NCERT MIND MAP FOR 12TH BOARDS

- Subject - Chemistry
- Chapter – Haloalkanes & Haloarenes

(One Shot)

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Today's Targets

1. Classification, Nomenclature
2. MOP of Haloalkanes & Haloarenes
3. Physical Properties
4. Chemical Properties
5. Polyhalogen Compounds

Introduction

Haloalkanes & Haloarenes

Halogen + Alkanes

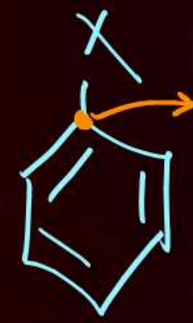
$C_nH_{2n+2} \xrightarrow[+X]{-H} C_nH_{2n+1}X$

Haloalkanes or Alkyl halides

$\rightarrow X \rightarrow sp^3$ hybz. C

Halogen + Arenes

$\xrightarrow[+X]{-H}$



Haloarenes / Aryl halides

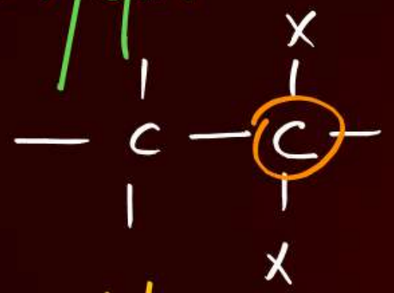
Classification

1. On the basis of no. of halogen atoms:

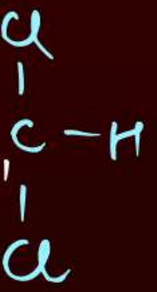
- Monohaloalkanes & Monohaloarenes
  - e.g. CH_3-Cl, C_2H_5-Br,  etc.
  - → $CH_3-CH_2-CH_2-CH_2-Cl$ (1° alkyl halide)
  - → $CH_3-CH(Cl)-CH_2-CH_3$ (2° alkyl halide)
  - → $CH_3-C(CH_3)_2-Cl$ (3° alkyl halide)
- Dihaloalkanes & Dihaloarenes
  - e.g. CH_2Cl-CH_2Cl ; CH_3-CHCl_2 ; 
- Polyhaloalkanes & Polyhaloarenes
  - e.g. $CHCl_3$, $CHBr_3$, CHI_3, CCl_4 etc.

Dihaloalkanes

Geminal / Gem.-dihalide

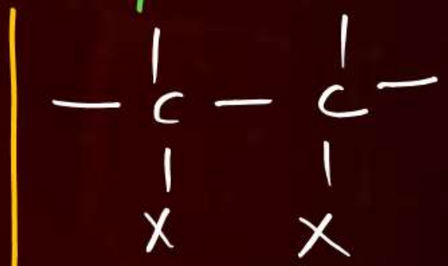


→ Also k/a Alkylidene halide

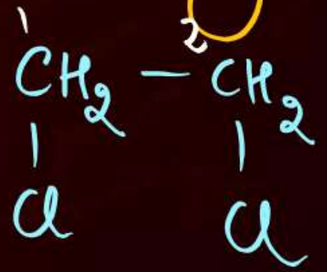
eg. CH_3-CHCl_2 or 

1,1-Dichloroethane (Ethylidene chloride)

Vicinal / Vic.-dihalide



→ Also k/a Alkylene dihalide

eg. 

1,2-Dichloroethane (Ethylene dichloride)

2. On the basis of hybz. of C attached with halogen:

- $Csp^3 - X$
  - Alkyl halides
    - eg: CH_3-I
    - sp^3
  - Allylic halides
    - $CH_2=CH-CH_2Cl$
    - CH_2 → sp^3
  - Benzylic halides
    - $sp^3 \leftarrow CH_2-Cl$
- $Csp^2 - X$
  - Vinylic halides
    - eg:
    - $CH_2=\overset{sp^2}{\overset{\nearrow}{CH}}-Cl$
  - Aryl halides
    - Cl → sp^2

Nomenclature

Common Name : Alkyl halide

IUPAC Name : 2°P + 1°P + Word Root + 1°S + 2°S

- ane
- ene
- yne

Halogens → added as 2° Prefix → Halo

→ Haloalkane

e.g. ① CH_3Cl

Chloromethane

[Methyl chloride]

② $\overset{1}{C}H_3-\overset{2}{C}H(Br)-\overset{3}{C}H_3$

2-Bromopropane

③ 

1-Chlorocyclopentane

(4) $CH_2^1=CH^2-CH_2^3Cl$

3-Chloropropene

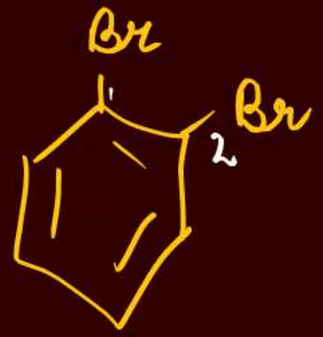
(5) $CH_3^1-CH^2(Cl)-CH^3(Cl)-CH_3^4$

2,3-Dichlorobutane

(6)

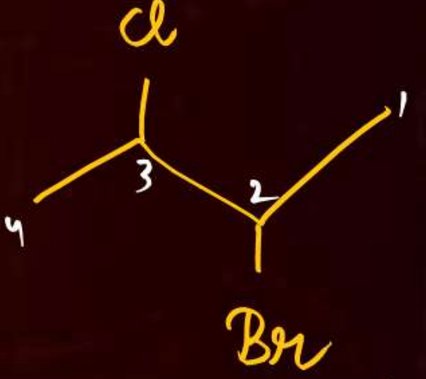
Bromobenzene

(7)



1,2-Dibromobenzene

(8)



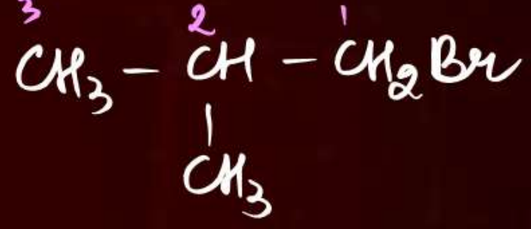
2-Bromo-3-chloro butane

Isomerism :

Chain isomerism :

C_4H_9Br :

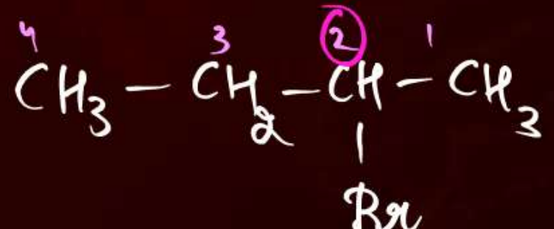
1-Bromobutane



1-Bromo-2-methylpropane

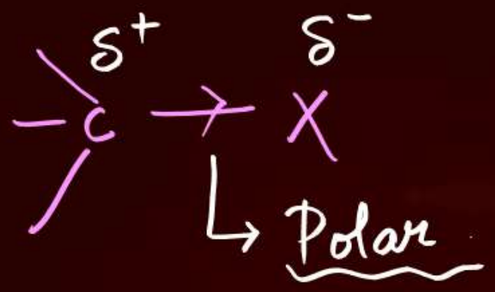
Position isomerism :

