Methods to prepare Haloalkanes–

(III) From alkenes:

$CH_2=CH_2 + Br_2 \longrightarrow CH_2(Br)-CH_2(Br)$ vicinal dihalide

↑ sym. alkene ↑ sym. reagent

$CH_3-CH=CH_2 + Br-Br \longrightarrow CH_3-CH(Br)-CH_2(Br)$ → Same ↓ one product

Unsym. Alkene ↑ sym. reagent

+ $CH_3-CH(Br)-CH_2(Br)$

Ex!: $CH_3-CH=CH_2 + HBr \longrightarrow$

↑ Unsym. alkene ↑ Unsym. reagent

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

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

+ diff. prod.

One of the product is major product and the other product is minor product.

↓

Which rule governs the major product?

↓

Markovnikov's rule.

↓

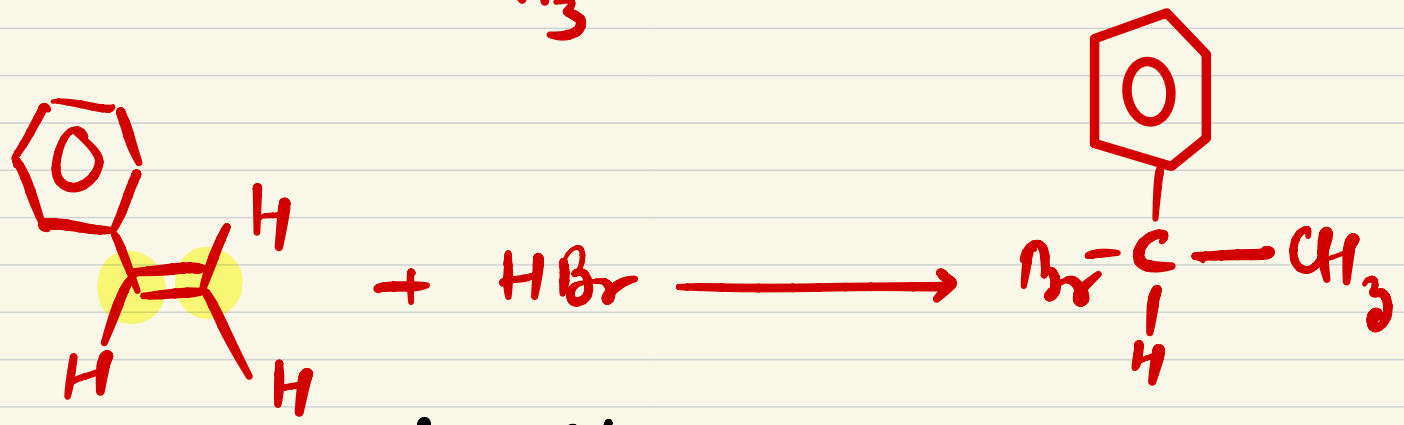
Major prod:- Negative part of HX (X^-) is added to that double bonded C-atom which has less no of H-atom.

In Ex1: Which is major product A or B?

B is the major product.

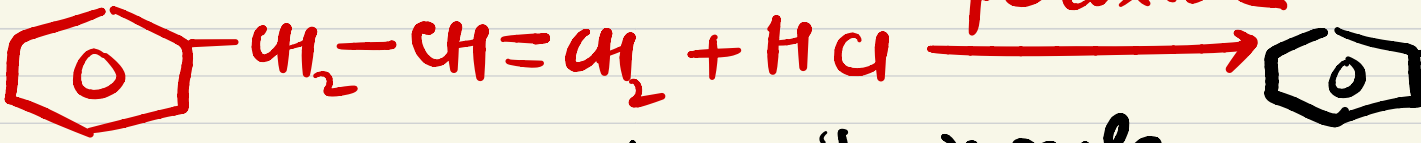
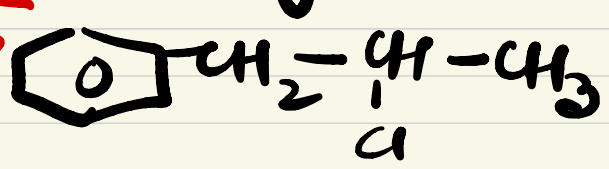
Q. Write the products (major) for the following reactions:—

