MIND MAP FOR JEE ASPIRANTS

Organic Chemistry

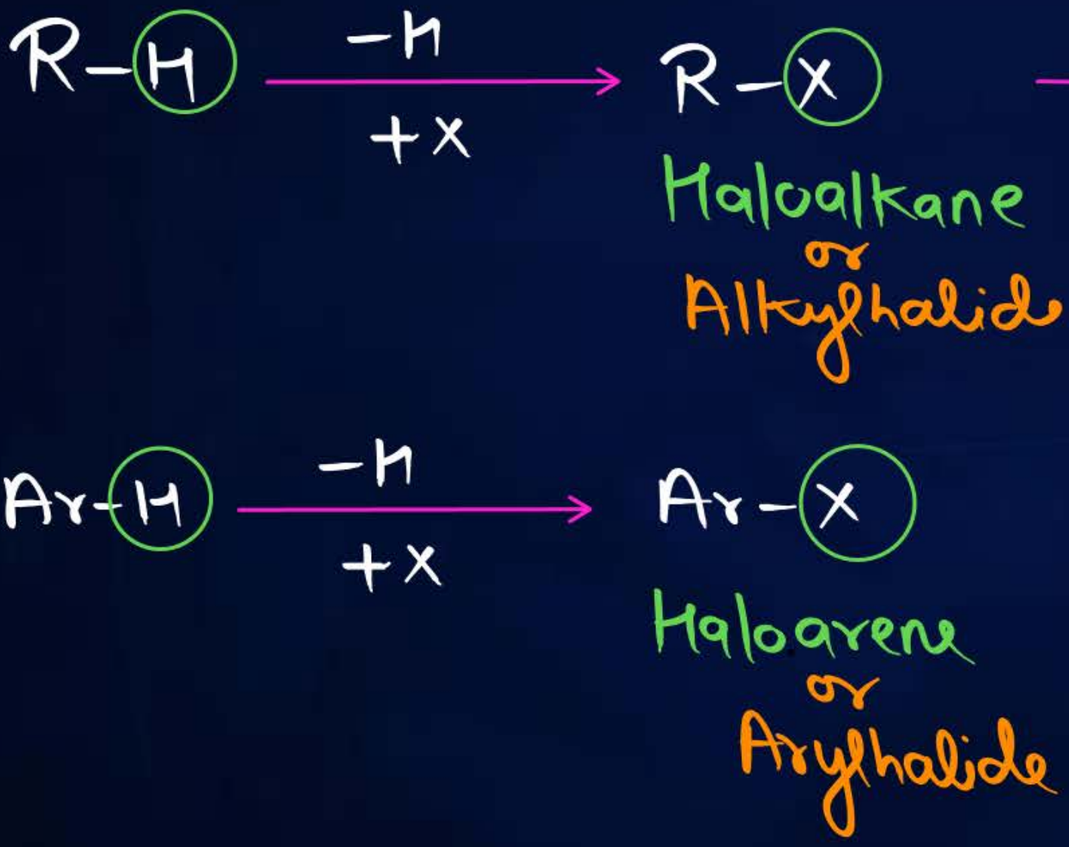
Haloalkane and Haloarenes

By- Yogesh Jain (YJ) Sir

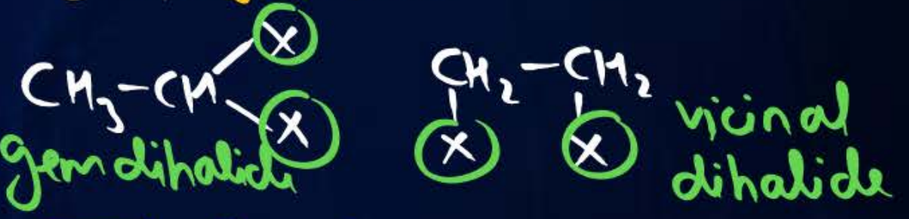
Today's Targets

1. Haloalkane and Haloarenes

Haloalkanes and Haloarenes



- Monohaloalkane
  CH_3-X, CH_3-CH_2-X etc.
- Dihaloalkane



- Trihaloalkane
  $CHCl_3$, $CHBr_3$, CHI_3
- Tetrahaloalkane
  CCl_4

Chemical properties of Haloalkane

- Nucleophilic Substitution Rxn. (S_N rxn.)
  - SN_1, SN_2, SN_i, SN_{NGP}
- Elimination Rxn.
  - E_1, E_2, E_{1cB}
- Rxn. with Metal

Nucleophilic substitution Reaction

S_N1

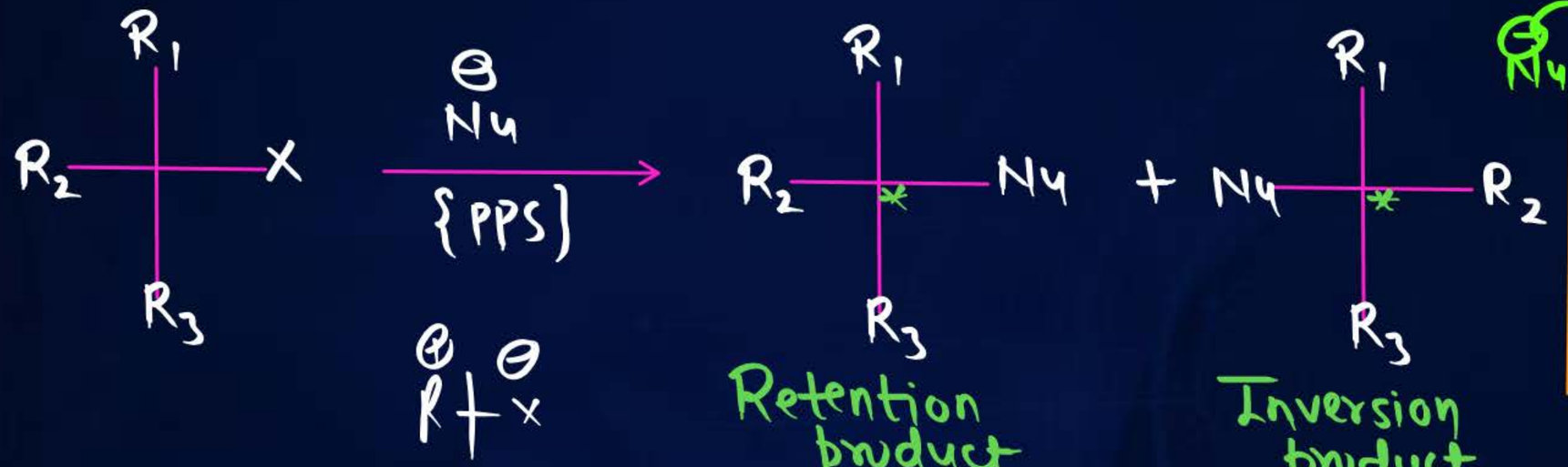
{Unimolecular $\overset{\ominus}{Nu}$ Subst^n Rxn.}

S_N2

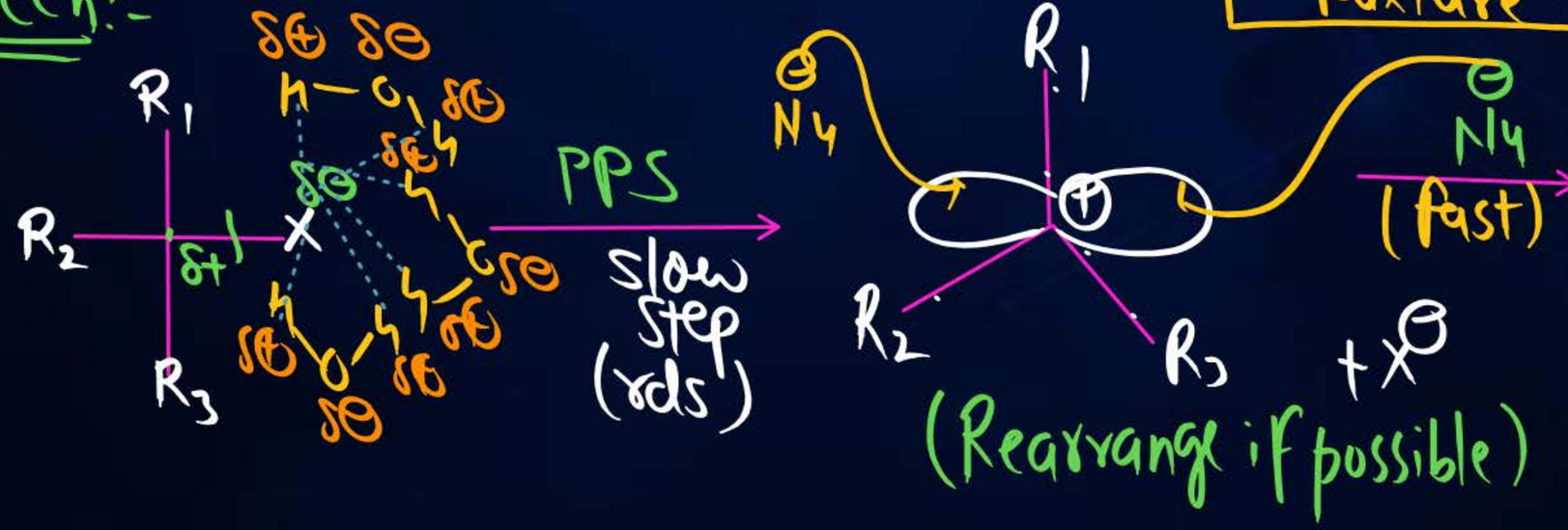
{ Bimolecular $\overset{\ominus}{Nu}$ Subst^n Rxn.}

S_N1 Rxn :- { Unimolecular $\overset{\ominus}{Nu}$ Subst^n Rxn. }

Rxn :-



Mech^n :-

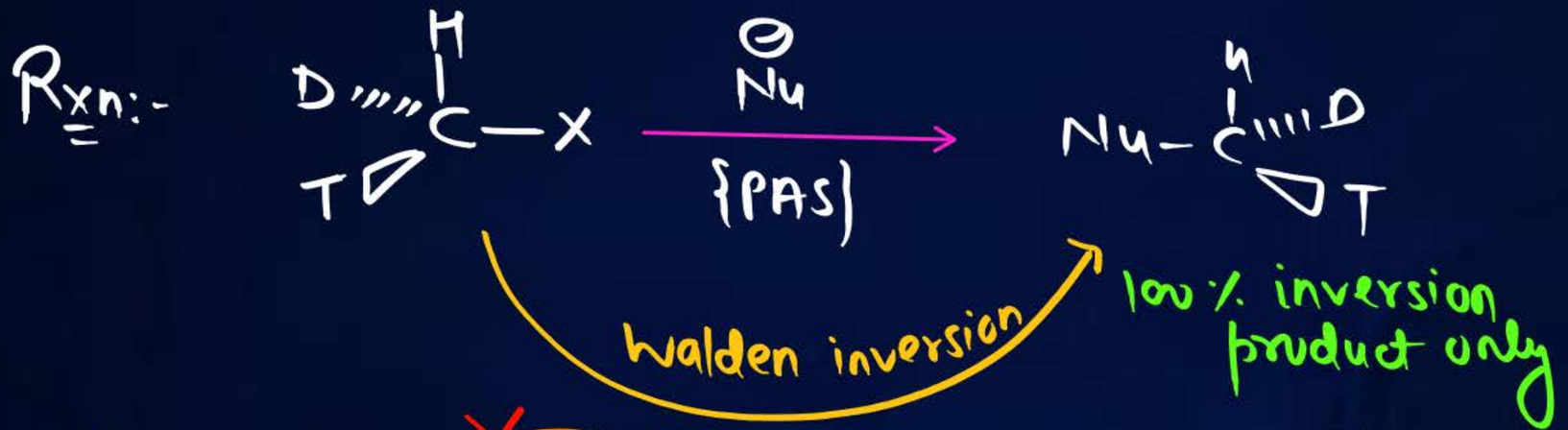


Rate $\propto k[R\text{-}X]$

$[H_2O]$

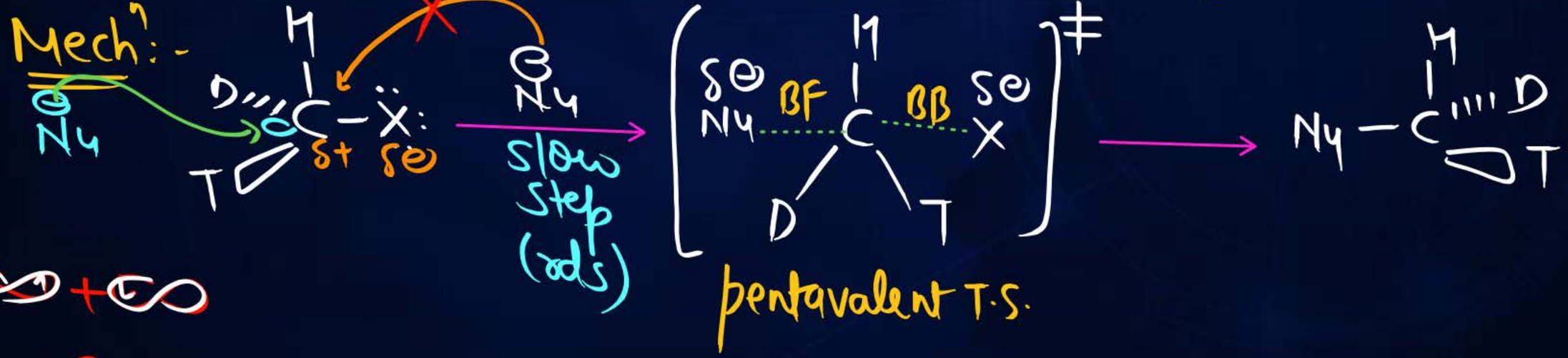
Rate $\propto k[R\text{-}X]^1$

S_N2 rxn. {Bimolecular Nu Substⁿ Rxn.}



Rate $\propto k[R\text{-}X]^1[Nu^-]^1$

$\sigma = 2$



SN_1	SN_2
(1) Unimolecular $\overset{\ominus}{Nu}$ Substⁿ	(1) Bi molecular $\overset{\ominus}{Nu}$ Substⁿ
(2) Step → 2	(2) Step → 1
(3) Slow step → 1st	(3) Slow step → 1st
(4) Int → $C^{\oplus}$	(4) Int → X T.S. ✓
(5) Rate $\propto k[R-X]^1$	(5) Rate $\propto k[R-X]^1[\overset{\ominus}{Nu}]^1$
(6) O = 1, M = 1	(6) O = 2, M = 2
(7) PPS	(7) PAS
(8) Rearr. ✓	(8) Rearr. X
(9) $\overset{\ominus}{Nu}$ poor	(9) $\overset{\ominus}{Nu}$ Strong