1-Bromobutane



2-Bromobutane

Nature of C–X bond :



(where X = F, Cl, Br or I)

(1) C–X bond length : $CH_3-F < CH_3-Cl < CH_3-Br < CH_3-I$

(2) Bond enthalpy (C–X) : $CH_3-F > CH_3-Cl > CH_3-Br > CH_3-I$

★★ (3) Dipole moment (μ) :

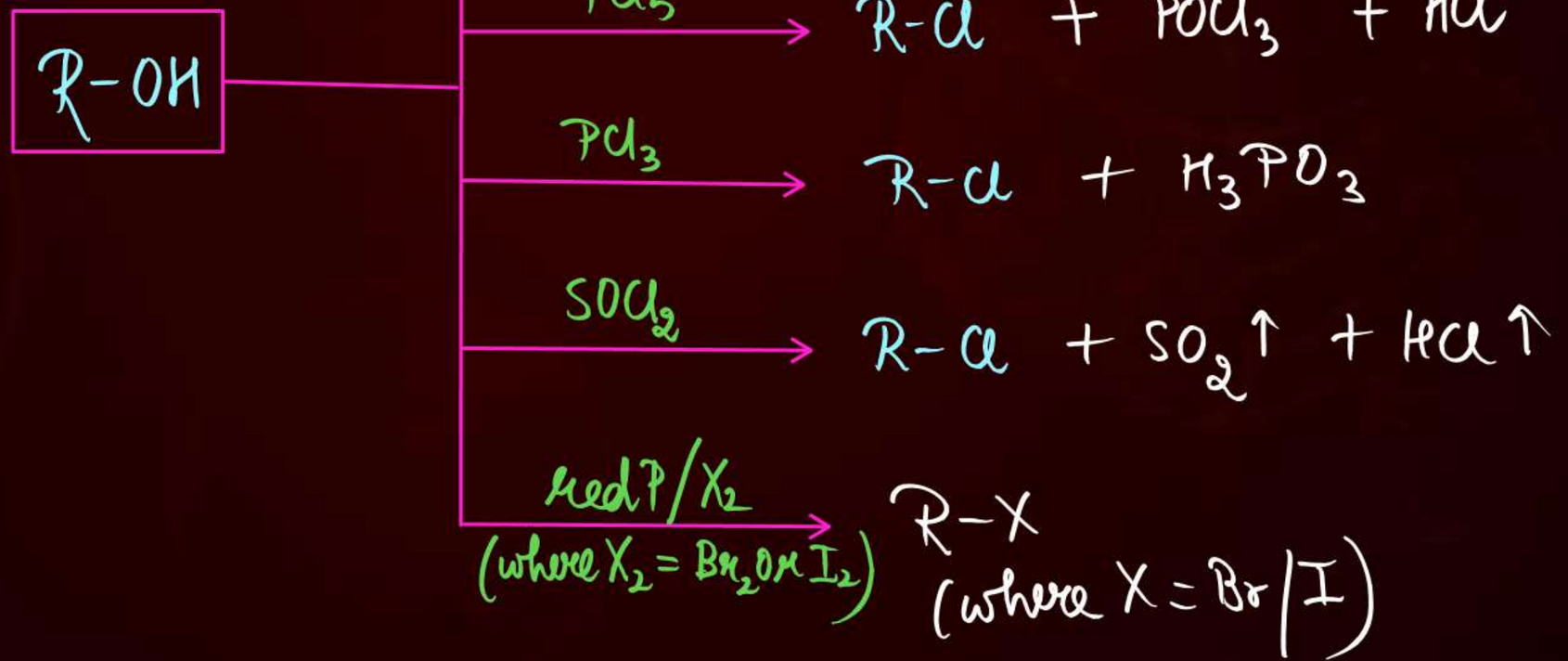
(1) $CH_3Cl > CH_3F > CH_3Br > CH_3I$

(2) $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

$$\mu = q \times d$$

MOP of Haloalkanes

1. From alcohols :



2. From hydrocarbons

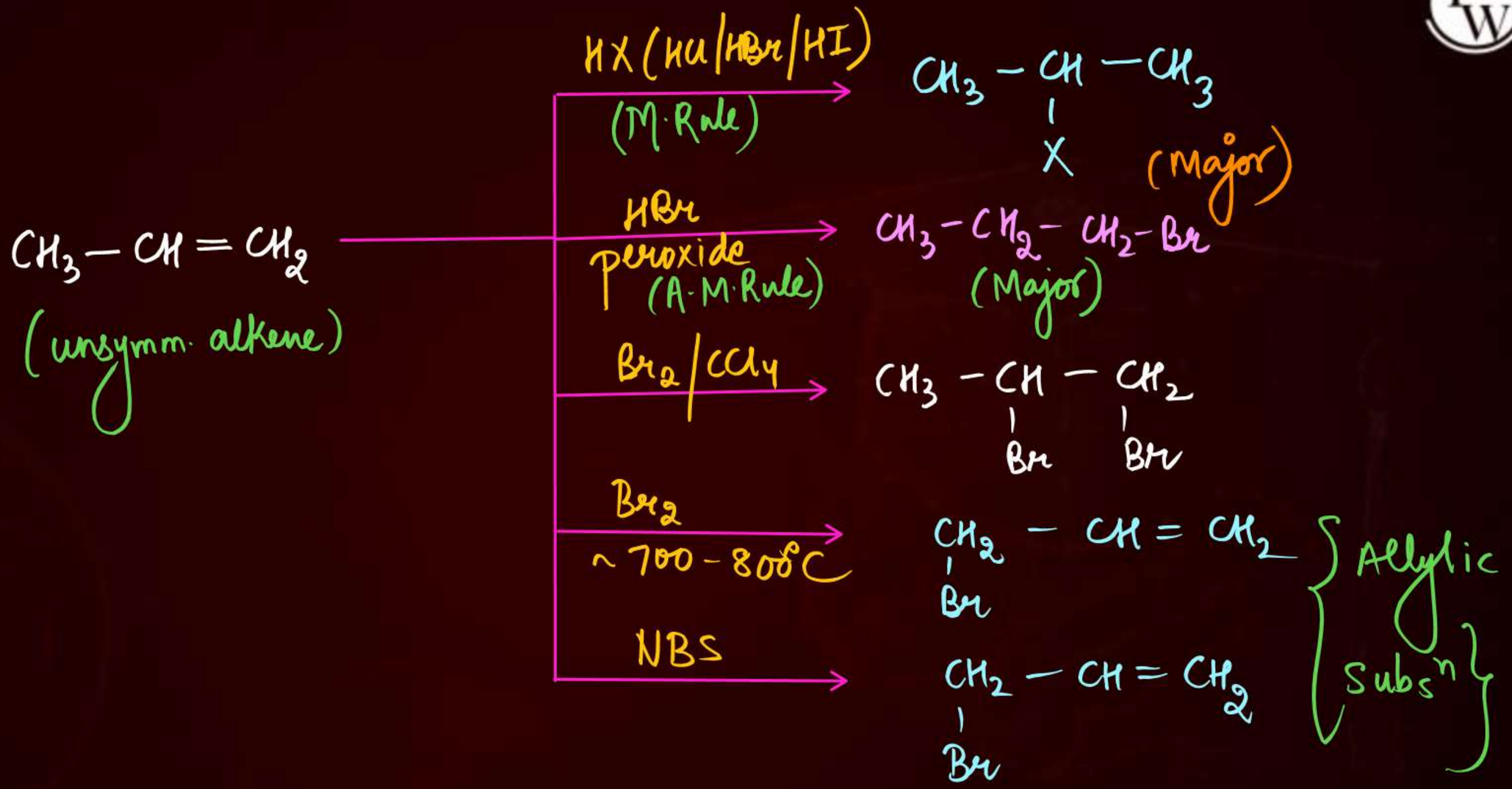
From Alkanes
(Free Radical Subs^{n} Rx^{n})