(i) $CH_3-CH=C(CH_3)_2 + HCl \longrightarrow CH_3-CH_2-C(Cl)(CH_3)_2$

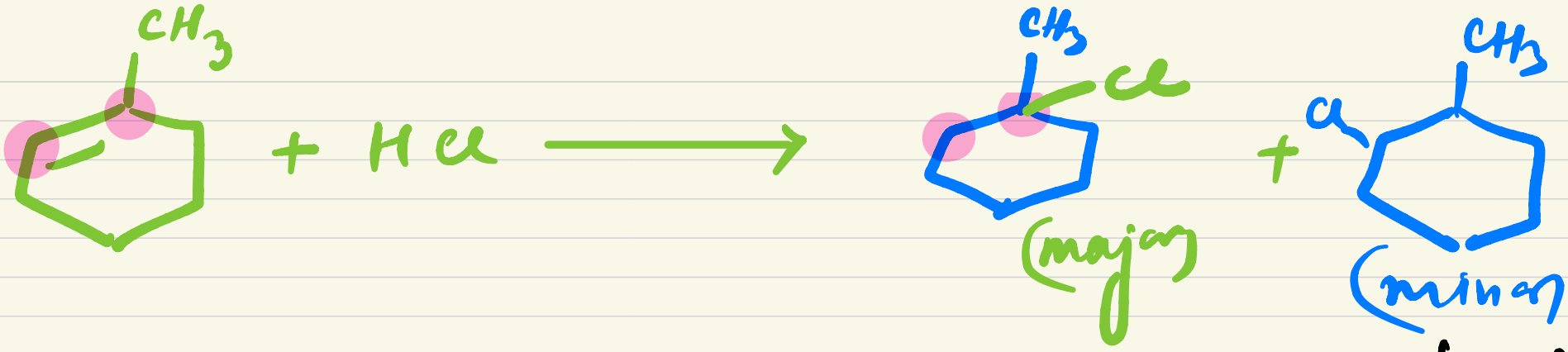
(ii)  $+ HBr \longrightarrow$

(iii) $CH_3-CH=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3-CH_2-CH_2-Br$ (major)

peroxide effect or anti-Markownikoff rule or Saytzeff rule.

(iv)  $\xrightarrow{\text{peroxide}}$ 

Markownikov's rule.