SN_1

(10) L.grp → moderate, good

(11) Favourable cond^n :→ 3° R–X

(12) Rate of $SN_1 \propto$ St. of $C^{\oplus}$

Rate of SN_1 :→ 3° R–X > 2° R–X > 1° R–X > ~~CH_3–X~~

ii) If alkyl grp. is same

Rate of $SN_1 \propto$ L.grp. ability

Rate of SN_1 :→ R–I > R–Br > R–Cl > ~~R–F~~

(13) Racemic Mixture

SN_2

(10) L.grp → moderate, good

(11) Favourable cond^n → CH_3–X ✓

(12) Rate of $SN_2 \propto \frac{1}{\text{Steric hindrance at R–X}}$

Rate of SN_2 :→ CH_3–X > 1° R–X > 2° R–X >> ~~3° R–X~~

ii) If alkyl grp. is same

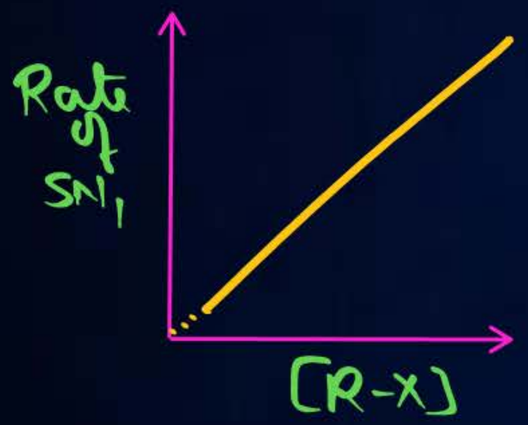
Rate of $SN_2 \propto$ L.grp. ability

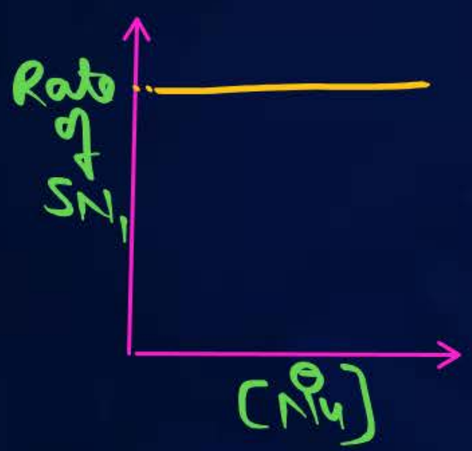
Rate of SN_2 :→ R–I > R–Br > R–Cl > ~~R–F~~

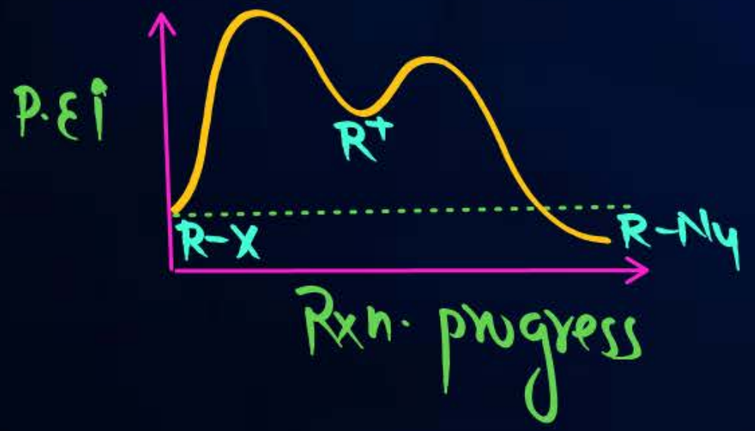
(13) 100% Inversion product

S_N1

(14) Rate $\propto k[R-X]^1$

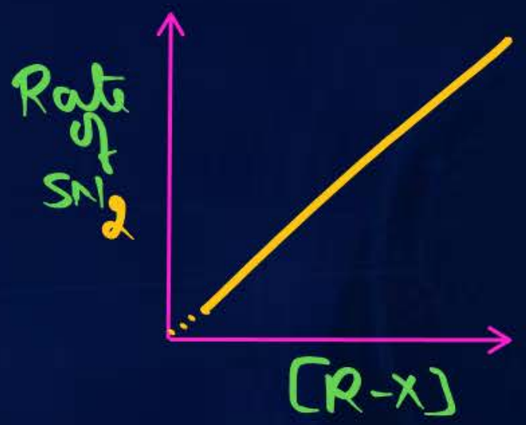


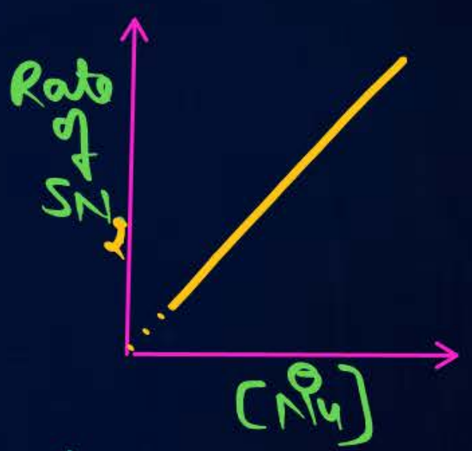


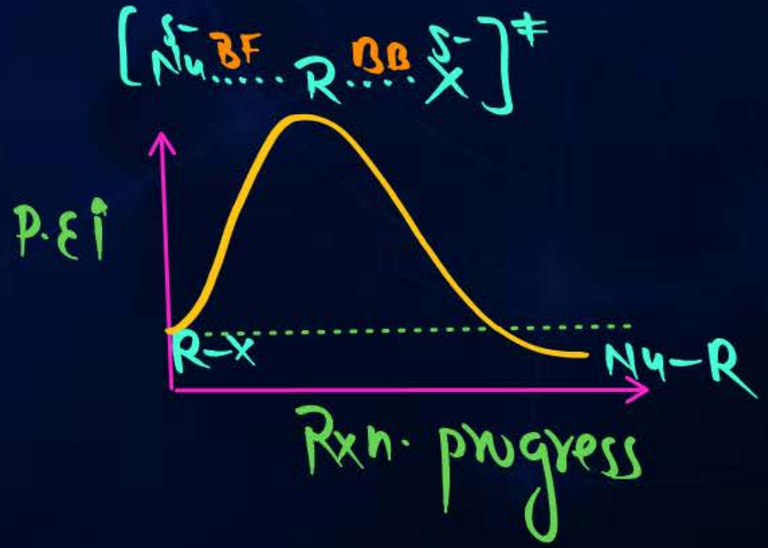


S_N2

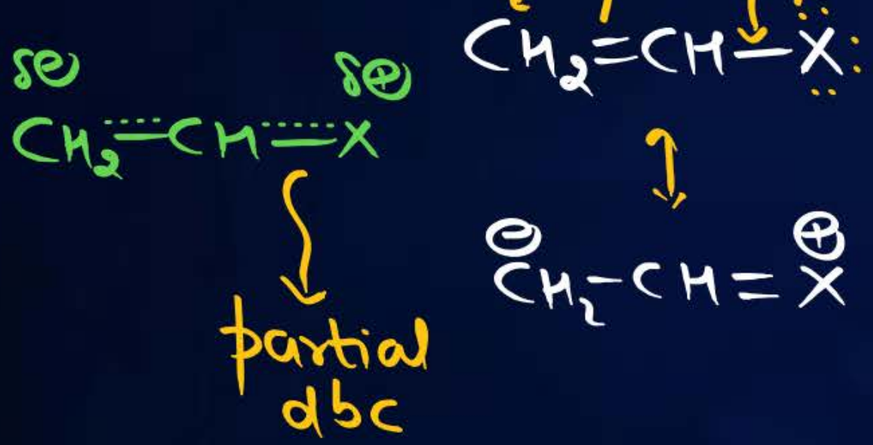
(14) Rate $\propto k[R-X]^1[\overset{\oplus}{N}H_4]^1$

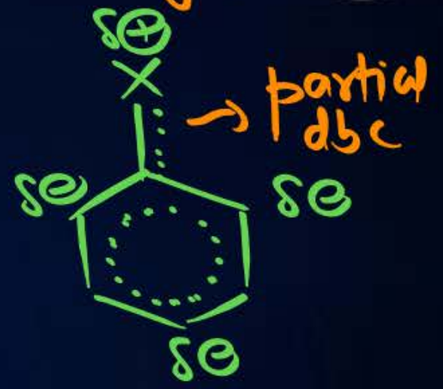






Que: Vinyl halide and aryl halide does not give S_N Rxn Why?

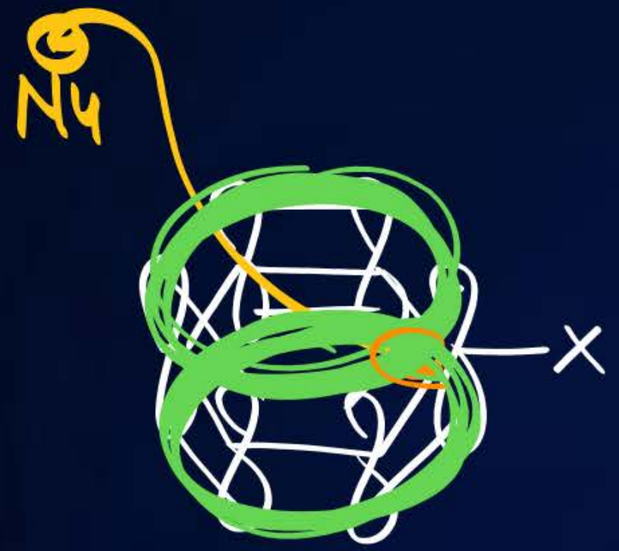


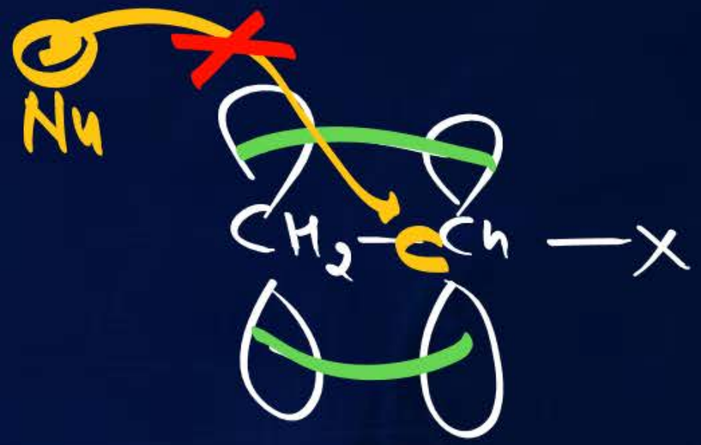


(1) Due to Resonance partial double bond character arises in C–X bond so weak l.gp.

(2) Yadi aapke ziddi aagyi aapne bond tod diya $C^{\oplus}$ banaya lekin fir aapko dard aajayega kyunki $C^{\oplus}$ unstable banaya.

(3)





Due to repln in $\ominus$ cloud of Benzene $\ominus$ Nu S_N2 not possible

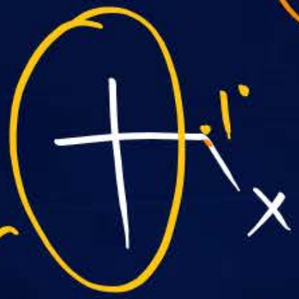
Following substrates does not gives S_N2 rxn :-

(1) 

(2) $CH_2=CH-X$

(3) 

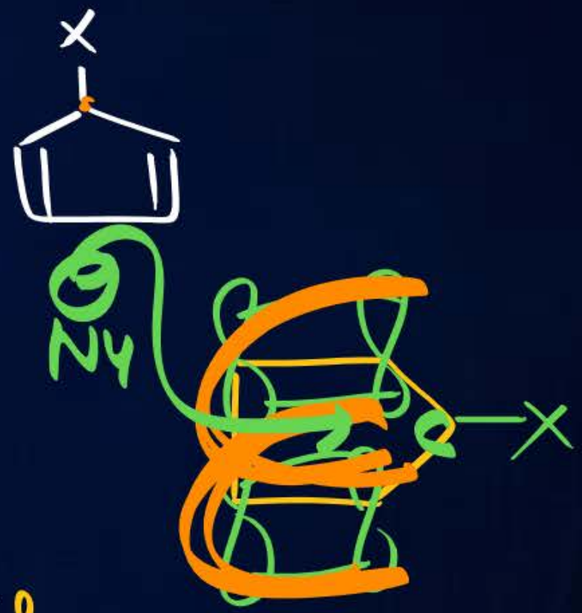
(4) 

(5) 