e.g. $CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl$

$CH_3\overset{a}{-}CH_2\overset{b}{-}CH_3 \xrightarrow[h\nu]{Cl_2} CH_3-CH_2-CH_2Cl + CH_3-\underset{Cl}{CH}-CH_3$

From Alkenes

- Addition of HX
- Addition of X_2
- Allylic Substitution


$CH_3 - CH = CH_2$
(unsymm. alkene)
HX (HCl/HBr/HI)
(M·Rule)
$CH_3 - CH(X) - CH_3$ (Major)
HBr
peroxide
(A·M·Rule)
$CH_3 - CH_2 - CH_2 - Br$
(Major)
Br_2/CCl_4
$CH_3 - CH(Br) - CH_2(Br)$
Br_2
~700 - 800°C
$CH_2(Br) - CH = CH_2$
NBS
$CH_2(Br) - CH = CH_2$
Allylic Substⁿ

3. By halogen exchange:

→ Finkelstein rxn:

$$R-X + NaI \xrightarrow[\text{reflux}]{\text{acetone}} R-I + NaX$$

→ Swarts Rxn:

$$R-Br + AgF \longrightarrow R-F + AgBr$$

↓

we can also use

Hg_2F_2 | SbF_3 | CoF_3

4. From silver salts of carboxylic acids :

Borodine - Hunsdiecker Rxn :

$$CH_3COOAg + Br_2 \xrightarrow{CCl_4} \underset{\text{Bromo methane}}{CH_3Br} + CO_2\uparrow + AgBr$$

MOP of Haloarenes

(i) E·S·Rxn:

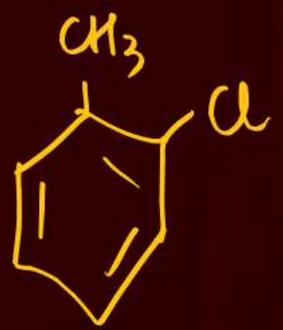
+ Cl_2 $\xrightarrow[FeCl_3]{\text{anhyd. } AlCl_3 \text{ or}}$

+ HCl

(ii)

(Toluene)

+ Cl_2 $\xrightarrow[(\text{dark})]{Fe}$



+

(iii) By diazonium salts:

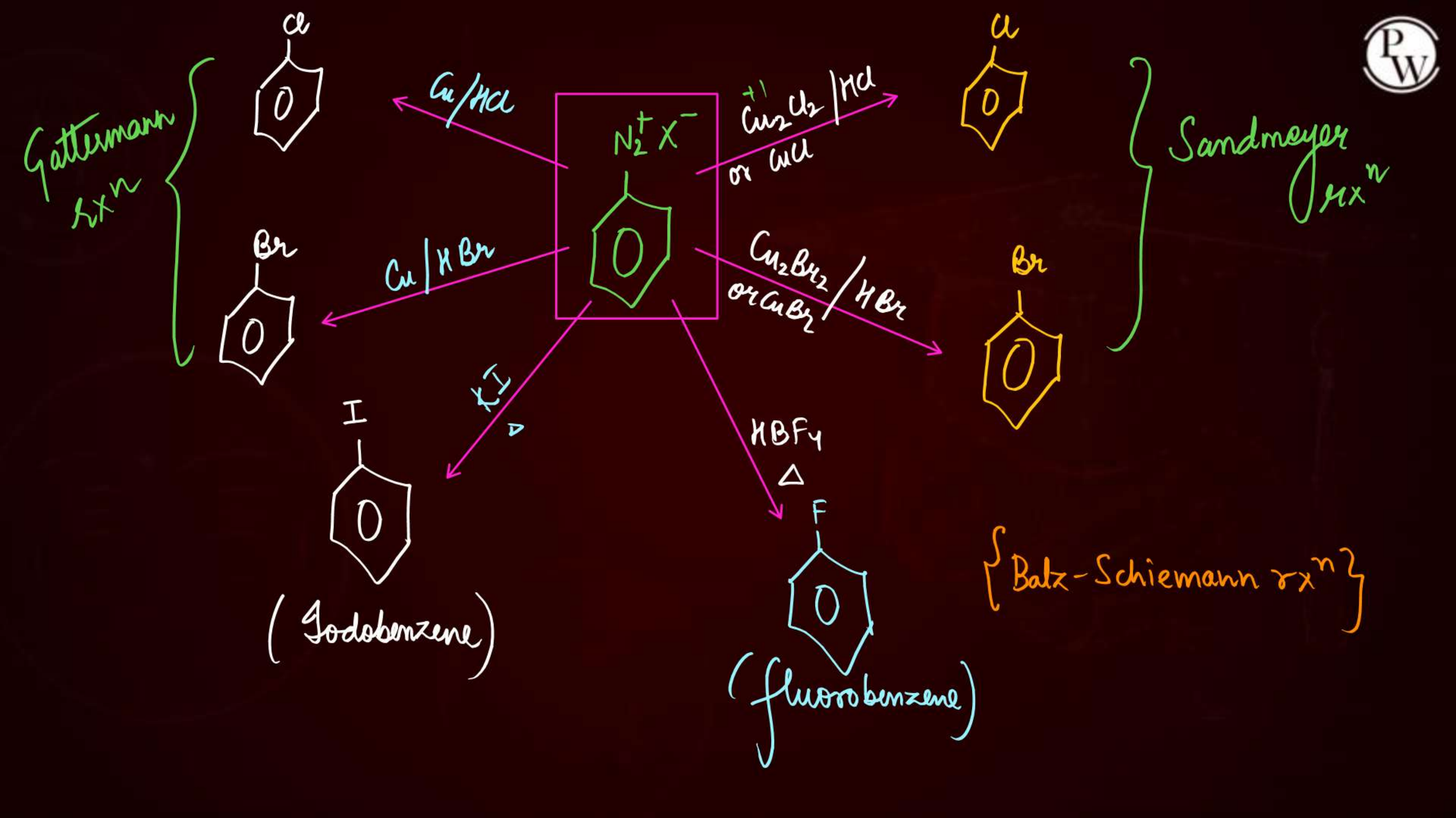
$\xrightarrow[+\text{ conc. } H_2SO_4]{\text{conc. } HNO_3}$