(4) **By Halogen Exchange :-**

↑ to make R-F & R-I

preparation of R-F is highly exothermic

R-I

Finkelstein reaction →

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

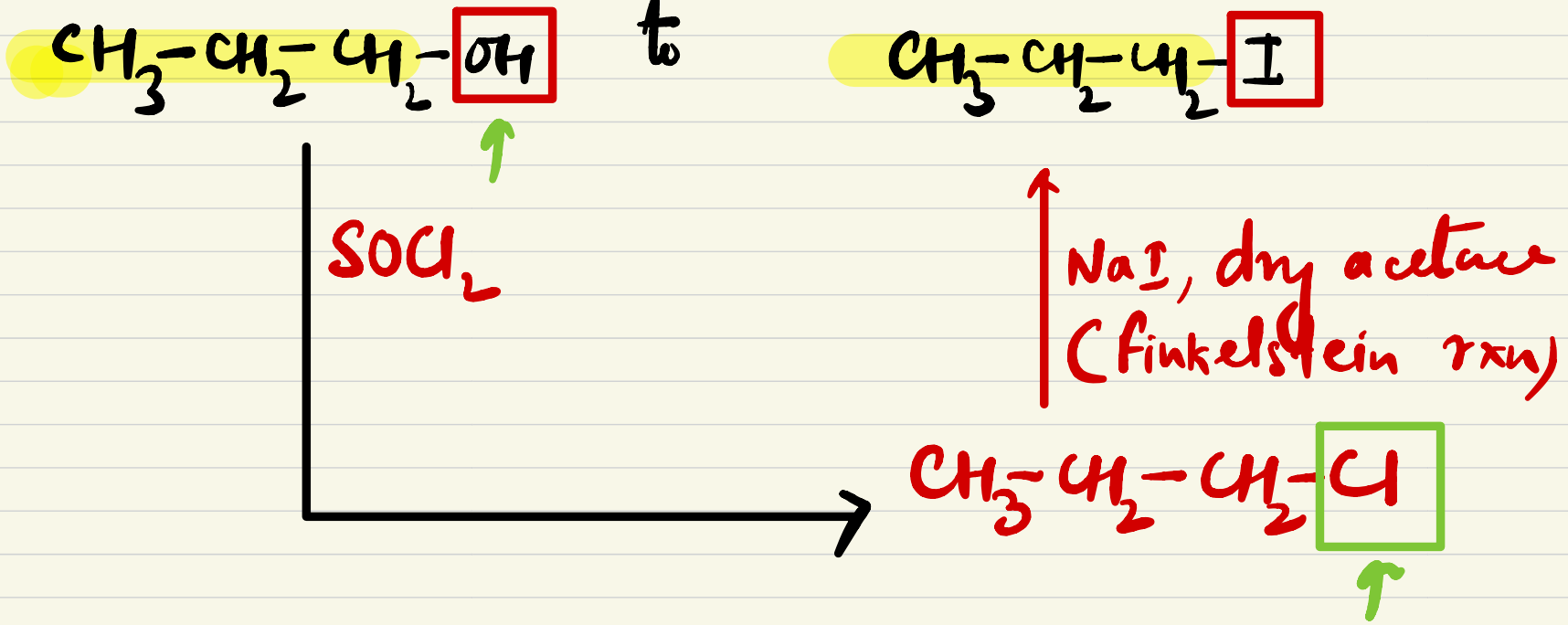
(X = Cl, Br)

Swarts reaction :-

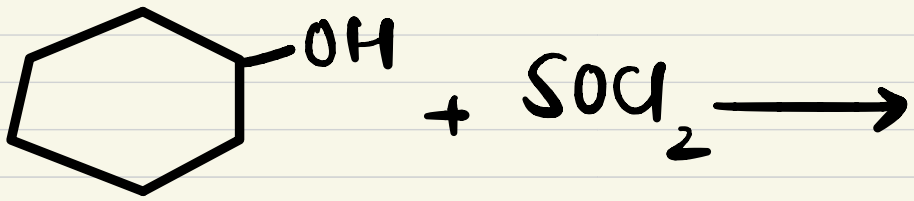
$$R\text{-}X + AgF \longrightarrow R\text{-}F + AgX$$

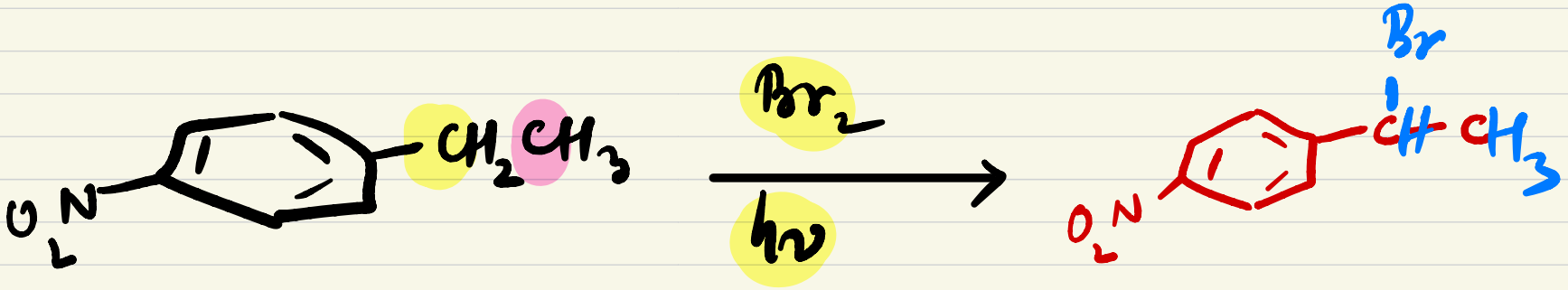
(X = Cl, Br)