(6) CH_3-F

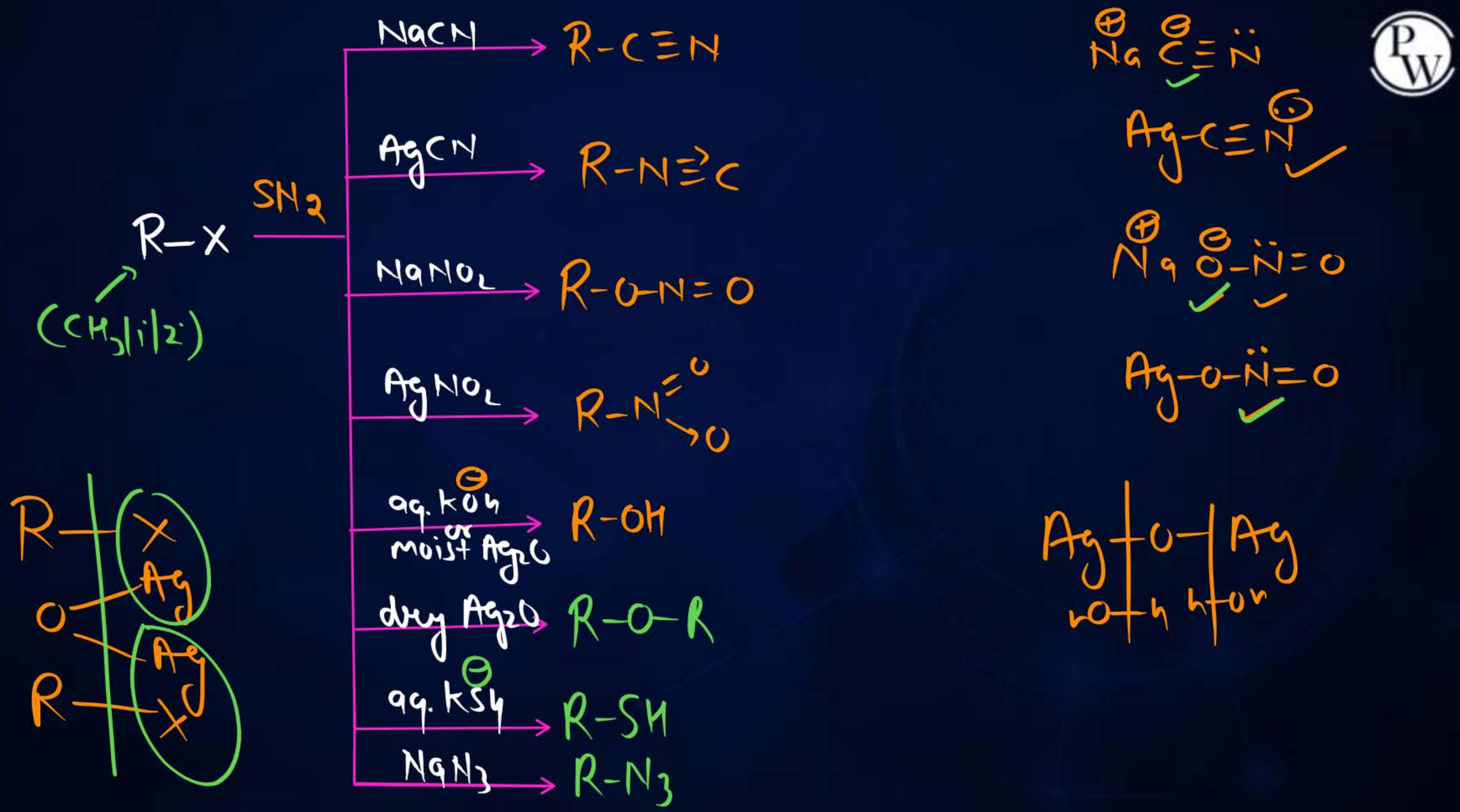
(7) 

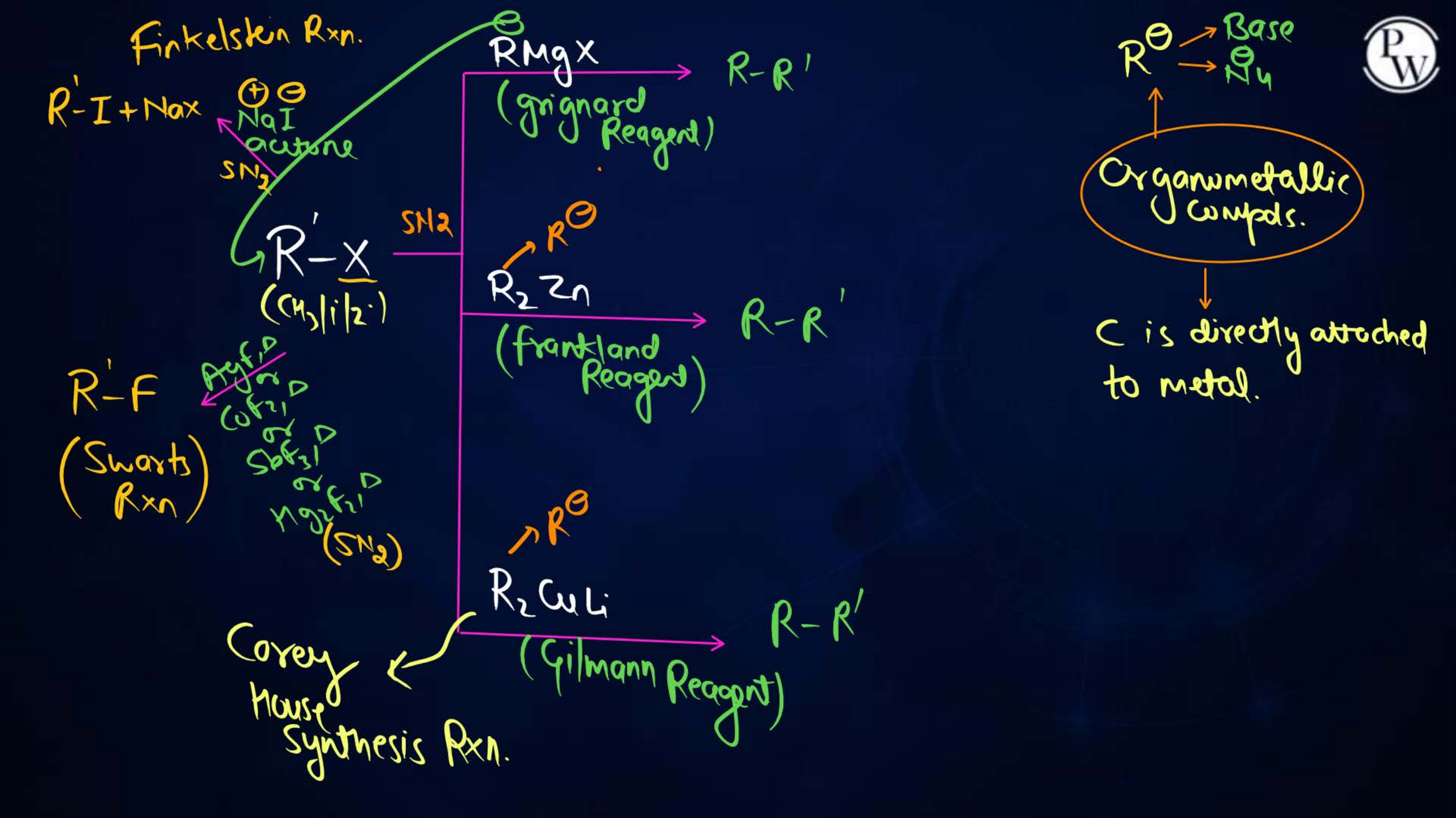
Neopentyl halide



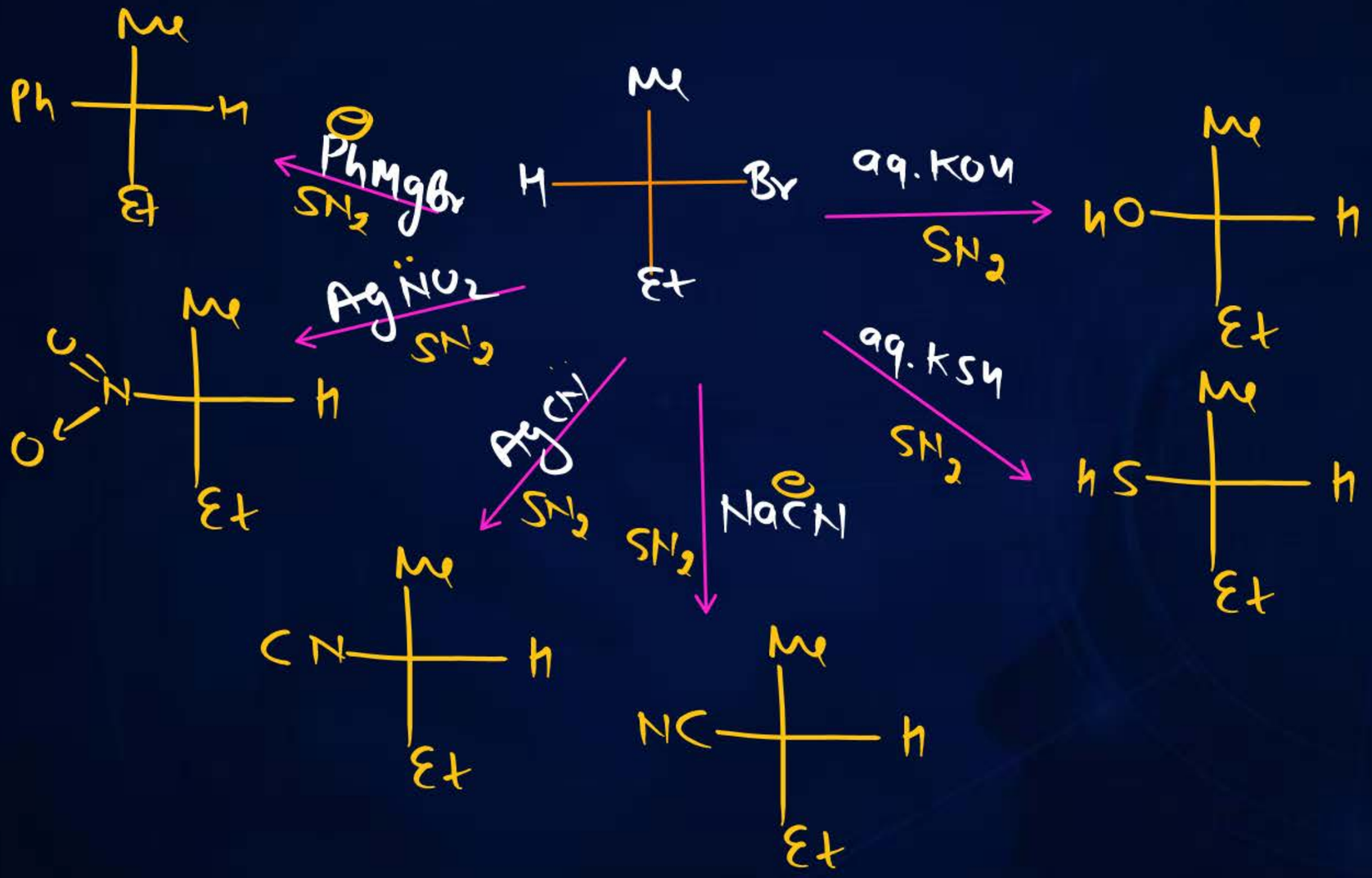
Substrate	S_N1	S_N2
① CH_3-X $(X \neq F)$	✗	Excellent
② $R-CH_2-X$	✗	✓
③ $R-\underset{R}{\overset{\overset{2^\circ}{|}}{CH}}-X$	✓ (PPS)	✓ (PAS)
④ $R-\underset{R}{\overset{R}{\overset{|}{\overset{3^\circ}{C}}}}-X$	✓	✗
⑤ $R\underset{-I}{-O}-\overset{\delta+}{C}H_2-X$	$R\ddot{O}-\overset{\oplus}{C}H_2$ ✓ (PPS)	✓ (PAS)
⑥ $R-\underset{\underset{-I}{O}}{\overset{\overset{\delta+}{\leftarrow}}{C}}CH_2-X$	✗	✓ (Excellent)

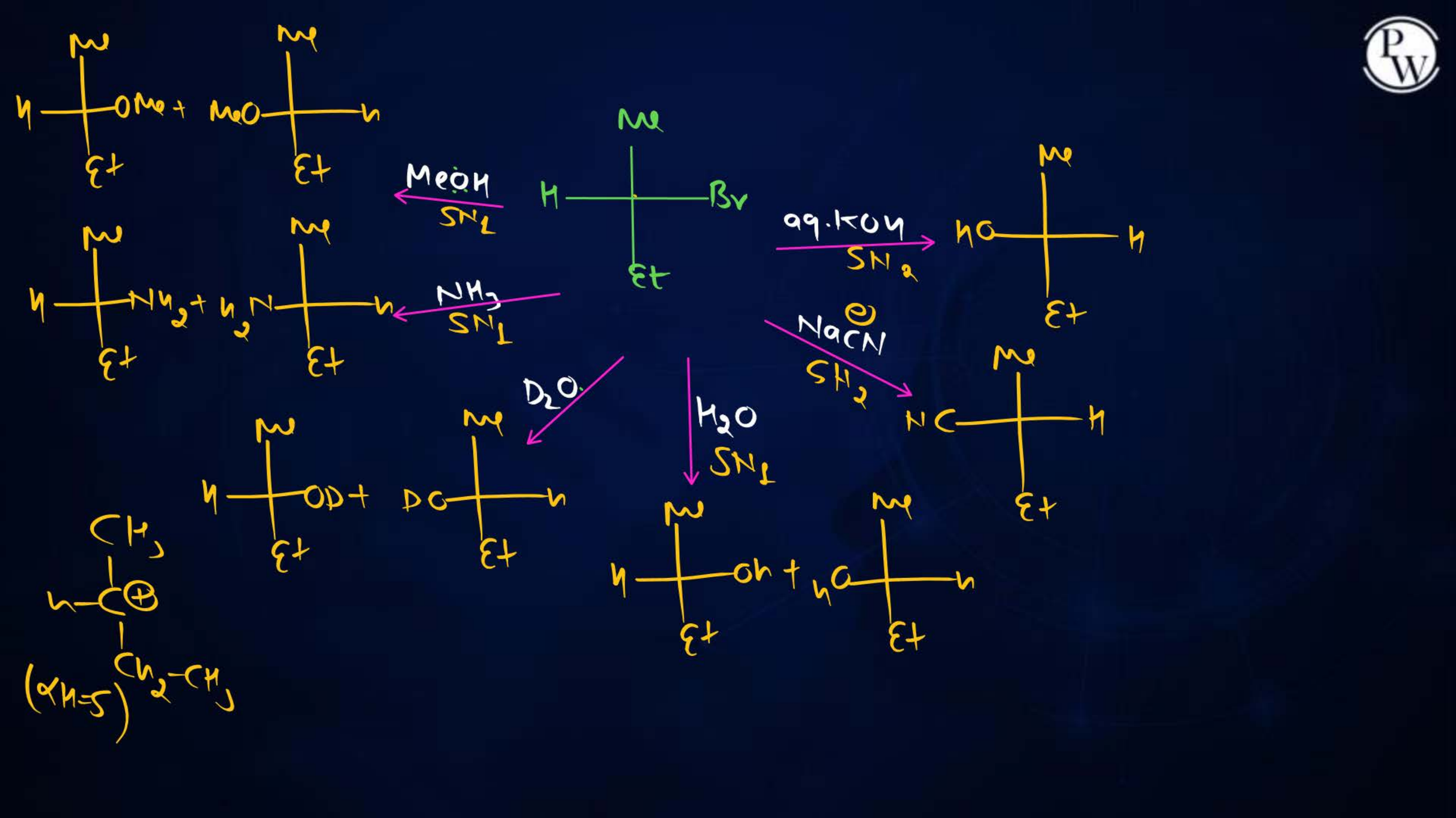
Substrate	S_N1	S_N2
(7) 	✗	✗
(8) $CH_2=CH-X$	✗	✗
(9) 	✗ Bredt's rule violate	✗
(10) $R-\overset{-I}{CH}=CH-\overset{\delta+}{CH_2}-X$	✓ (PPS)	✓ (PAS)
(11) 	✓ (PPS)	✓ (PAS)
(12) 	✗ Antiaw	✗


R–X
(CH3Li/Zn)
SN2
NaCN
R–C≡N
AgCN
R–N≡C
NaNO2
R–O–N=O
AgNO2
R–N=O
O
aq. KOH
or
moist Ag2O
R–OH
dry Ag2O
R–O–R
aq. KSH
R–SH
NaN3
R–N3
R
X
Ag
O
Ag
R
X
Na C≡N
Ag–C≡N
Na O–N=O
Ag–O–N=O
Ag–O–Ag
both
both


Finkelstein Rxn.
R'-I + NaX
NaI
acetone
SN2
R'-X
(Cl/I/Br)
SN2
RMgX
(grignard Reagent)
R-R'
R⊖
R2Zn
(frankland Reagent)
R-R'
R'-F
(Swarts Rxn)
AgF, Δ
or
CoF2, Δ
or
SbF3, Δ
or
Hg2F2, Δ
(SN2)
R⊖
R2CuLi
(Gilmann Reagent)
R-R'
Corey House Synthesis Rxn.
R⊖ → Base
R⊖ → N4
Organometallic Compds.
C is directly attached to metal.