$\xrightarrow{Sn/HCl}$

Aniline

$\xrightarrow[(0-5^\circ C)]{NaNO_2 + HCl}$

Benzene diazonium Chloride


Gattermann rxn
Cl
Cu/HCl
$N_2^+X^-$
Cu_2Cl_2/HCl or CuCl
Cl
Sandmeyer rxn
Br
Cu/HBr
Cu_2Br_2/HBr or $CuBr_2$
Br
KI
Δ
I
(Iodobenzene)
HBF_4
Δ
F
(fluorobenzene)
{Balz-Schiemann rxn}

Physical Properties

→ R-X : v. less soluble in water

↳ more soluble in organic solvents

→ ★ B.Pt :

B.Pt ∝ Mol. mass

B.Pt ∝ $\frac{1}{\text{Branching}}$

(1) For same alkyl gp; B.Pt : R-I > R-Br > R-Cl > R-F

e.g. $CH_3I > CH_3Br > CH_3Cl > CH_3F$

(2) For same halogen but diff. alkyl gps; no. of C-atoms ↑ ; M.M. ↑ ; B.Pt ↑

e.g. B.Pt: $CH_3Cl < CH_3CH_2Cl < CH_3CH_2CH_2Cl$

→ M.Pt :

bcz of symmetry ; it fits very well in crystal lattice & ∴ has higher M.Pt.

★ Q. p-dichlorobenzene has higher M.Pt than o or m-isomer. Why ?

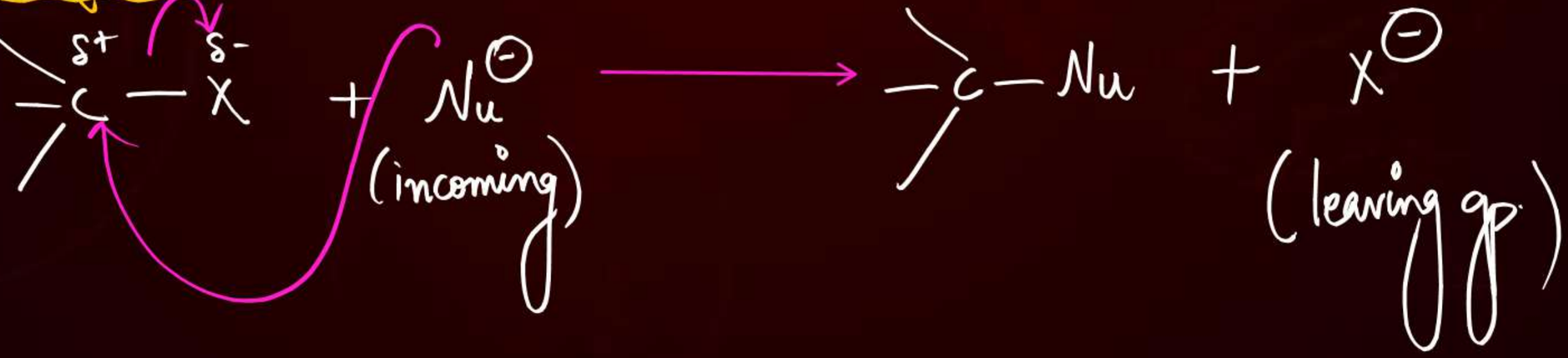
→ density :

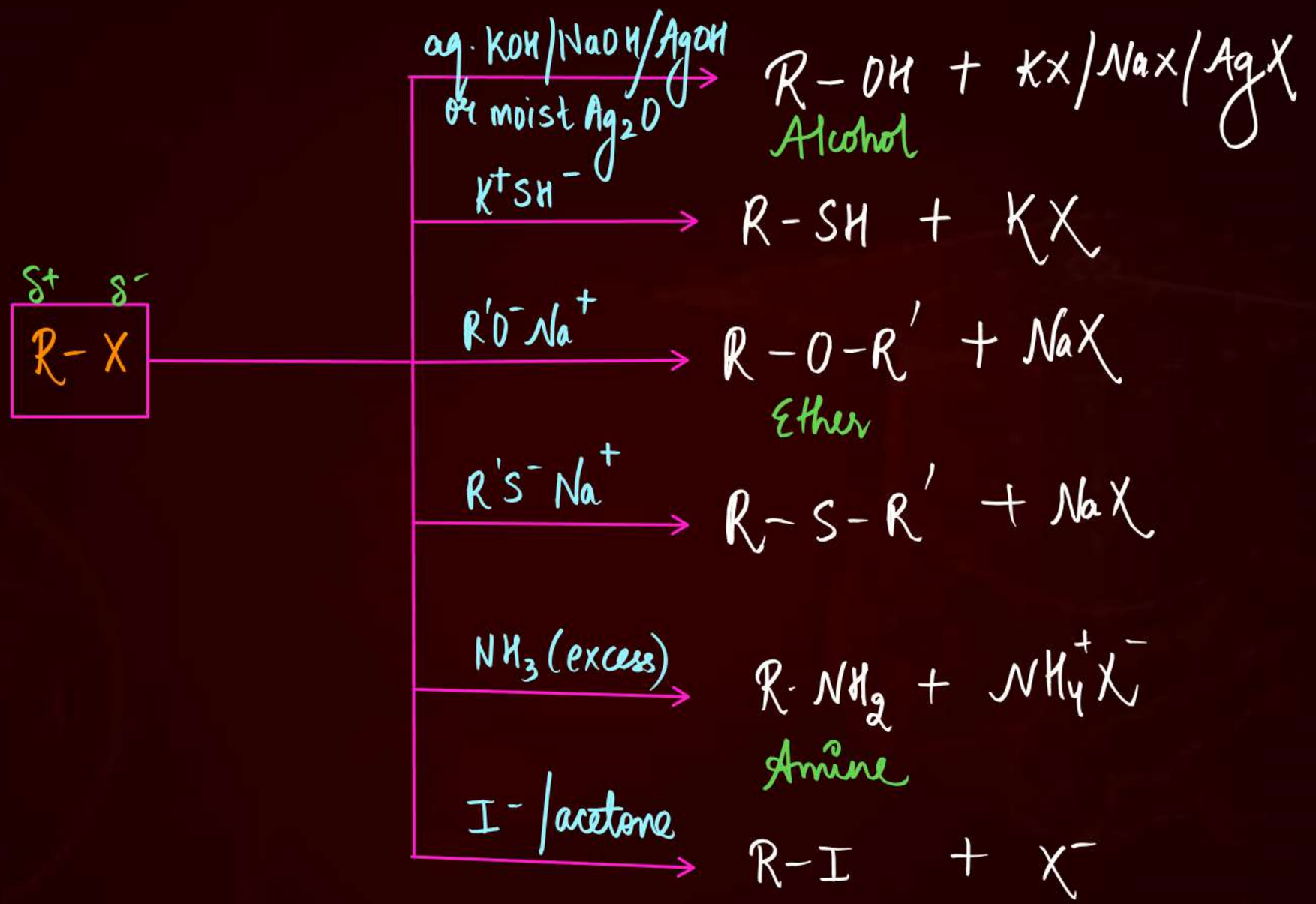
density : $n\text{-}C_3H_7Cl < n\text{-}C_3H_7Br < n\text{-}C_3H_7I$