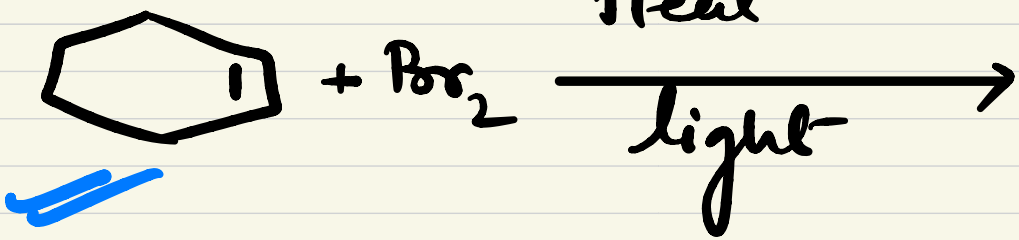
Convert : propan-1-ol to iodopropane.

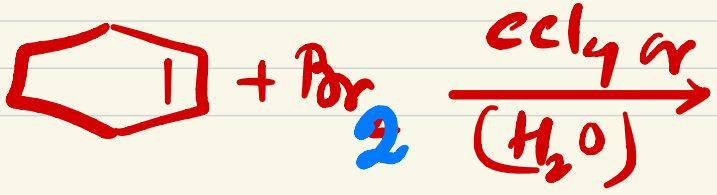


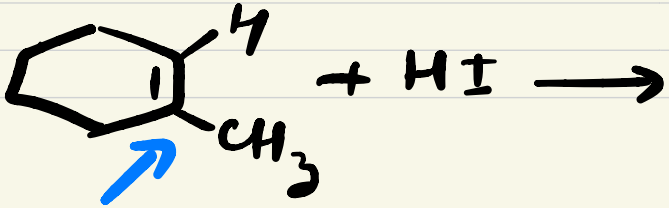
Q Draw the structures of major products in each of the following reactions:-

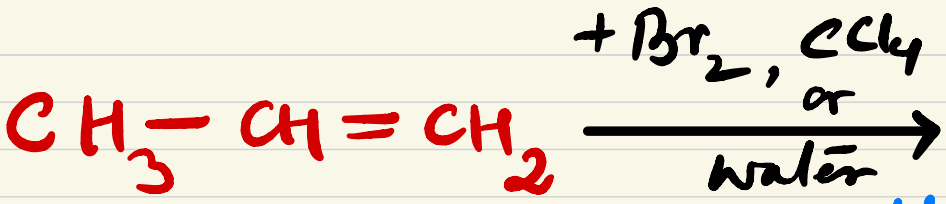
(i) 

(ii) 

(iii) 

(iv) 

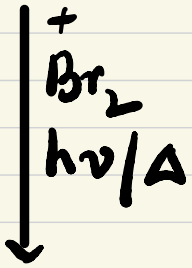
(v) 



addition rxn

$C\equiv C-\overset{\uparrow}{C}-\overset{\uparrow}{C}-X$

allylic substⁿ

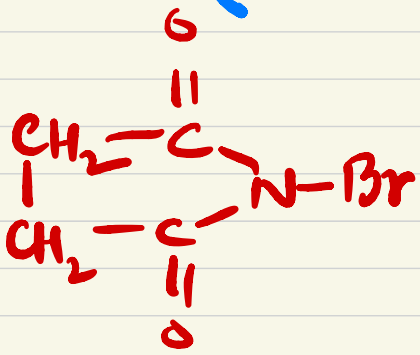


(High Temp.)