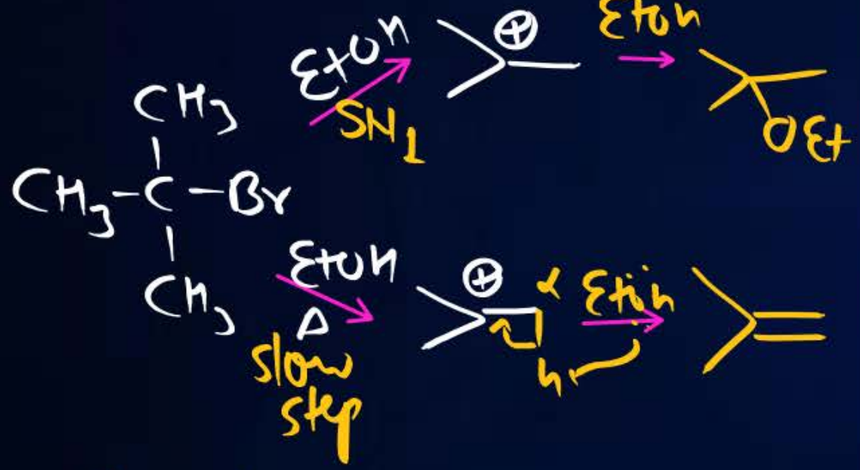
(3)


Me
Ph
H
Et
PhMgBr
SN2
H
Br
aq. KOH
SN2
HO
AgNO2
SN2
O
N
O
AgCN
SN2
NaCN
SN2
aq. KSH
SN2
HS
CN
NC


MeOH
SN1
aq. KOH
SN2
NH3
SN1
NaCN
SN2
D2O
H2O
SN1

Elimination Rxn:

E_1 rxn.



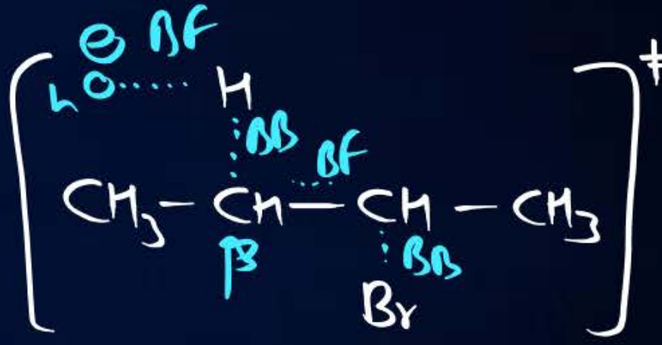
low temp + solvolysis → SN_1

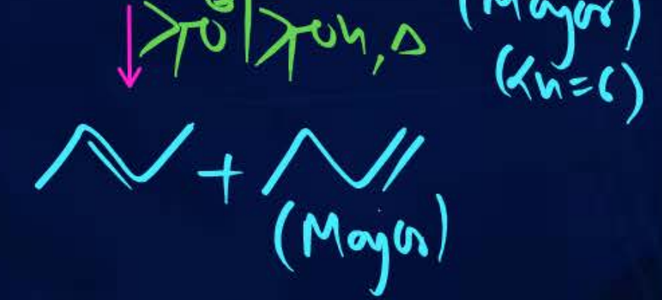
high temp + solvolysis → E_1

1. Step → 2
2. Slow step → 1
3. Int → $C^{\oplus}$
4. Rearr → ✓
5. Rate $\propto k[R\text{-}X]$
6. $O = 1$ $M = 1$
7. Rate $\propto$ St. of $1^{st} C^{\oplus}$
8. Major product St. alkene

E_2 rxn.

① Dehydrohalogenation {Anti elim}





Dehydrohalogenating Reagents:-

① (alc. KOH, Δ)

② $EtO^{\ominus}$ / EtOH, Δ

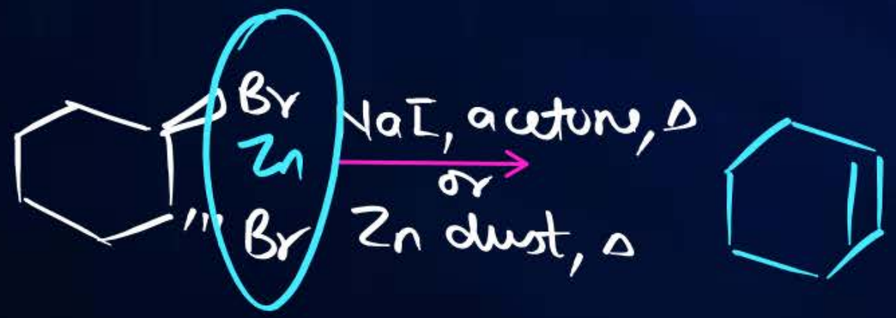
③ $tBuO^{\ominus}$ / tBuOH, Δ

④ $NaNH_2$, Δ

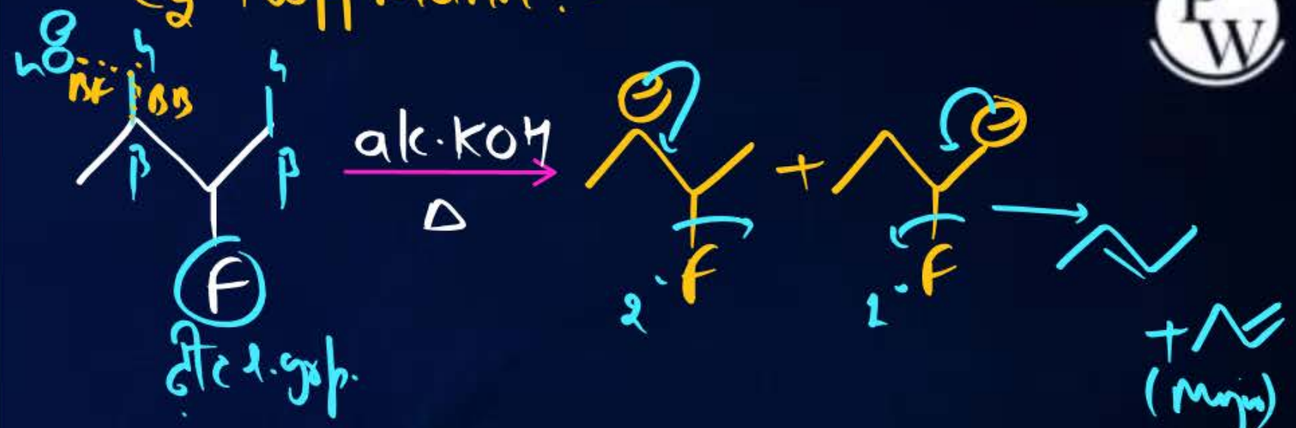
Dehalogenation Rxn.

(E_2 rxn.) (Anti elim^n)

Ex:-

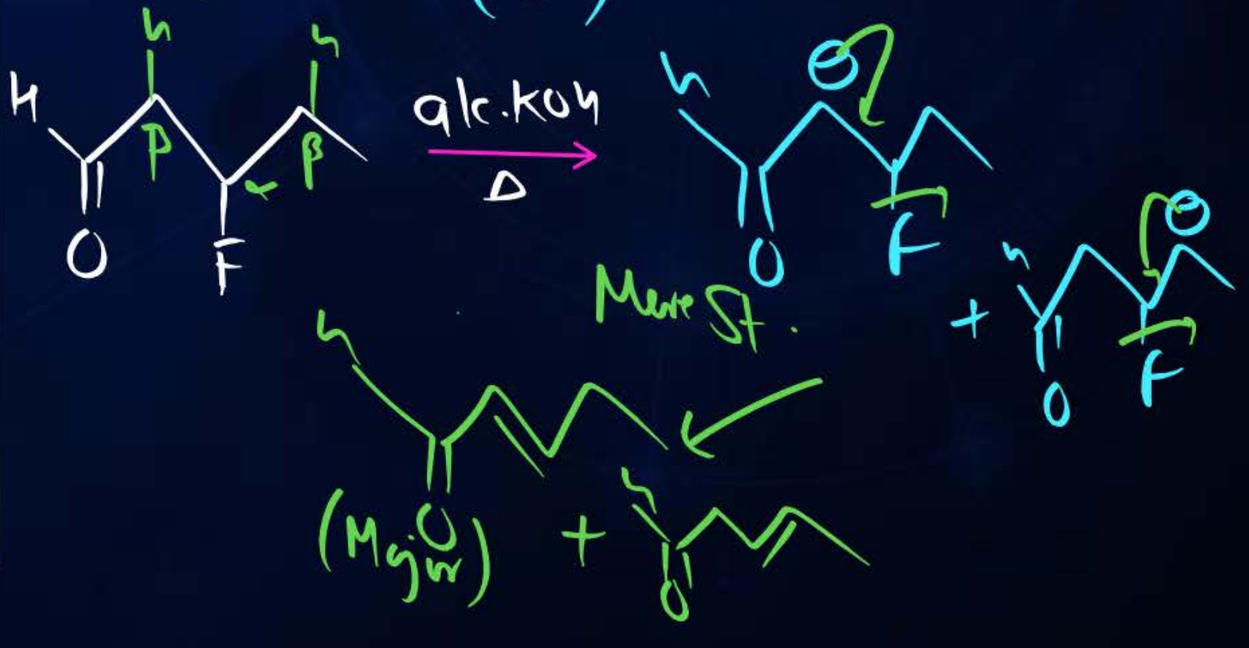


E_2 Huffmann :-



Gehri Baat :- Major product will be decided by st. of partial $C^\ominus$

E_{1cB} Rxn :- ($C^\ominus$)



Comparison of $SN_1 / SN_2 / E_1 / E_2$

SN_1 (PPS)

E_1 (PPS + Δ)

E_2 (Strong Base + Δ + β-H)