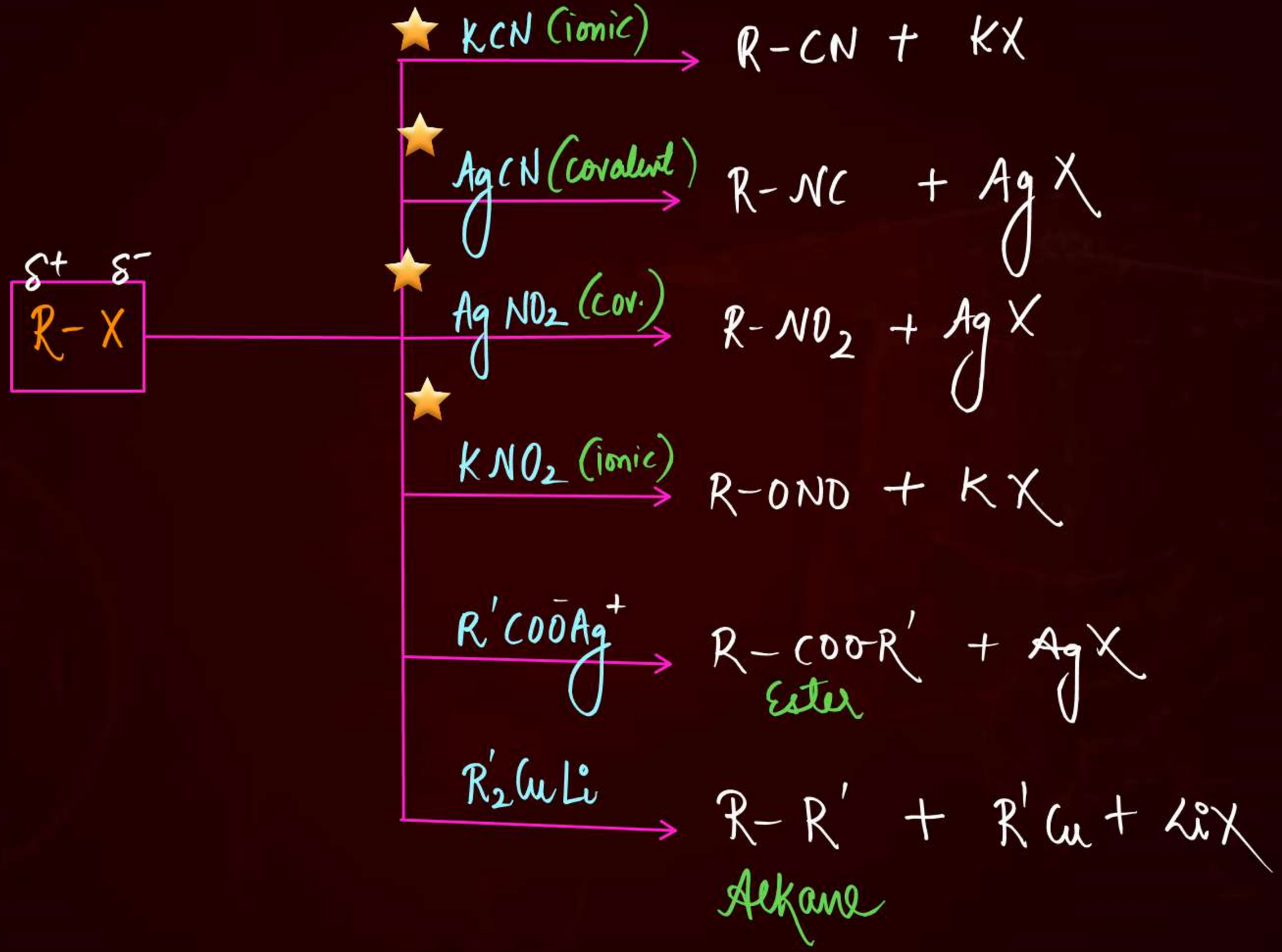
Chemical Properties of Haloalkanes

1. Nucleophilic Substitution Rxn (N.S.R.)
2. Elimination Rxn
3. Rxn with Metals

1. N.S.Rxn :




δ+ δ-
R - X
aq. KOH / NaOH / AgOH
or moist Ag_2O
$R-OH + KX/NaX/AgX$
Alcohol
K^+SH^-
$R-SH + KX$
$R'O^-Na^+$
$R-O-R' + NaX$
Ether
$R'S^-Na^+$
$R-S-R' + NaX$
NH_3 (excess)
$R-NH_2 + NH_4^+X^-$
Amine
I^- / acetone
$R-I + X^-$


δ+ δ−
R – X
KCN (ionic)
R – CN + KX
AgCN (covalent)
R – NC + AgX
AgNO2 (cov.)
R – NO2 + AgX
KNO2 (ionic)
R – ONO + KX
R'COO⁻Ag⁺
R – COOR' + AgX
Ester
R'2CuLi
R – R' + R'Cu + LiX
Alkane

N.S. Rxn

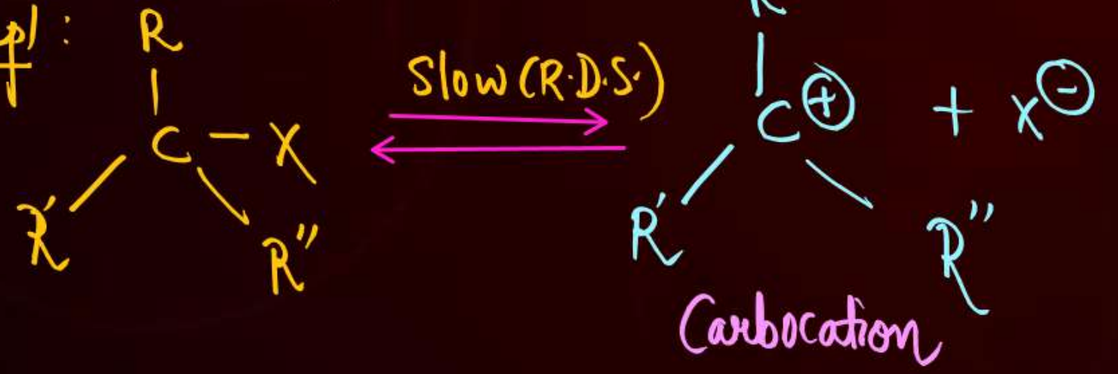
S_N1

→ Unimolecular

→ favoured in polar protic solvent such as H_2O, CH_3COOH etc.