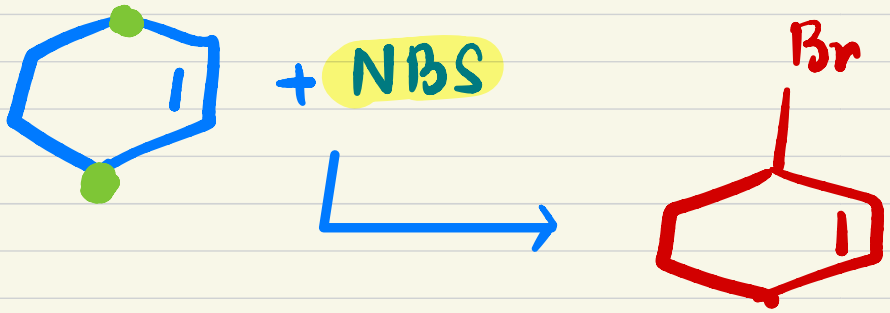
$CH_2(Br)-CH=CH_2$

allylic substⁿ

Reagent :- NBS (N-Bromo succinimide)



allylic substⁿ

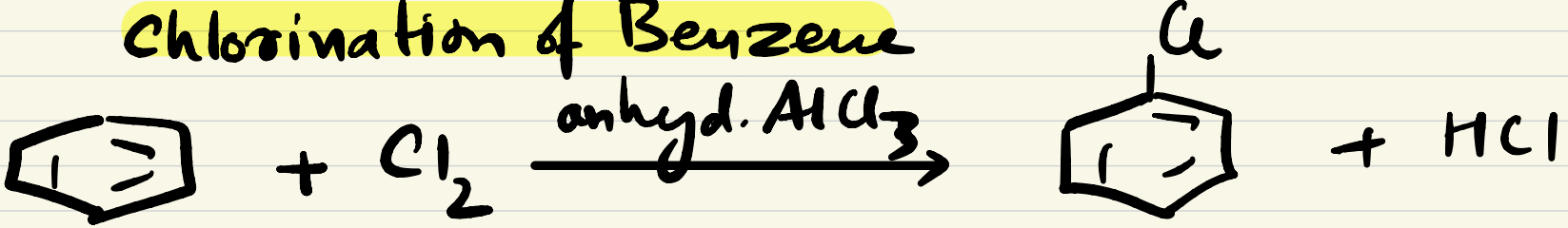


Preparation of Haloarenes :→

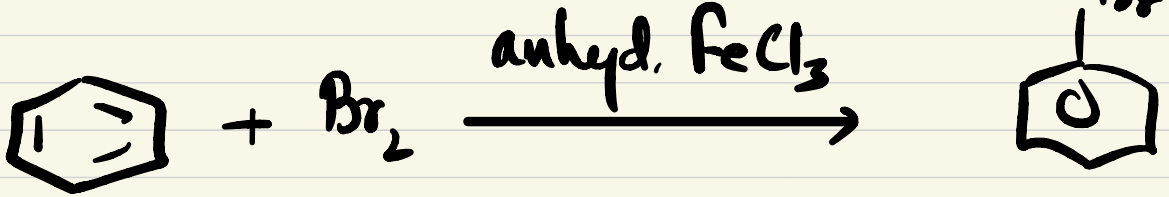
(i) From benzene (ii) From Diazonium salt.

From Benzene :- $E_{Ar}S$ rxn.

Chlorination of Benzene



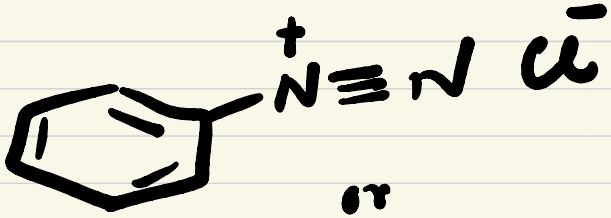
Bromination of Benzene :-



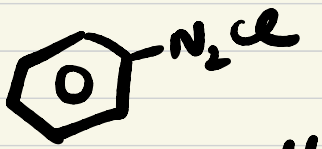
Iodination of Benzene :-

Q. How to carry out iodination of Benzene?

By using strong oxidising agents like HIO_3 or HNO_3 acid.