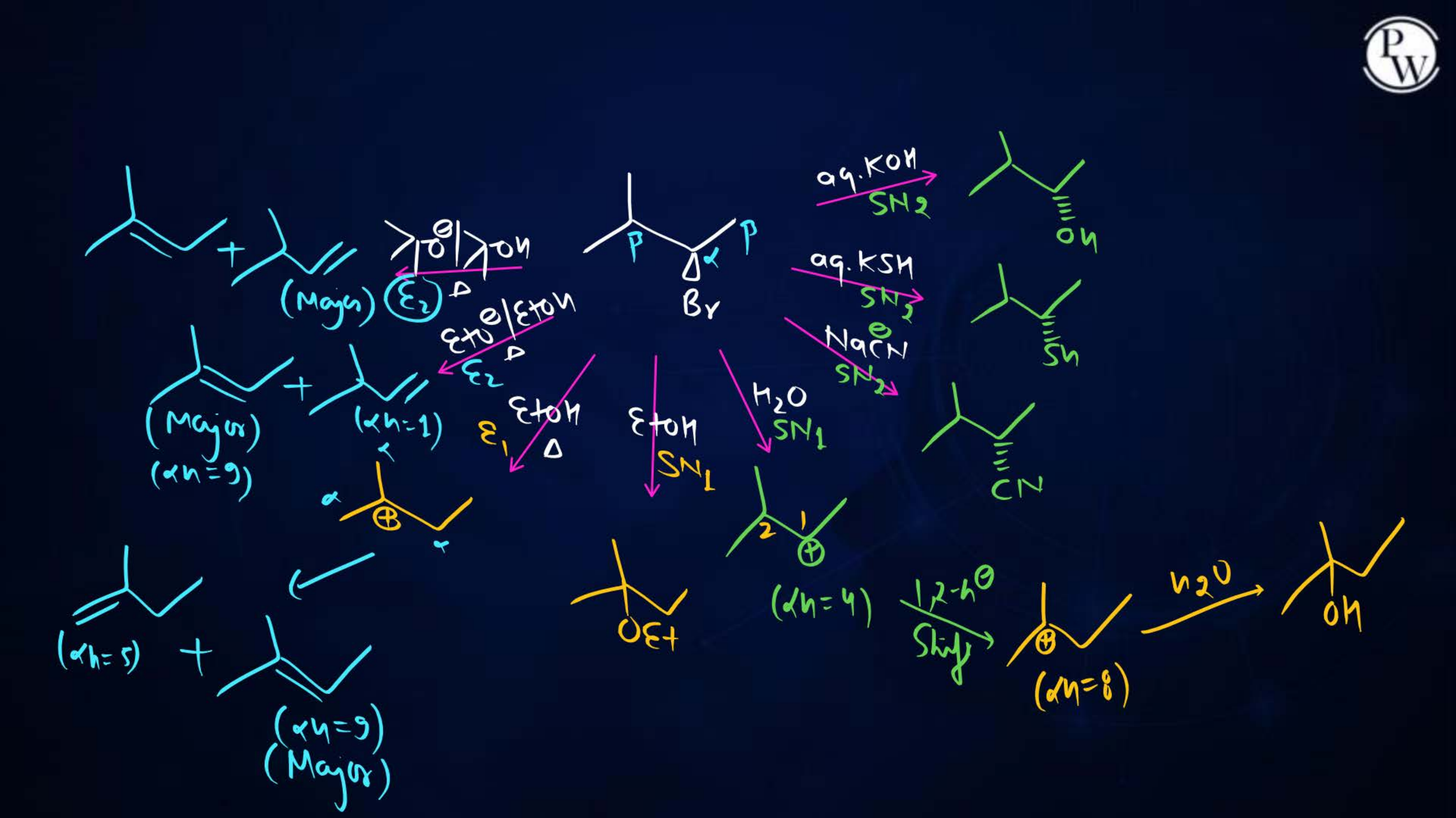
① CH_3-X → Excellent SN_2 only

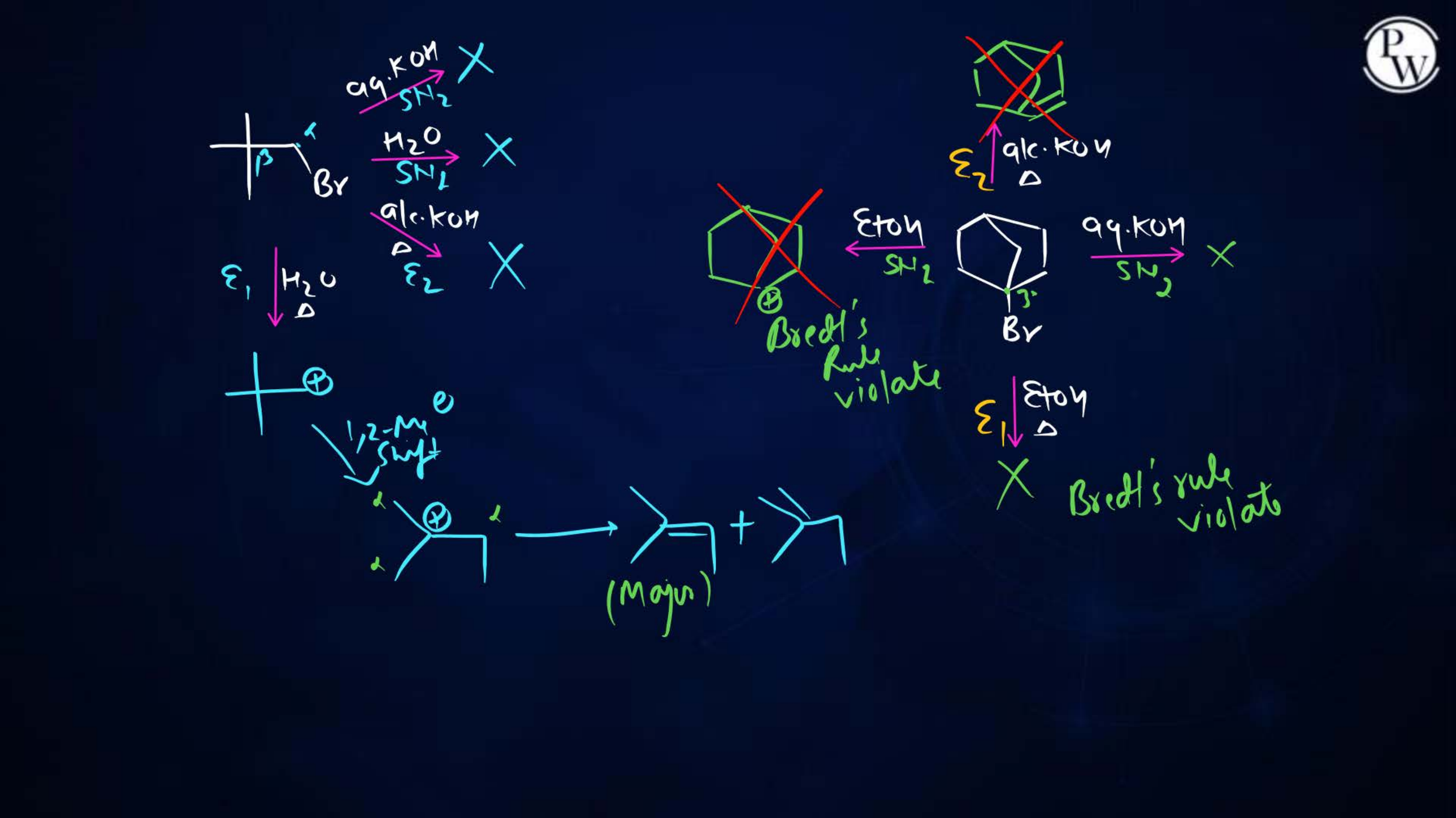
② $R-\overset{1^\circ}{C}H_2-X$

- SN_2 {Strong $N_4^{\ominus}$} {aq.KOH, aq.KSH, NaCN, KCN, AgCN, $NaNO_2$, RMgX}
- E_2 {Strong Base + β-H} {(Alc.KOH, Δ), ($EtO^{\ominus}$/EtOH, Δ), ($\langle\rangle O^{\ominus}$/$\langle\rangle$OH, Δ), ($NaNH_2$, Δ)}

③ $R-\overset{2^\circ}{C}H-X$ (R)

- SN_1 (PPS) {H_2O, R-OH, NH_3, D_2O, EtOH etc.}
- E_1 (PPS + Δ) {H_2O (Δ), R-OH (Δ), NH_3 (Δ) etc.}
- SN_2 (Strong $N_4^{\ominus}$)
- E_2 (Base + Δ + β-H)


(Major)
E_2
$\ominus$ / EtOH
Δ
E_2
(Major)
(αH=9)
(αH=1)
EtOH
Δ
E_1
EtOH
S_N1
H_2O
S_N1
aq. KOH
S_N2
aq. KSH
S_N2
NaCN
S_N2
Br
P
P
α
OH
SH
CN
OEt
(αH=4)
1,2-H Shift
(αH=8)
H_2O
OH
(αH=5)
(αH=9)
(Major)

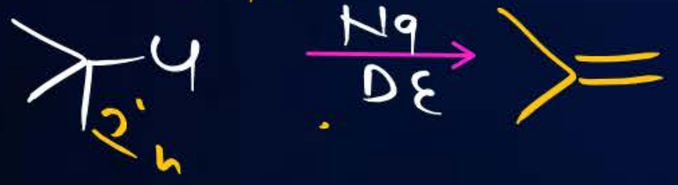

aq.KOH
SN2
X
H2O
SN1
X
alc.KOH
Δ
E2
X
E1
H2O
Δ
1,2-H shift
(Major)
+
E2
alc.KOH
Δ
EtOH
SN1
Bredt's Rule violate
aq.KOH
SN2
X
Br
E1
EtOH
Δ
X
Bredt's rule violate

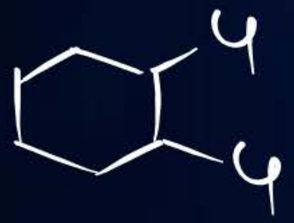
③ Rxn. with Metal

① Wurtz Rxn:-

Rxn:- ① $2\,R{-}X \xrightarrow[D\varepsilon]{Na} R^{\cdot} + {}^{\cdot}R \longrightarrow R{-}R$

(CH_3I/I_2)

②  $\xrightarrow[D\varepsilon]{Na}$

③  $\xrightarrow[D\varepsilon]{Na}$ 

④  $\xrightarrow[D\varepsilon]{Na}$ 

⑤ 

$\xrightarrow{Na,\,D\varepsilon}$ 

Non-arn

② Prepr^n of Grignard Reagent:

Rxn:- $R{-}X \xrightarrow[D\varepsilon]{Mg} RMgX$

$Mg \longrightarrow Mg^{+2} + 2e^{\ominus}$

$R{-}X \xrightarrow{2e^{\ominus}} R^{\ominus} + X^{\ominus}$

$R{-}X + Mg \longrightarrow RMgX$

Ex:-  $\xrightarrow[D\varepsilon]{Mg}$ 

Method of preparation of Halwalkane

- From Hydrocarbon
  1. From Alkane
  2. from alkene
  3. from alkyne
- From Alcohol
- From Halogen Exchange {Already done}
  - → Finkelstein Rxn.
  - → Swartz Rxn.

① From Alkane (Photohalogenation of Alkane)

$n_p = 12$
$n_s = 0$
$n_t = 2$

$\gamma_p \rightarrow$ rate of $1^\circ H$
$\gamma_s \rightarrow$ " — $2^\circ H$
$\gamma_t \rightarrow$ " — $3^\circ H$

$n_p \rightarrow$ no. of $1^\circ H$
$n_s \rightarrow$ " — $2^\circ H$
$n_t \rightarrow$ " — $3^\circ H$

	Rate of H		
	$1^\circ H$	$2^\circ H$	$3^\circ H$
F_2	1	1	1
Cl_2	1	3.8	5 ✓
Br_2	1	82	1600