→ 2 steps

Step I:

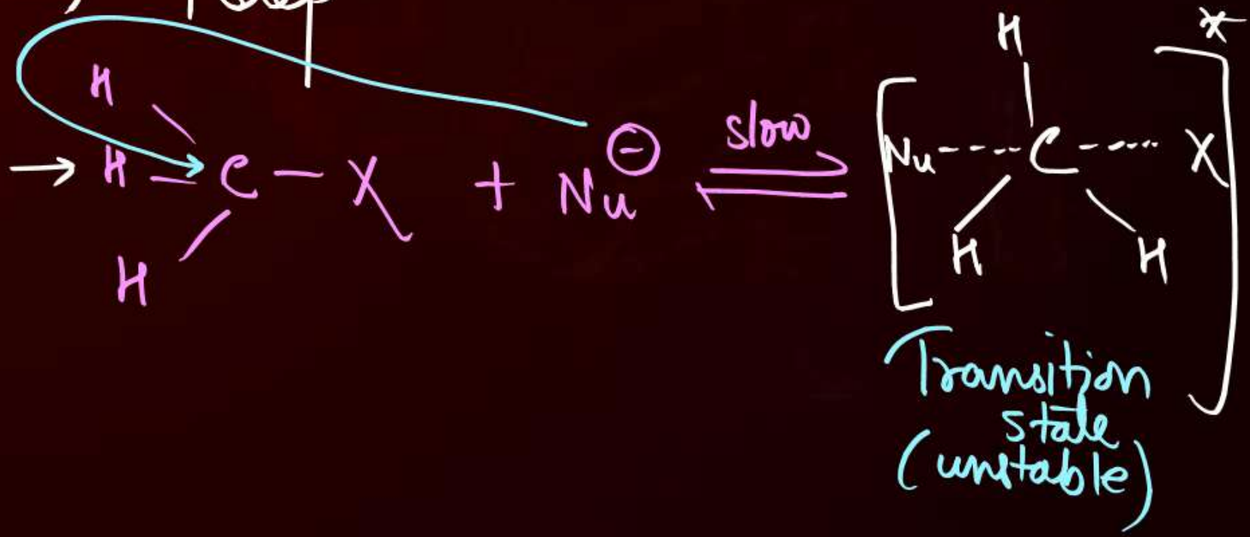


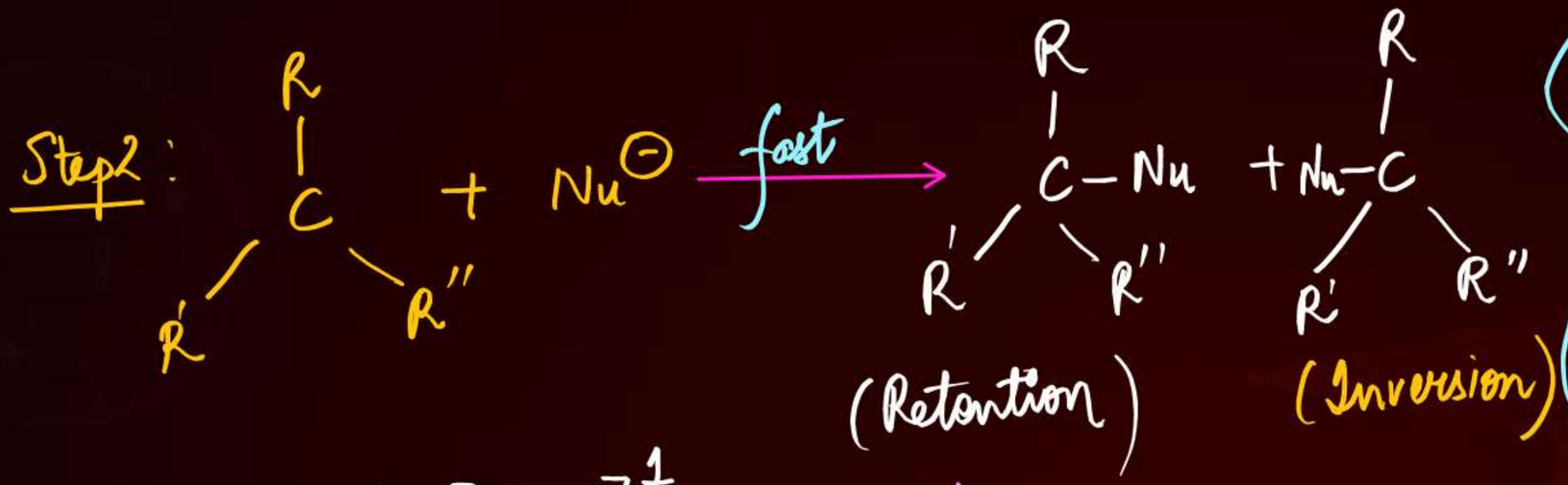
S_N2

→ Bimolecular

→ favoured in polar aprotic solvent such as DMF, DMSO, CH_3CN etc.