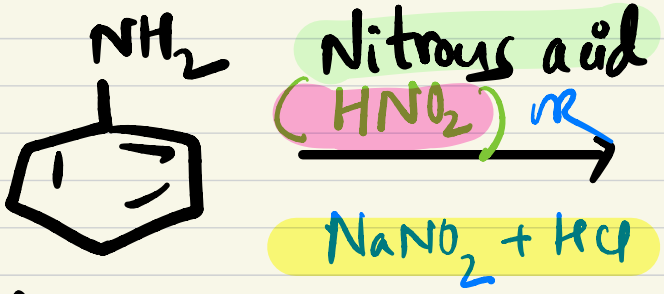


or

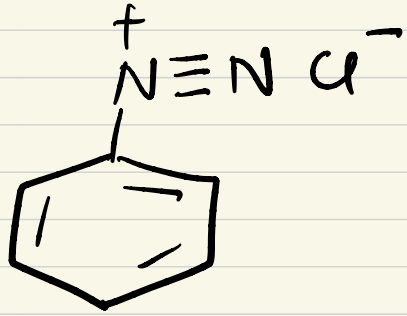


Diazonium salt of benzene.

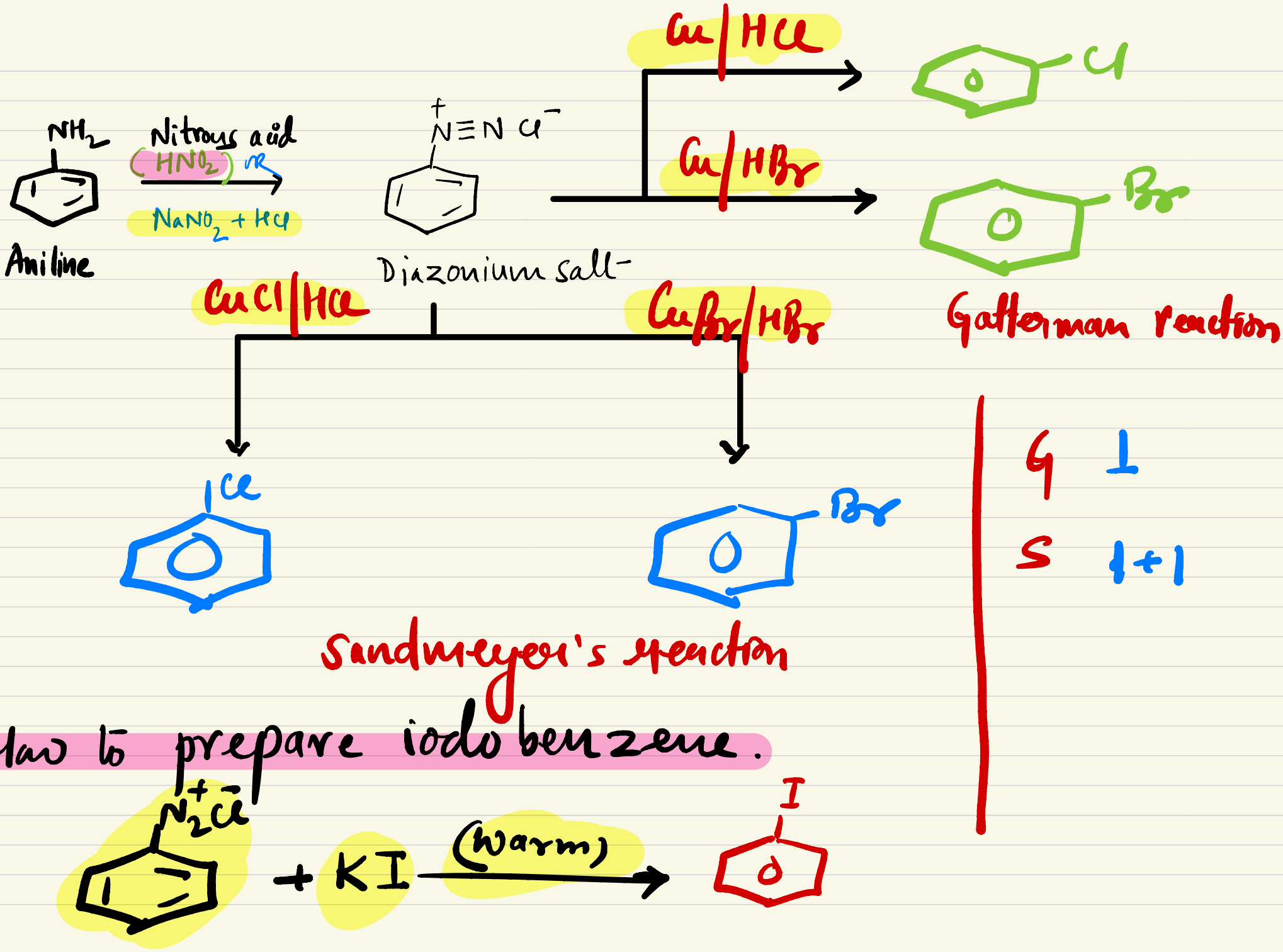
I) From Diazonium salt :-



Aniline



Diazonium salt


Cu/HCl
Cu/HBr
Aniline
Nitrous acid
(HNO2)
NaNO2 + HCl
Diazonium salt
CuCl/HCl
CuBr/HBr
Gatterman reaction
Sandmeyer's reaction
How to prepare iodobenzene.
(warm)

G	1
S	1+1

Physical properties of –

(I) Haloalkanes – (i) B.P (ii) Solubility (iii) dipole moment.

Boiling Point :–

a, b, c, d, e

branched

straight chain

H-Bond > polar & non-polar > Molecular mass > Straight chain > Branching

(a) $CH_3-CH_2-CH_2-CH_2-OH$; (b) $CH_3-CH_2-CH_2-CH_2-Cl$,

(c) $CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-Cl$, (d) $CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-Cl$

Ting order of boiling point :–

d < c < b < a

Ex:→ CH_3Cl (a), CH_3Br (b), $CHCl_3$ (c) & $CHBr_3$ (d) (↑ing order of B.P)

(a) ↑ Chloromethane