$F_2, h\nu$ →

$\%p = n_p\gamma_p = 12\times1 = 12$ > $\%t = n_t\gamma_t = 2\times1 = 2$

$Cl_2, h\nu$ →

$\%p = n_p\gamma_p = 12\times1 = 12$ > $\%t = n_t\gamma_t = 2\times5 = 10$

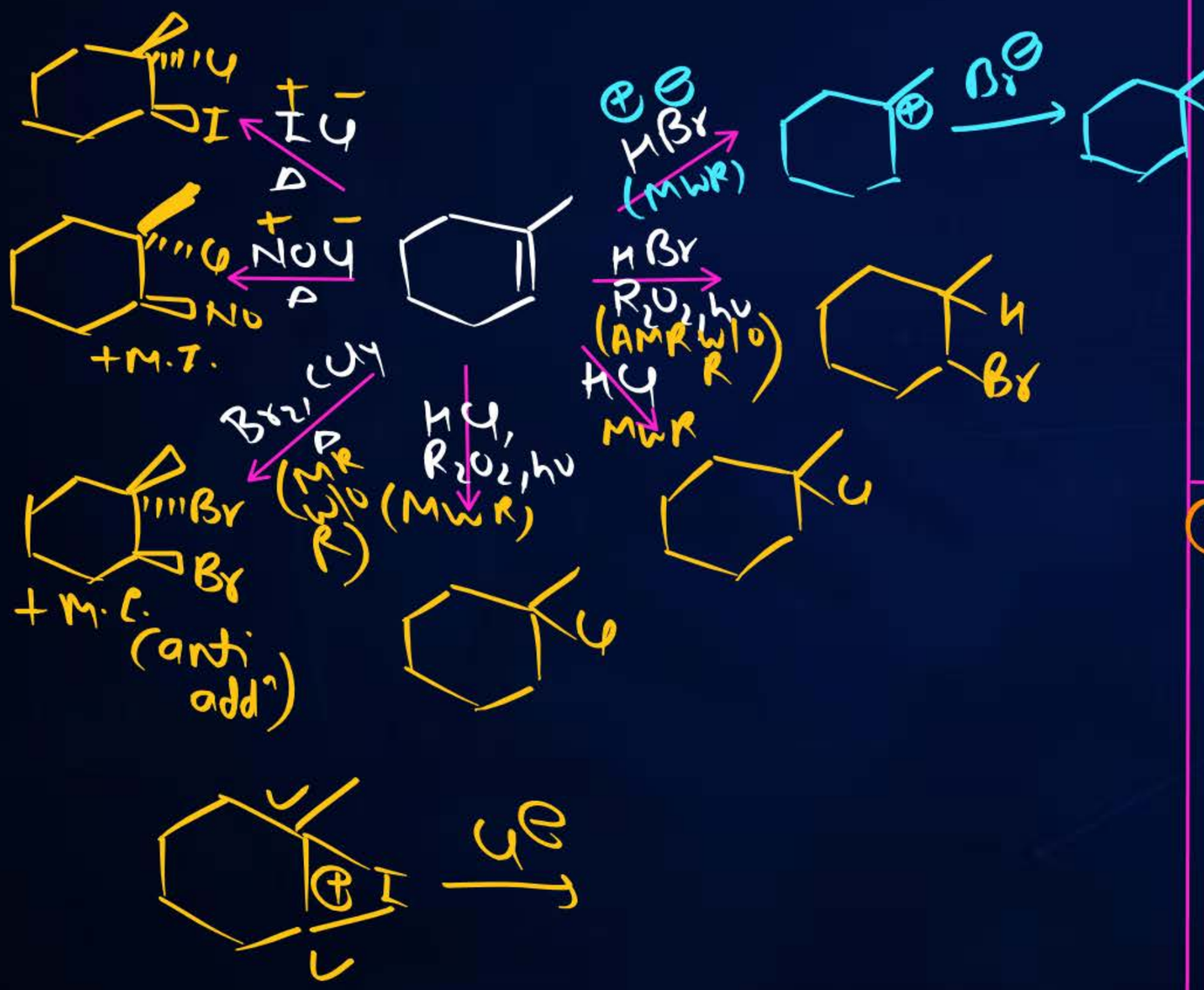
$Br_2, h\nu$ →

$\%p = n_p\gamma_p = 12\times1 = 12$ < $\%t = n_t\gamma_t = 2\times1600 = 3200$

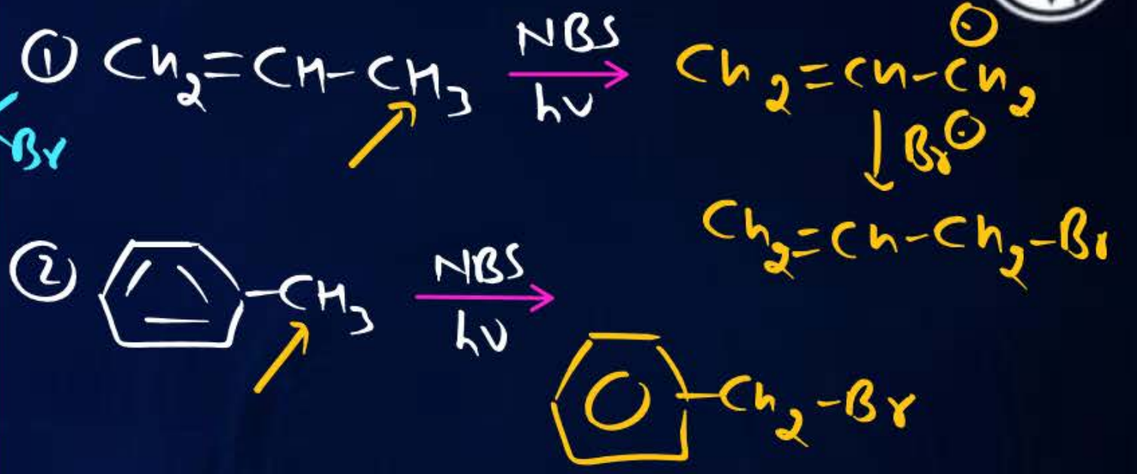
Reed's Rxn :-

$R-H \xrightarrow[h\nu]{SO_2Cl_2} R-Cl$

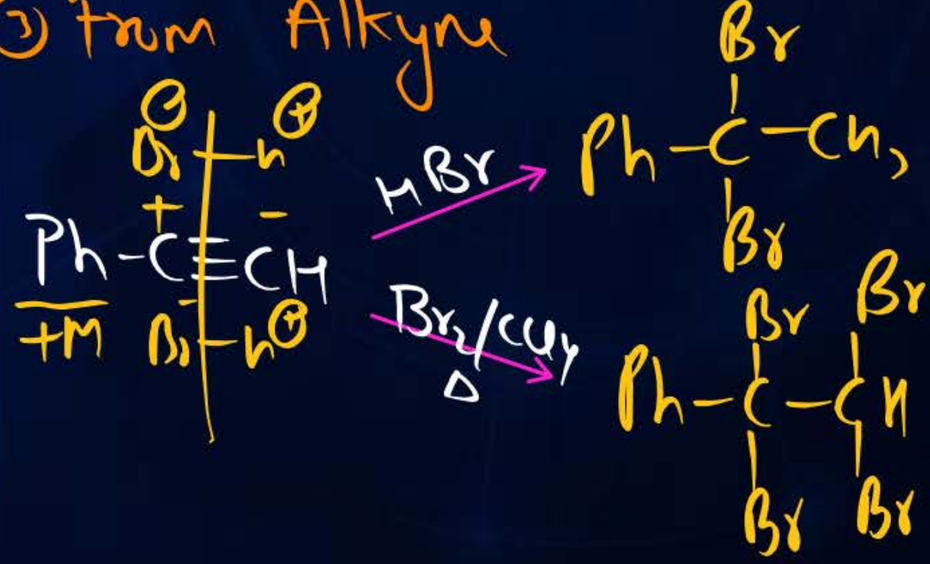
② From Alkene



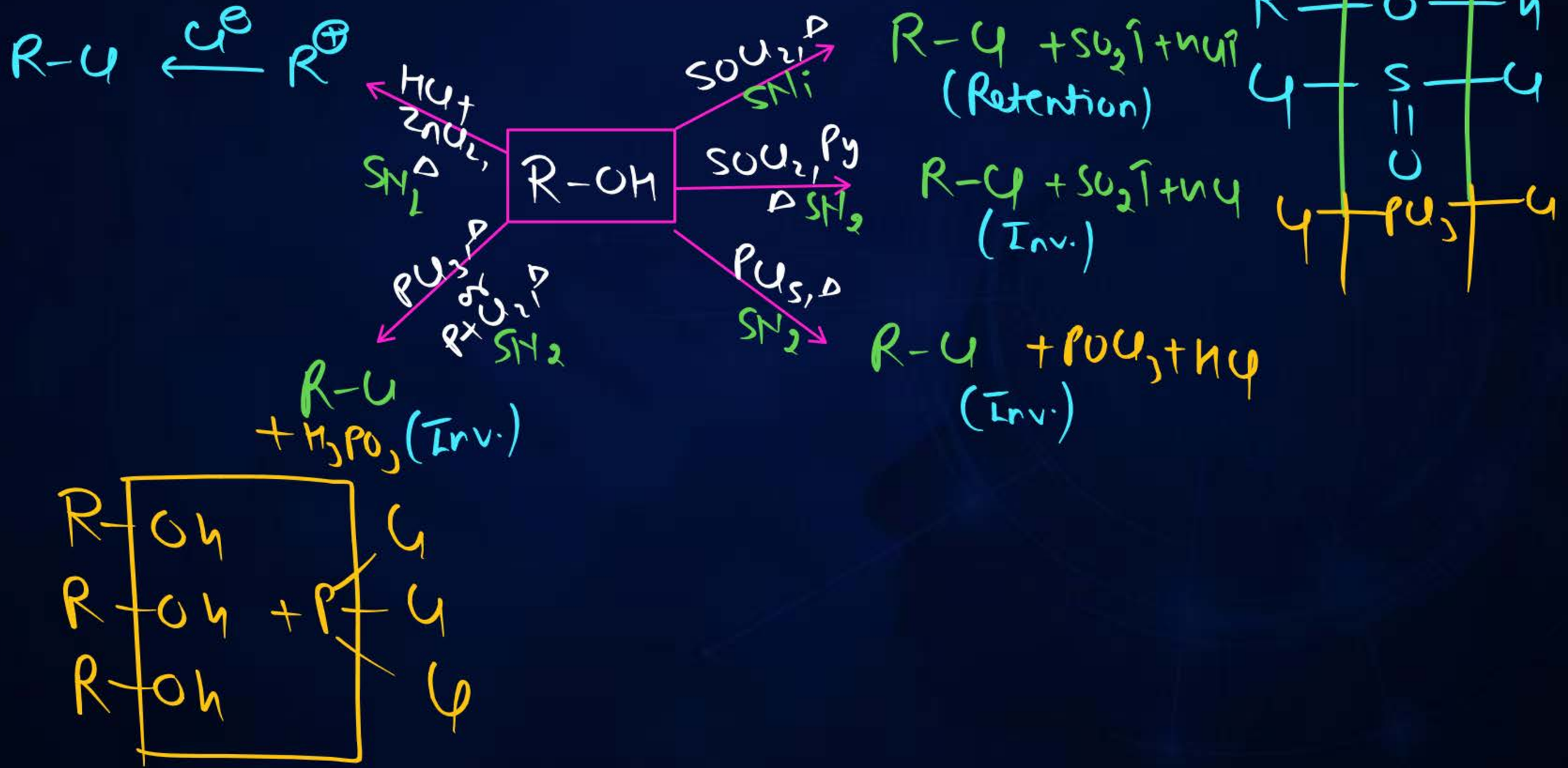
Rxn. with NBS, hν :-

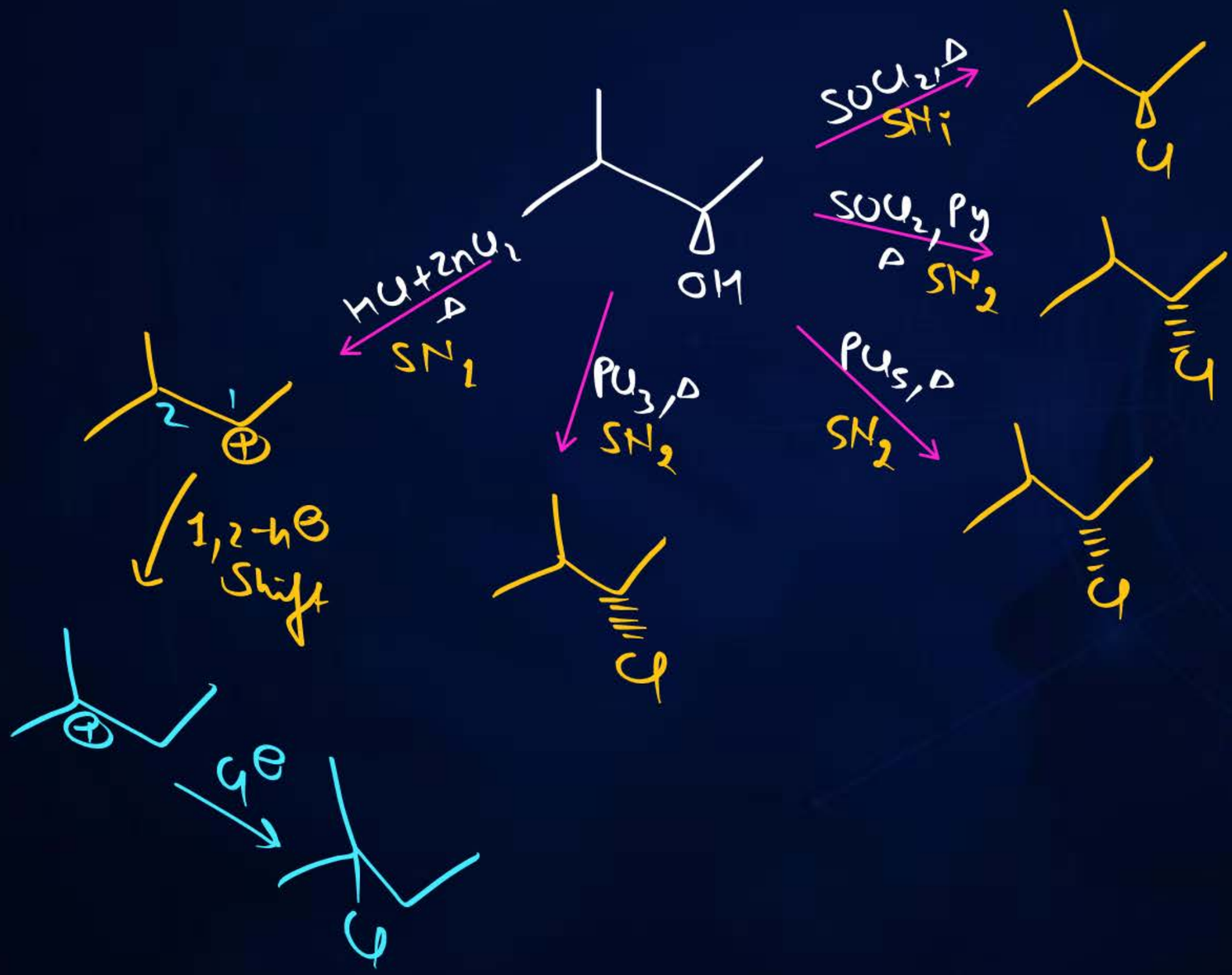


③ From Alkyne



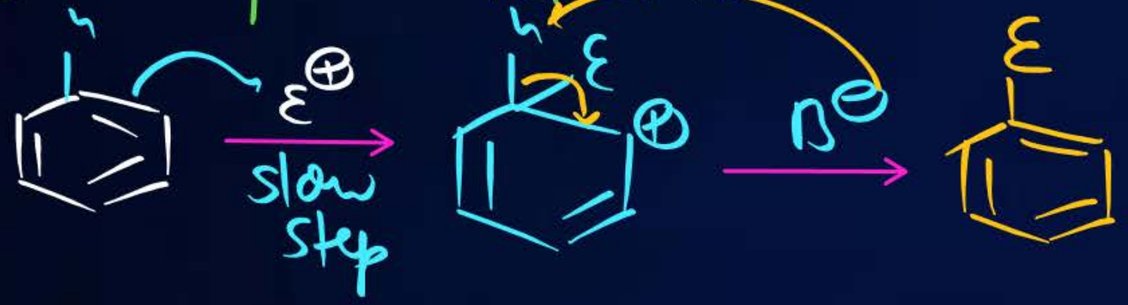
② From Alcohol

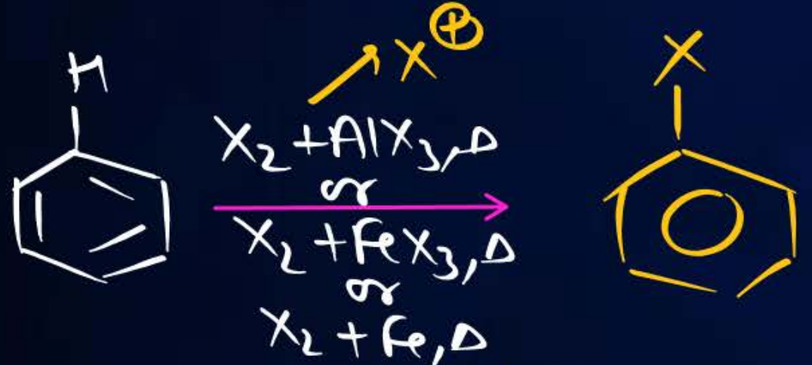


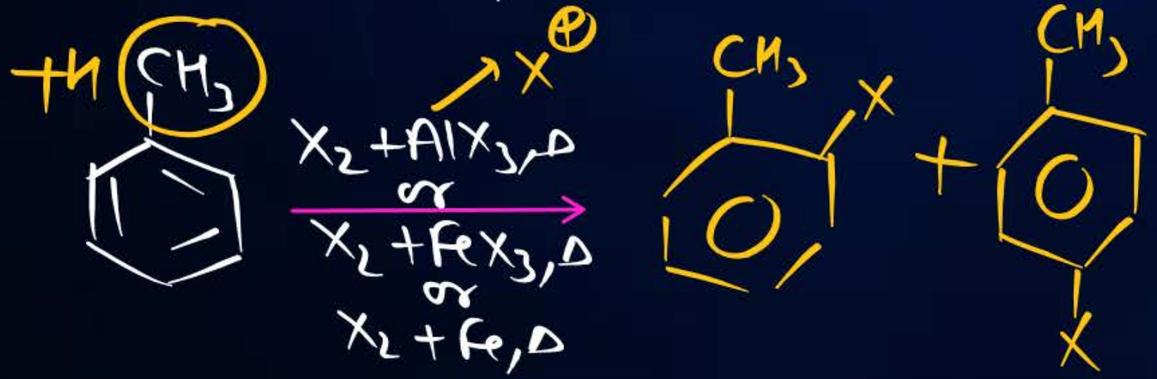

OH
SOCl2, Δ
SNi
Cl
SOCl2, Py
Δ
SN2
Cl
HCl+ZnCl2
Δ
SN1
PCl3, Δ
SN2
PCl5, Δ
SN2
1,2-H⊖
Shift
Cl⊖
Cl

MOP of Halwarene

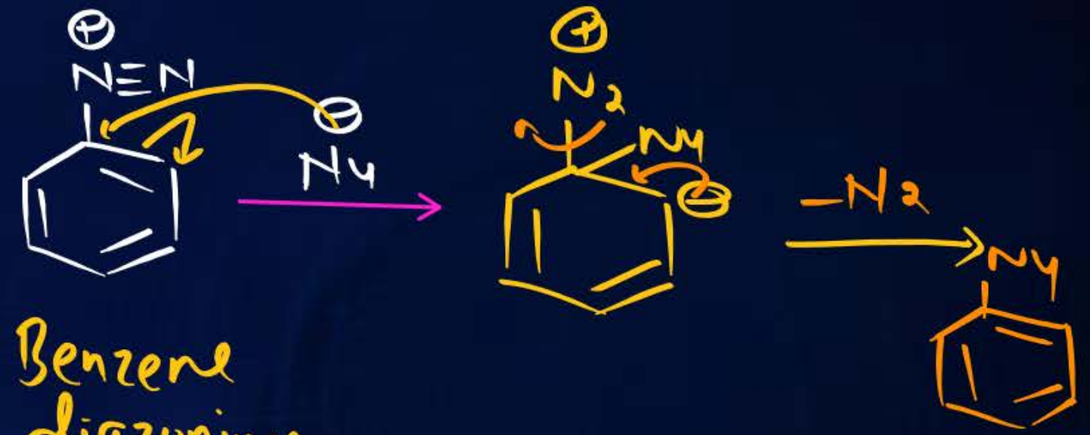
① Electrophilic Substⁿ Rxn.



