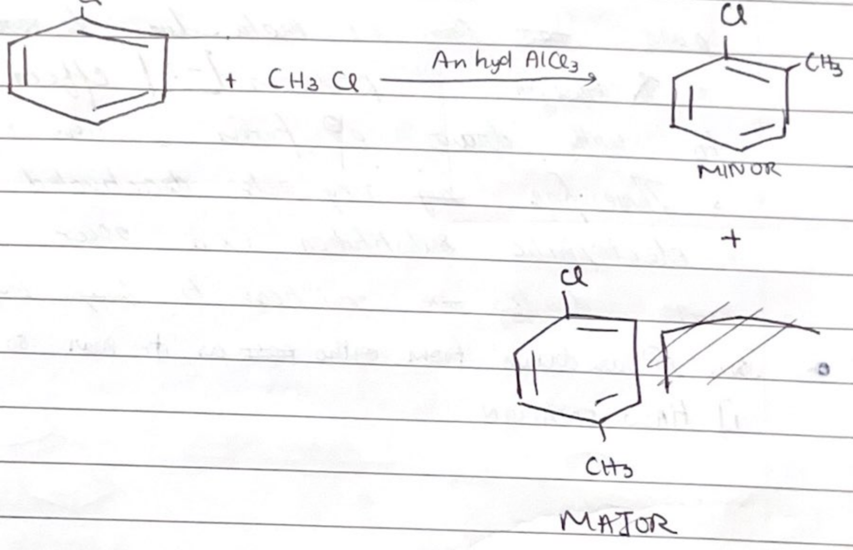


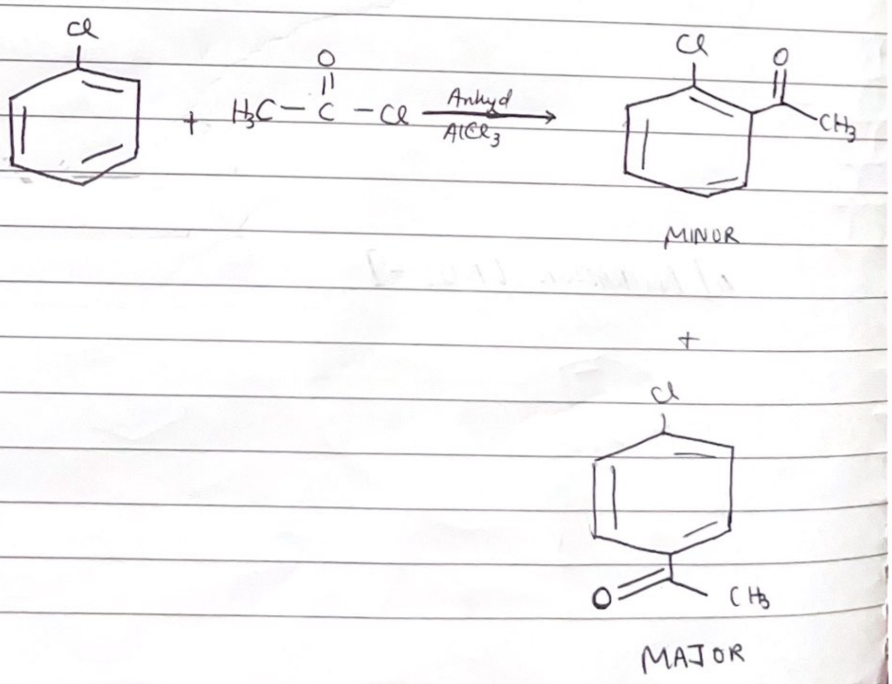
MINOR MAJOR

III] SULPHONATION [$-SO_3H$ *] → sulphonic acid



IV] FRIEDEL CRAFTS RxN(Reaction) :





REACTION WITH METALS :