(b) ↑ Bromomethane

(c) ↑ Chloroform

(d) ↑ Bromoform

$a < b < c < d$

Ex: Chloropropane, isopropyl chloride, 1-chloro butane.

Arrange them in increasing order of Boiling Point.

⇒ $CH_3-CH_2-CH_2-Cl$; $H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-Cl$; $CH_3-CH_2-CH_2-CH_2-Cl$.

(a) C_3H_7Cl

(b) C_3H_7Cl

(c) C_4H_9Cl

$b < a < c$

(II) Solubility :- "Like dissolves like"

Polar solute is soluble in polar solvent

OR

Non-polar solute is soluble in non-polar solvent.

CH_3-Cl polar

In general, R-X (alkyl halide) is polar in nature & water is also polar in nature.

Our expectation is that R-X is soluble or miscible in water.

In actual practice RX is slightly soluble (or insoluble) or immiscible in

water

Q. Alkyl halides, though polar, are immiscible in water. Why?

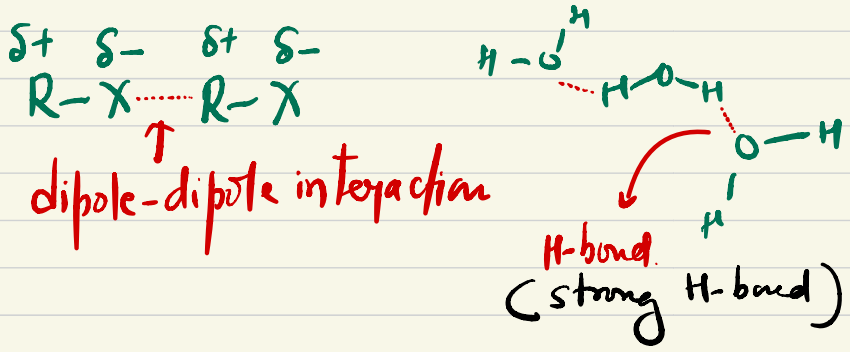
Ans: RX do not form H-bond with H_2O. And RX can't break the H-bond of two water molecules & interact.