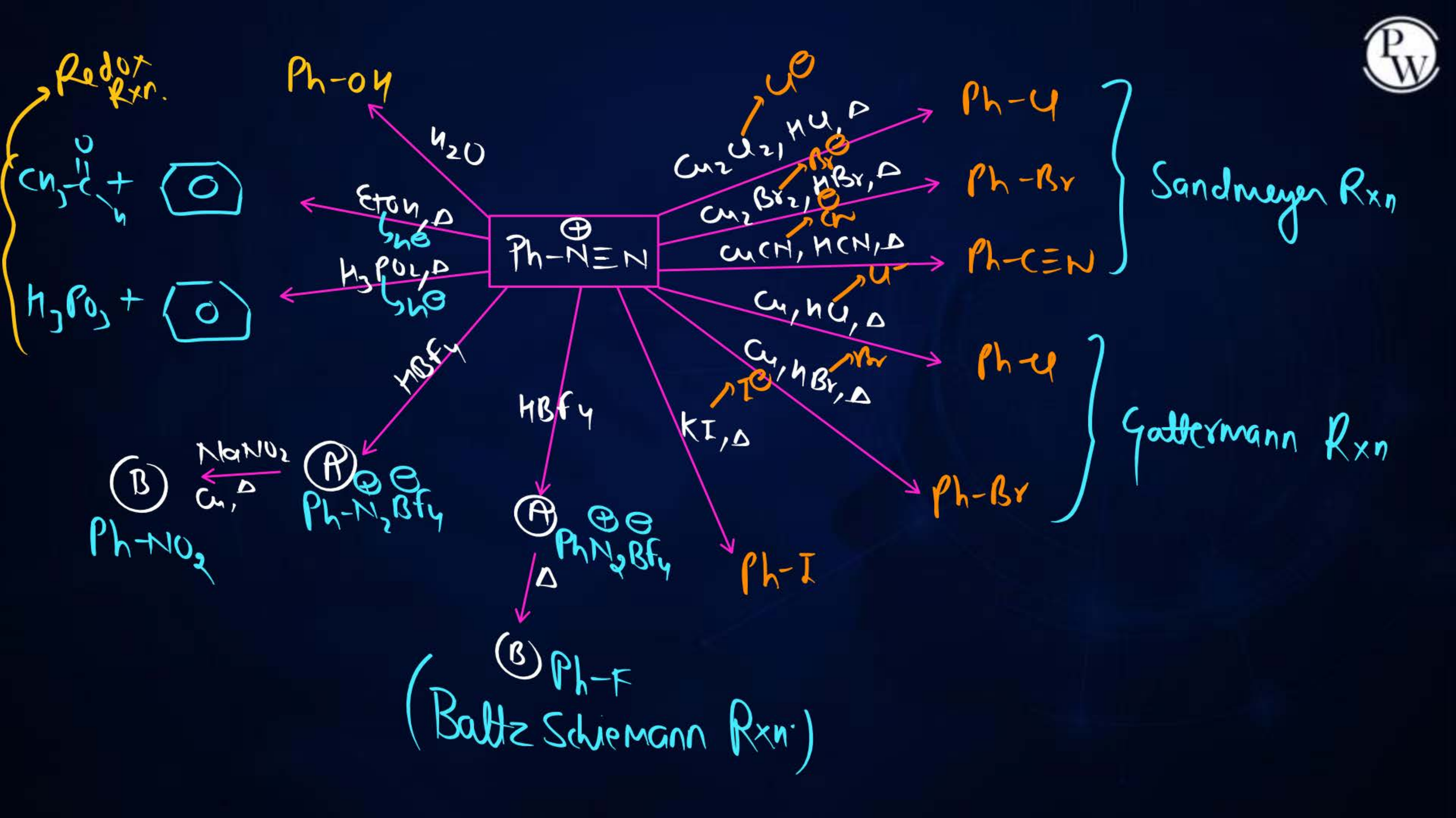




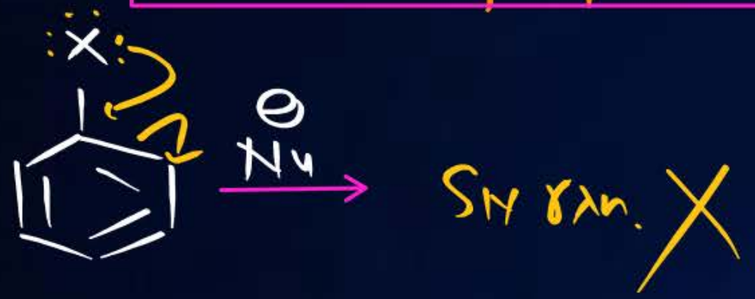
② Nu⊖ Substⁿ Rxn:-



Benzene diazonium salt

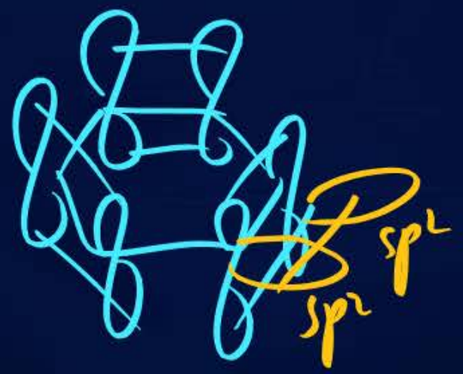

Redox Rxn.
Ph-OH
H_2O
EtOH, Δ
H_3PO_2, Δ
HBF_4
$NaNO_2$
Cu, Δ
B
$Ph-NO_2$
A
$Ph-N_2BF_4$
HBF_4
A
PhN_2BF_4
Δ
B
Ph-F
(Baltz Schiemann Rxn.)
Cu_2Cl_2, HCl, Δ
Cu_2Br_2, HBr, Δ
CuCN, HCN, Δ
Ph-Cl
Ph-Br
Ph-CN
Sandmeyer Rxn
Cu, HCl, Δ
Cu, HBr, Δ
KI, Δ
Ph-Cl
Ph-Br
Ph-I
Gattermann Rxn

Chemical properties of Haloarene



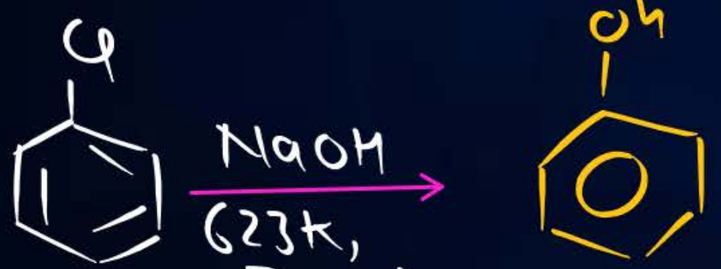
Mech^{n}:-

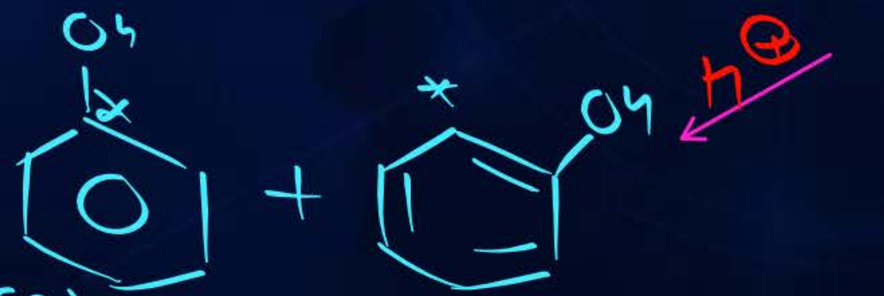
$C^{*} \equiv C^{H}$



Subs^{n}

Dow's process / Benzyne mech^{n} / SNEA mech^{n}

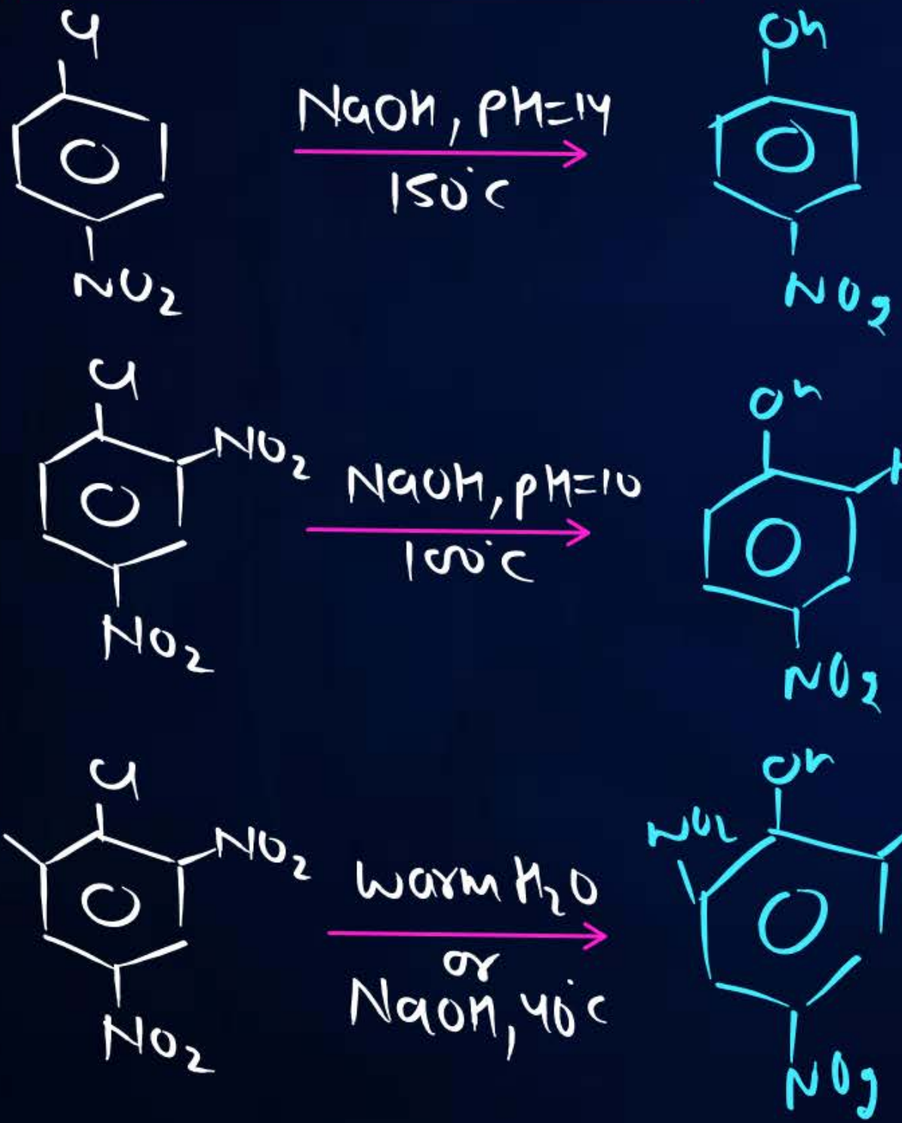




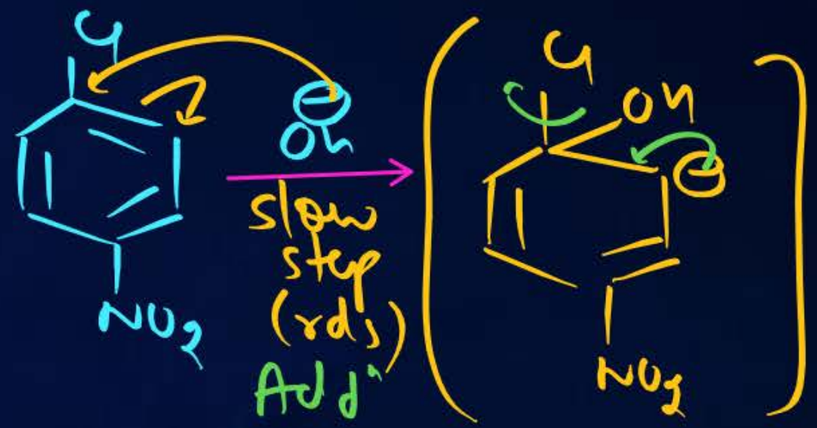
(DSP) Direct Substituted

(CSP) Cine substituted

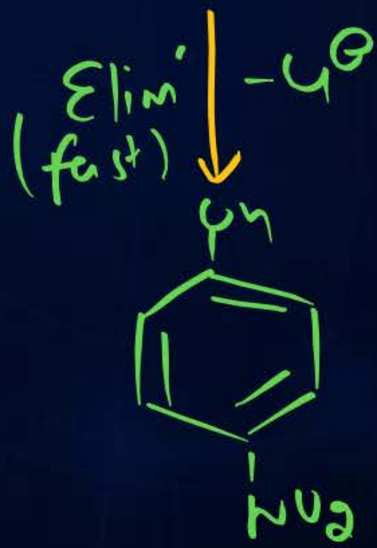
SN_2Ar | SNAE rxn.