A] WURTZ FITTIG RXN

- A reaction where

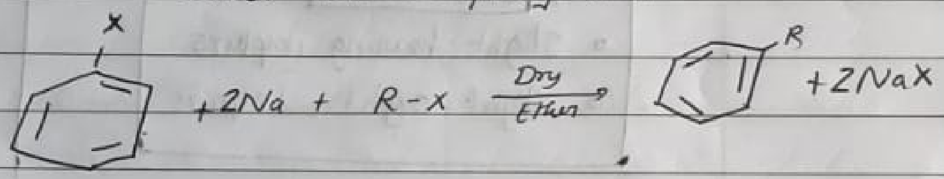
~~Alkyl Ar~~

Alkyl hallide + Aryl hallide

↓

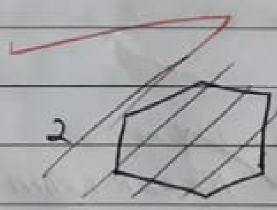
Alkyl arren

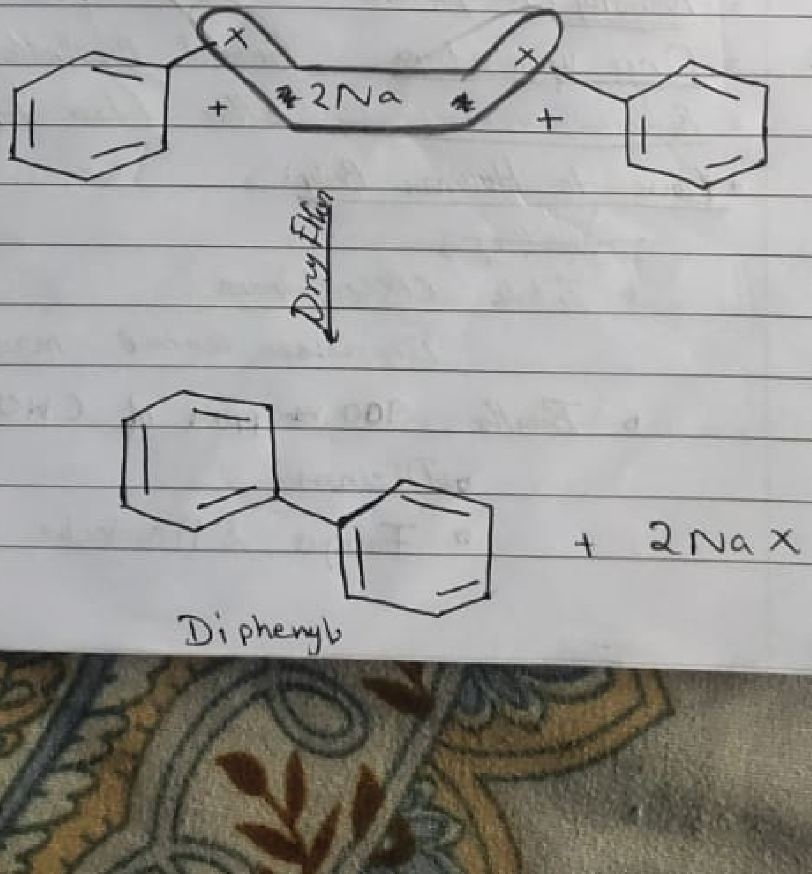
In presence of Na and Dry Ether is called wurtz fittig rxn



B] FITTIG RXN :

- Aryl Hallide + Aryl Hallide in presence of Na and dry ether is called fittig rxn.





Diphenyl

_/_/_

POLY HALOGEN COMPOUNDS [Have more than 1 Halogen atom]

- CN: Methylene Chloride

CH_2Cl_2

DICHLORO -METHANE

- Solvent of paint remover (thinner) and in manufacturing the drugs.
- Used for metal cleaning and finishing solvent
- Used as propellant in aerosols
-
- Cause to Human Body

Level of CH_2Cl_2

Low Level
- slight hearing impairs
- slight sight impairs

High Level
- Dizziness
- Skin Tingling
- Numbs fingers and toes

- Contact to skin: ~~tink~~
  intense burning, ~~ret~~ mild redening
- Contact to eyes:
  Burns out cornea

- CN: Chloroform

$CHCl_3$

TRICHLORO -METHANE

- Solvent in fats, Alkaloids, iodine, ..
- Majorly: to produce FERON REFRIGERANT R-22
- Once upon a time General Anesthetic
- Replaced anesthetic by Ether (Less toxic comparitively)
- Cause to Houman Body:
  - ~~Smelling~~
  - Inhale $CHCl_3$ vapours:
    Depresses central nervous system (CNS)
  - Breathe 900 ppm of $CHCl_3$:
    - Diziness,
    - Fatigue & Headache

- Chronic Chloroform:
  - Damages Liver since
    $CHCl_3 \longrightarrow$ Phosgene (poisonous)
  - Skin sores when skin immersed in $CHCl_3$
- $CHCl_3$ oxidises slowly in presence of light produces phosgene [Carbonyl chloride]

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\text{(Phosgene)}}{2COCl_2} + 2HCl$$

CHI_3

~~Trio~~ TRIIODOMETHANE

- CN: Iodoform
- Earlier : Antiseptic (due to liberation of free Iodine)
- Due to smell objection repaced by other Iodine derivatives

CCl_4

CARBON-TETRACHLORIDE

TETRACHLOROMETHANE

- CN: [Carbon tetra Chloride]
- Used to manufacture refrigerants
- Used to produce propellants for aerosol cans
- CFC ~~production~~, Pharmaceutical production.
- General solvent
- Degreasing agent ~~to~~ ~~to~~
- Cleaning fluid
- Depletes Ozone Layer [leads to skin cancer, eye disease]
- Spot remover
- Fire extinguisher.
- On Human body : Effects :
  - Liver Cancer
  - Dizziness
  - Vomiting
  - Coma
  - Death
  - Light headedness
  - Nausea
  - Permanent nerve cell damage
  - Unconciousness
  - Make heart to beat irregularly

FERON

- FERON = CFC of methane + CFC of ~~eth~~ ethane
- Highly Stable
- Non Reactive
- Non Toxic
- Non Corrosive
- Easily Liquifyable.
- Feron - 12 variant [CCl_2F_2] used ind industry
- To produce aresol propellants
- Used for refrigeration, ~~airconditioning~~ air conditioning
- Can ~~create~~ Initiate ~~radica~~ radical chain rxn in stratosphere that upset Natural Ozone Balance

DDT

para, para
-Dichloro
phenylthic
-holro
-ethane

- 1st Chlorinated Organic Inseeticide and discovered by Paul Muller
- effective against mosquito ~~and~~ that spread malaria and lice that carry typhus
- highly toxic to fish
- DDT slowly metabolises in animals so its gets deposited ~~in~~ and stored ~~as~~ in fatty tissues
- DDT builds up within the body of animal over time.
- US banned use of DDT in 1973