→ 1 step





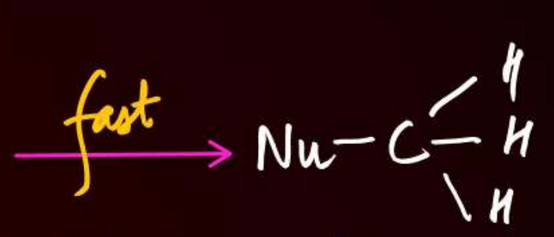
→ Rate = $K[R-X]^1$ Order = 1, Molecularity = 1

→ Reaction intermediate : Carbocation

→ Order of reactivity of R-X :

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

→ R–I > R–Br > R–Cl > R–F



→ Walden inversion

→ Rate = $K[R-X]^1[Nu^-]^1$

Order = 2

Molecularity = 2

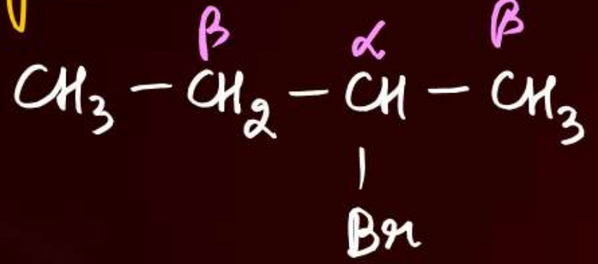
→ Reaction intermediate : Transition state

S_N2 : $CH_3X > 1^\circ > 2^\circ > 3^\circ$

R–I > R–Br > R–Cl > R–F

2. Elimination rxn :

Dehydrohalogen^{n} :



alc. KOH, Δ

or $C_2H_5O^-K^+$, Δ

$CH_3-CH_2-CH=CH_2$ + $CH_3-CH=CH-CH_3$

(Minor) (Major)

as per Saytzeff's Rule

★ $(CH_3)_3CO^-K^+$, Δ

bulky base

$CH_3-CH_2-CH=CH_2$ +

(Major)

$CH_3-CH=CH-CH_3$

(Minor)

3. Rxn with Metals :

(i) $R-X + Mg \xrightarrow{\text{dry ether}} \overset{-}{R}-\overset{+}{Mg}-X$

Grignard's Reagent

(ii) $R-X + 2Li \xrightarrow{"} R-Li + LiX$

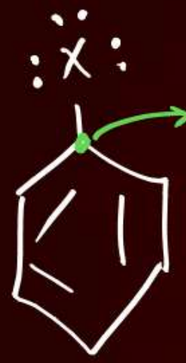
(iii) Wurtz Rxn :

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

Chemical Properties of Haloarenes

1. Nucleophilic Subs^{n} Rx^{n} :

→ Haloarenes



(33.33% s-char.)

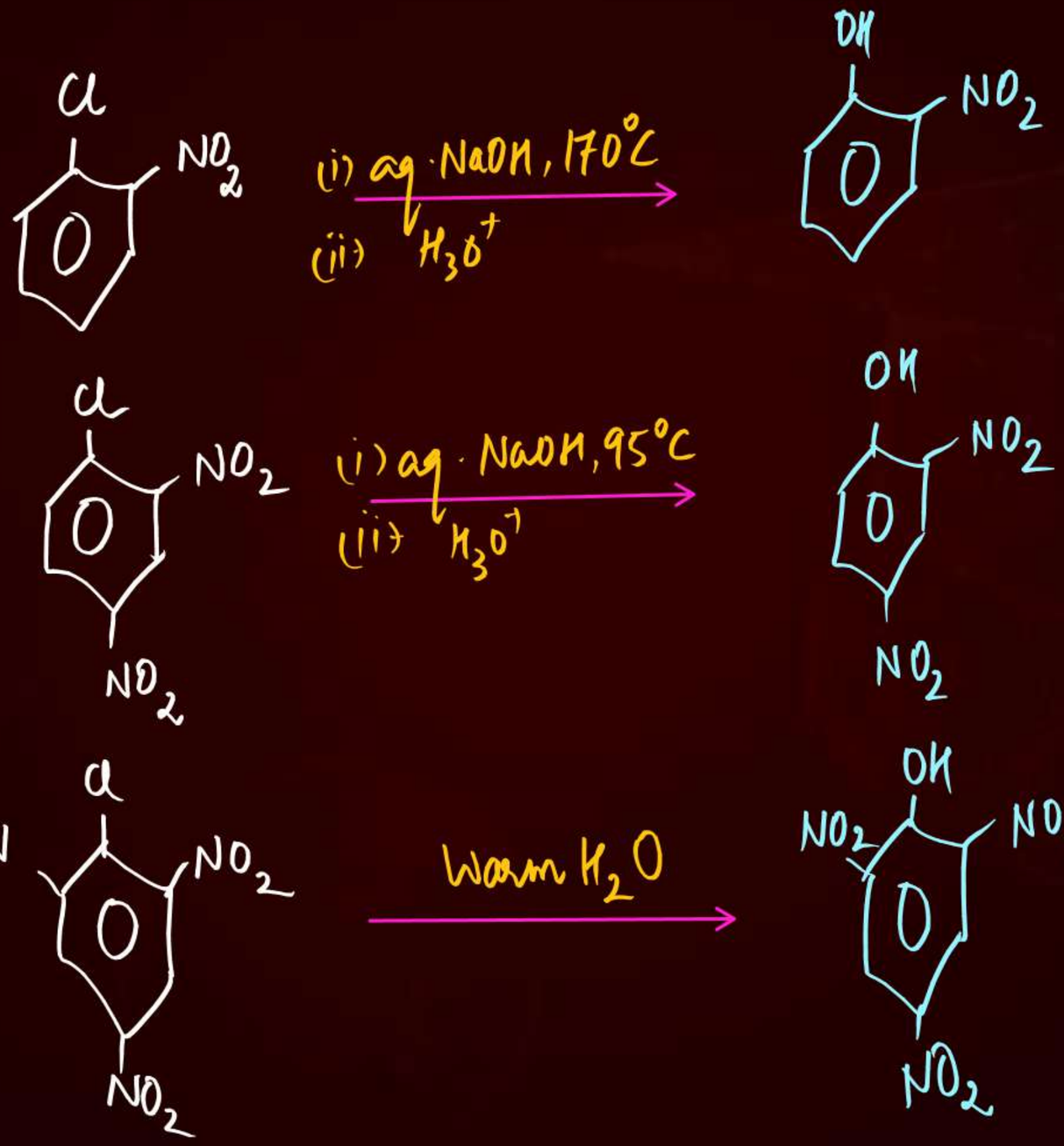
↓

→ don't undergo N.S.Rx^{n} easily

→ undergo N.S. Rx^{n} in extreme conditions.