Mech^n:-

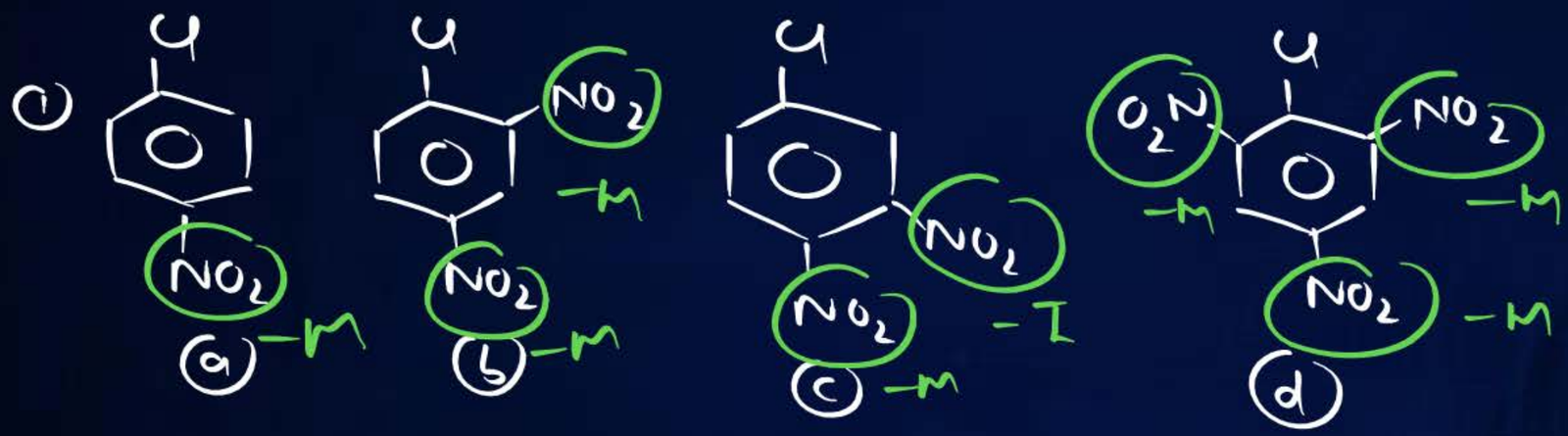


Meisenheimer complex



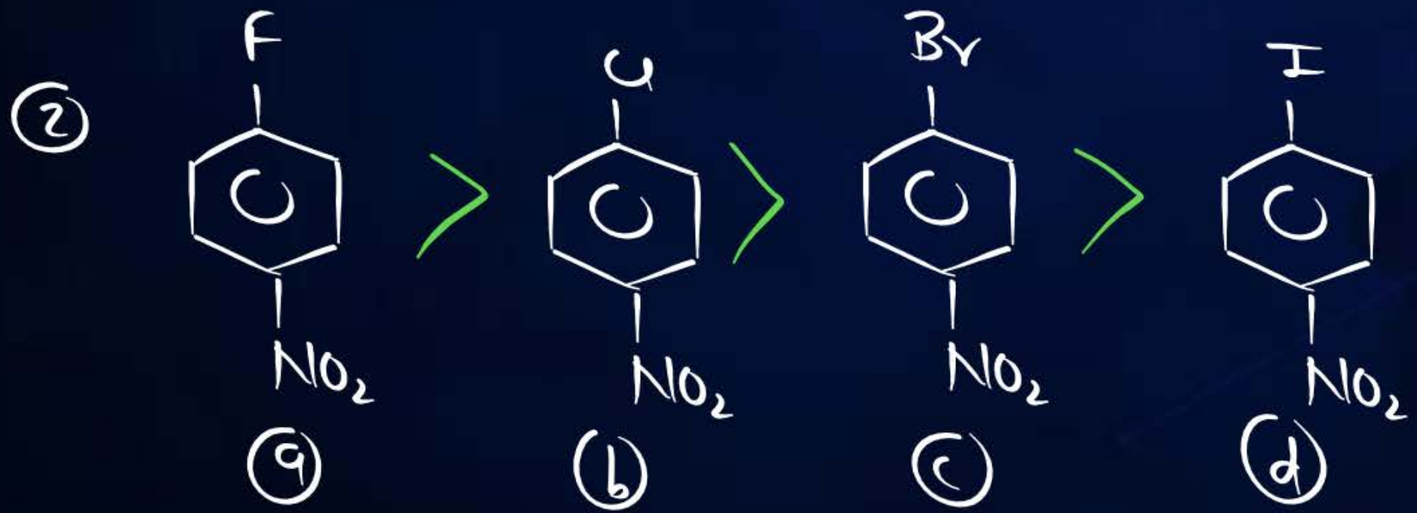
Qw. Compare rate of SN_2Ar or SNAE:-

(1)

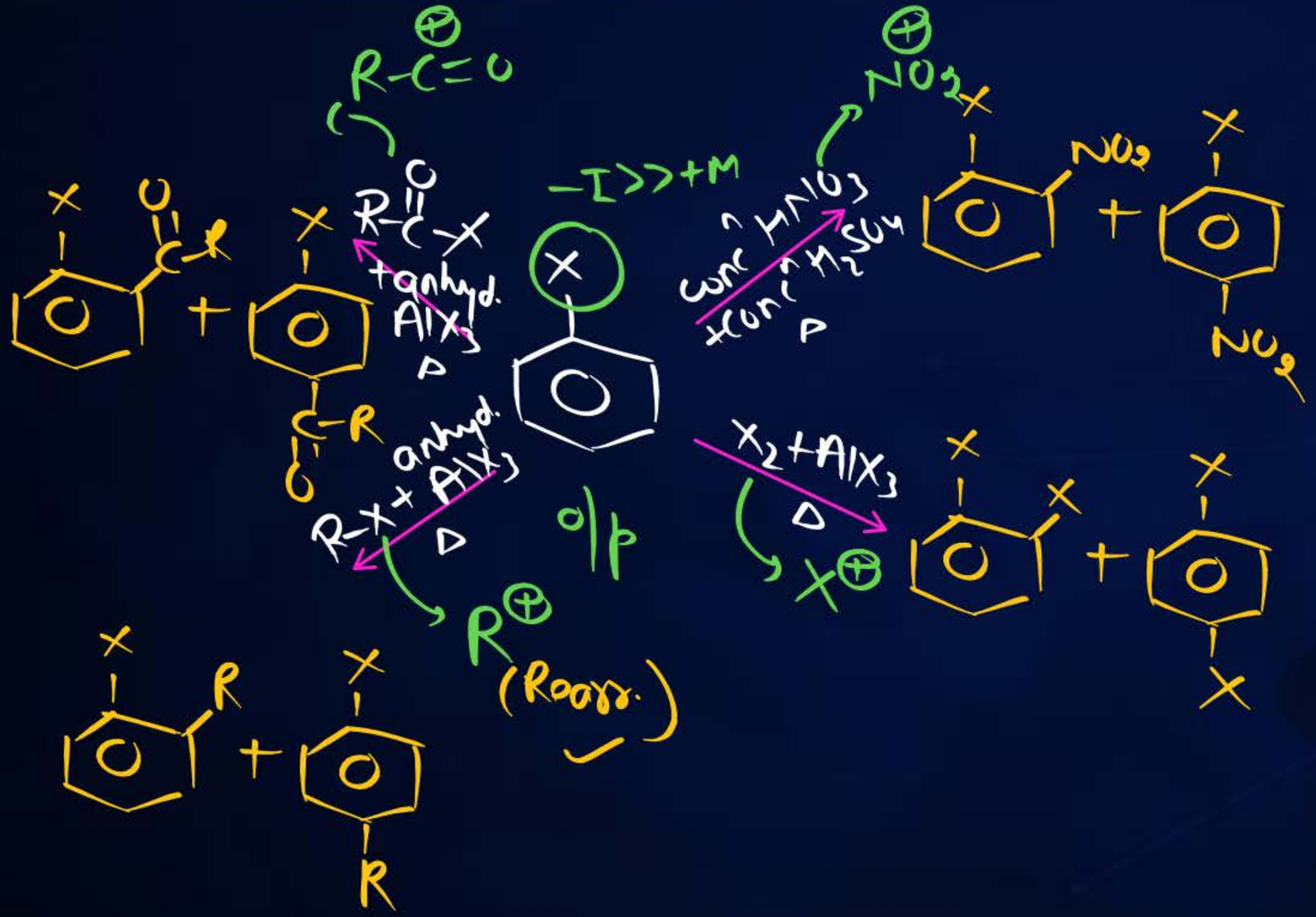


d > b > c > a

(2)

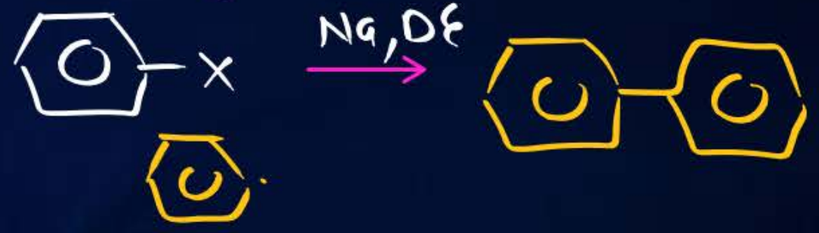


Electrophilic Substⁿ Rxn:-

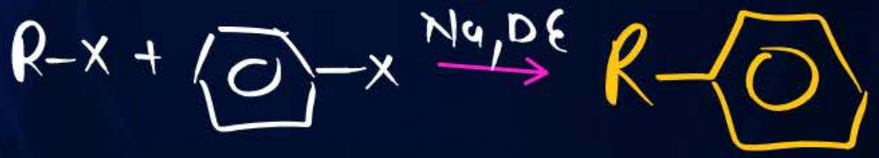


Rxn. with Metal

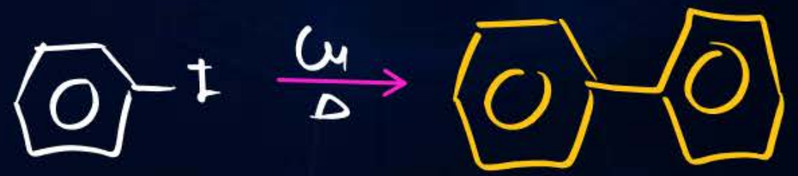
① Fittig Rxn:-

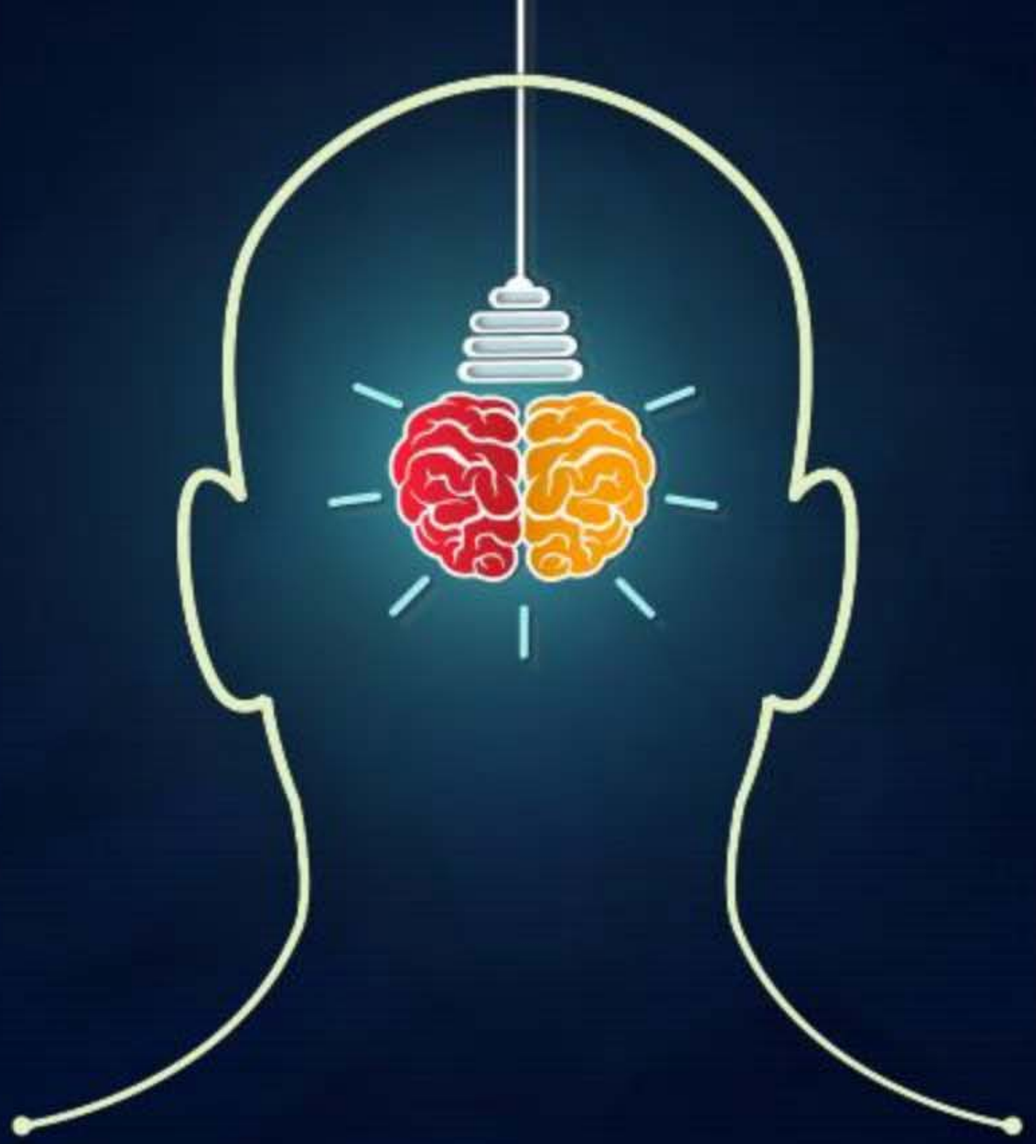


② Wurtz-fittig Rxn:-



③ Ulmann Rxn:-





THANK YOU