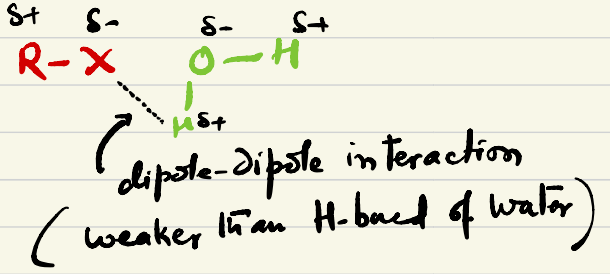
Extra

Solute - solute + Solvent - Solvent

↓

Solute - Solvent interaction





(II) Dipole Moment :

$\mu = q \times d$

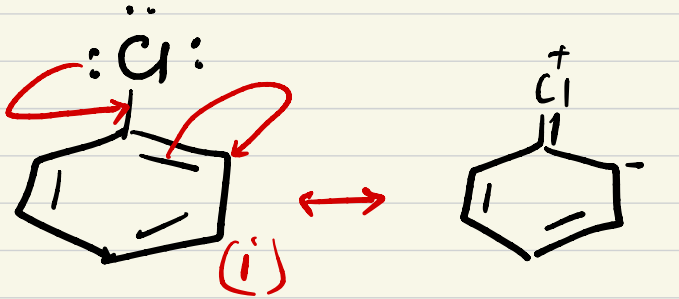
μ → Vector Quantity → magnitude, direction

Bonds

structure of molecule.

CO_2 $\quad O = C = O$

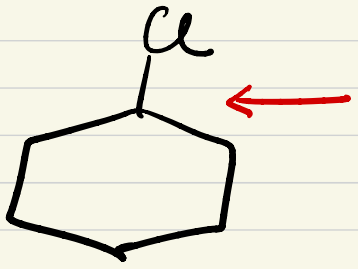
$\mu_{net} = 0$ ⇒ Non-polar molecule



(i)

C-Cl bond has partial double bond character.

Which is more polar & why ?

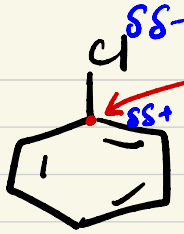


(ii)

C-Cl bond has pure single bond character.

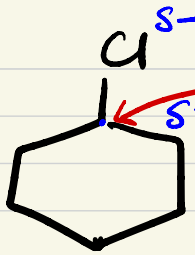
more E·N → least E·N

$sp\text{-}C > sp^2\text{-}C > c\text{-}sp^3$



sp^2-hybridised C-atom (greater s-character ∴ more E.N)

(II)



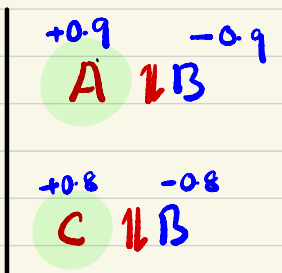
sp^3 (less s% - character ∴ least E.N)

(IV)

A, B, C | E.N :- B > C > A

A^{+L} → A has lost its e⁻ completely ⇅ B^{-1}

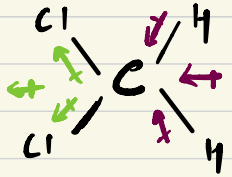
due to str. (ii) & (iv) combining effect; cyclohexylchloride is more polar than chlorobenzene

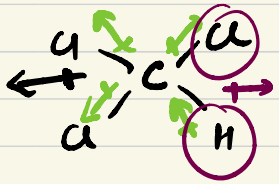


Q. Which one of the following has the highest dipole moment?

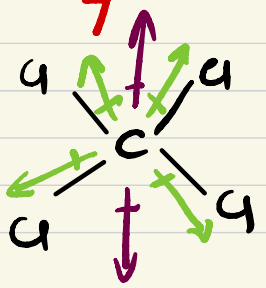
(i) > (ii) > (iii)

(i) CH_2Cl_2 (ii) $CHCl_3$ (iii) CCl_4 → non-polar





μ ≠ 0



μ = 0