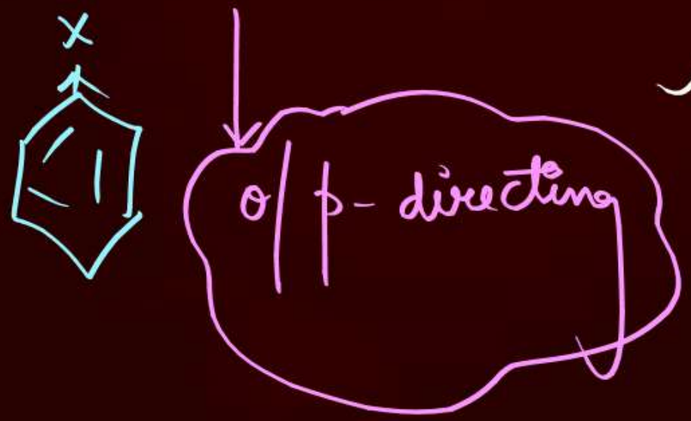
$C_{sp^2}-X$: less polar

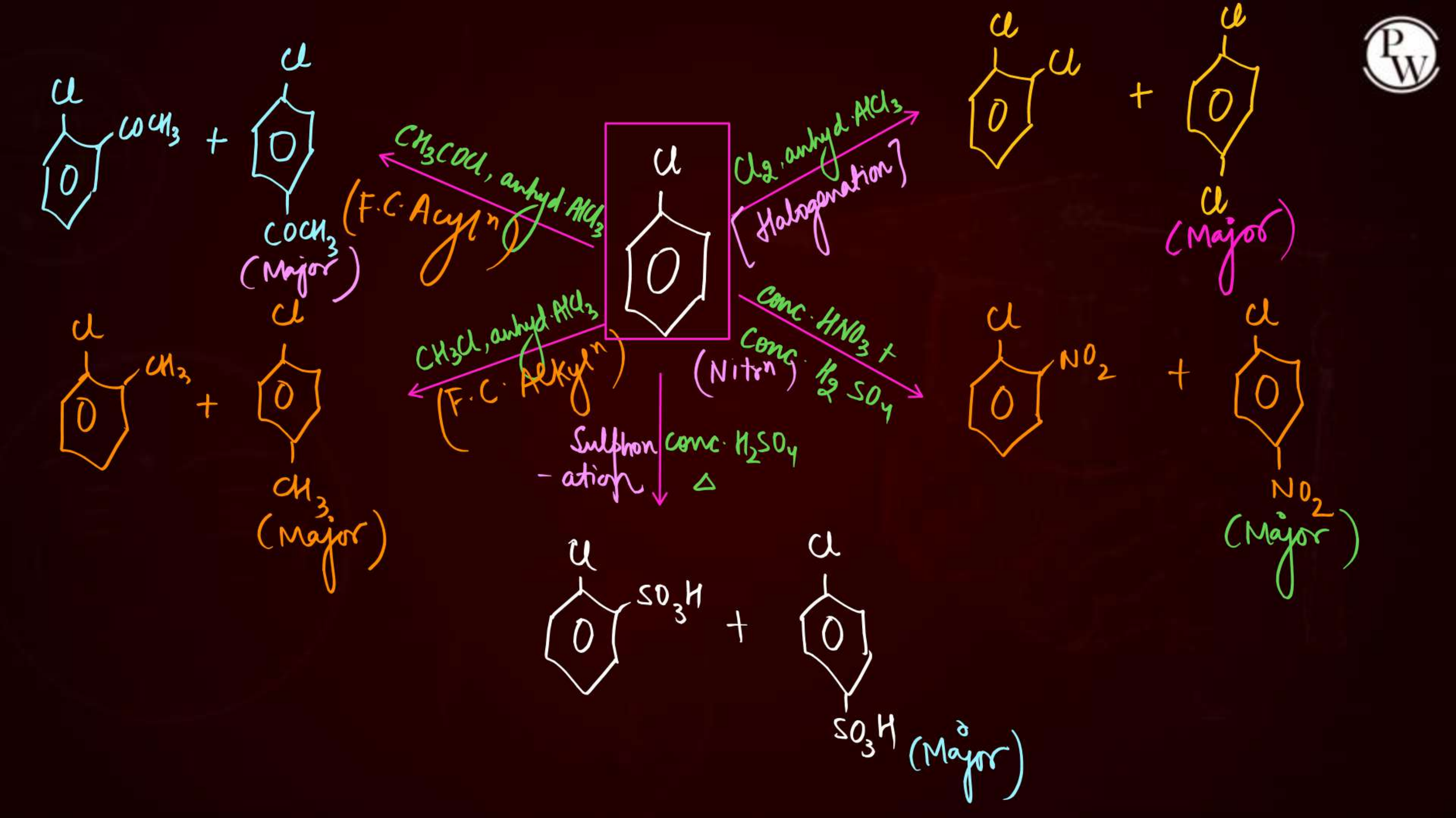
↳ partial double bond char. due to resonance


Cl
NO2
(i) aq. NaOH, 170°C
(ii) H3O+
OH
NO2
Cl
NO2
NO2
(i) aq. NaOH, 95°C
(ii) H3O+
OH
NO2
NO2
Cl
O2N
NO2
NO2
Warm H2O
OH
NO2
NO2
NO2

2. Electrophilic Subs^{n} Rx^{n} :

↳ Haloarenes : deactivating towards E·S Rx^{n} (due to −I effect)



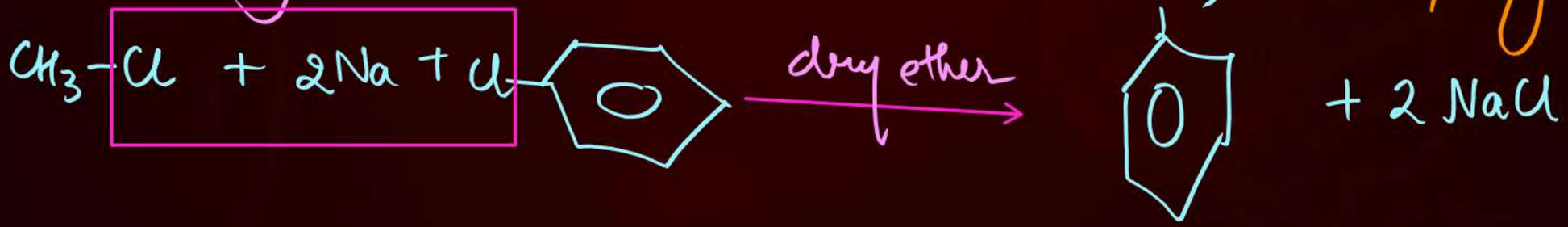

Cl
COCH3
(Major)
CH3COCl, anhyd. AlCl3
(F.C. Acylⁿ)
Cl2, anhyd. AlCl3
[Halogenation]
Cl
Cl
(Major)
CH3
CH3
(Major)
CH3Cl, anhyd. AlCl3
(F.C. Alkylⁿ)
Conc. HNO3 +
Conc. H2SO4
(Nitrⁿ)
NO2
NO2
(Major)
Sulphon-ation
conc. H2SO4
Δ
SO3H
SO3H
(Major)

3. Rxn with Metals :

(i) Fittig Rxn :

Biphenyl

(ii) Wurtz - Fittig Rxn :



Toluene

(iii.)

Grignard Reagent

(iv) Ullmann Rxn :

Biphenyl

Polyhalogen compounds

(i) CH_2Cl_2

(ii) $CHCl_3$

(iii) CHI_3

(iv) CCl_4

(v) Freons

(vi) DDT

$$CHCl_3 + \frac{1}{2}O_2 \xrightarrow{(air)} COCl_2 + HCl$$

(Phosgene)

↳ Highly toxic

Homework

→ Read NCERT

→ Solve NCERT Exercise

THANK YOU