MIND MAP FOR JEE ASPIRANTS

Organic Chemistry

Aldehydes Ketones & Carboxylic acids

By- Yogesh Jain (YJ) Sir

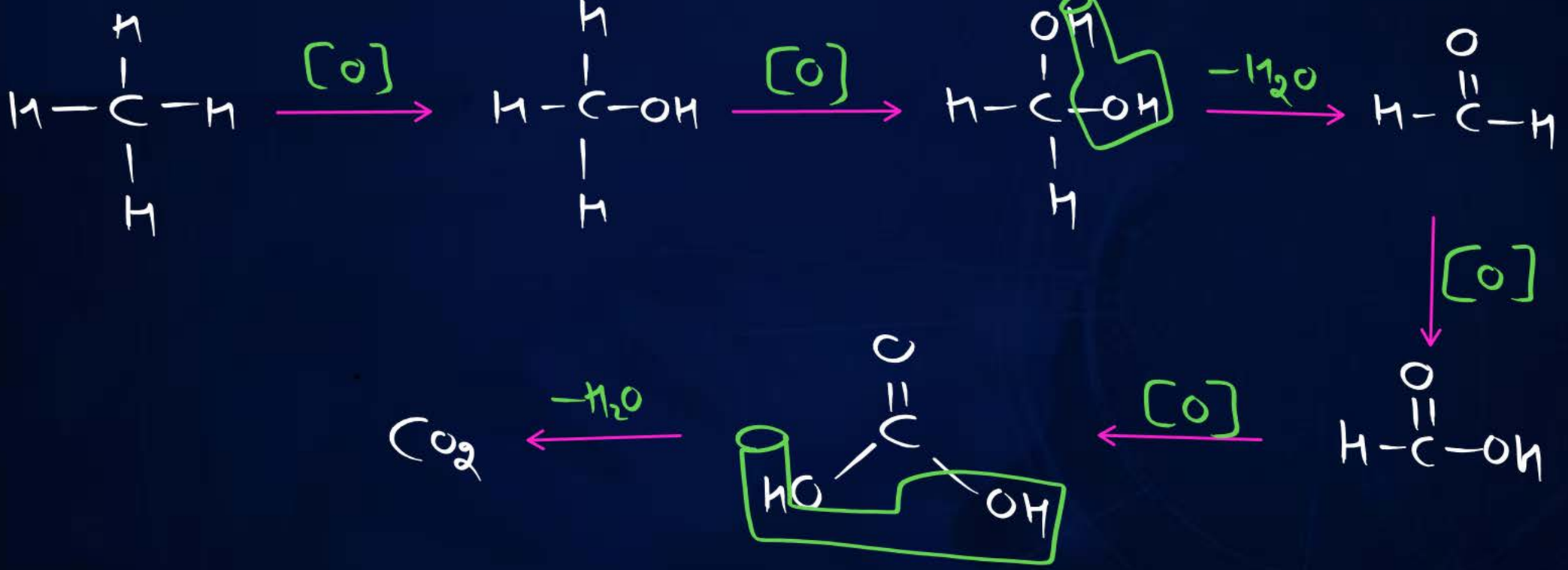
Today's Targets

1. Aldehydes Ketones and Carboxylic acids

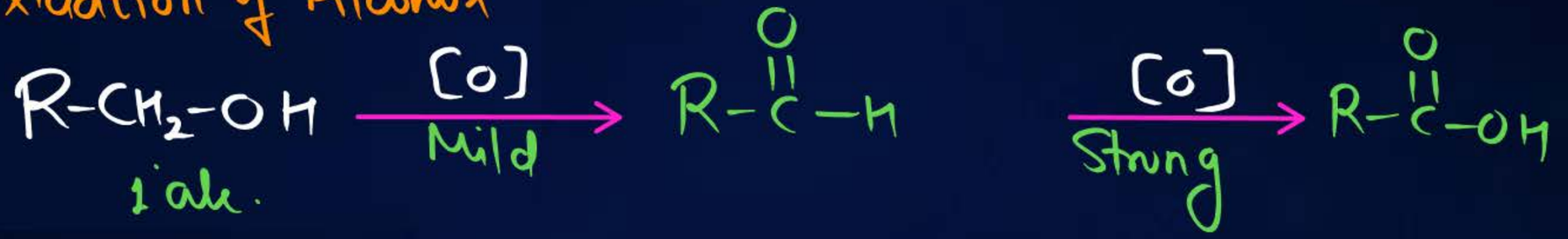
MOP of

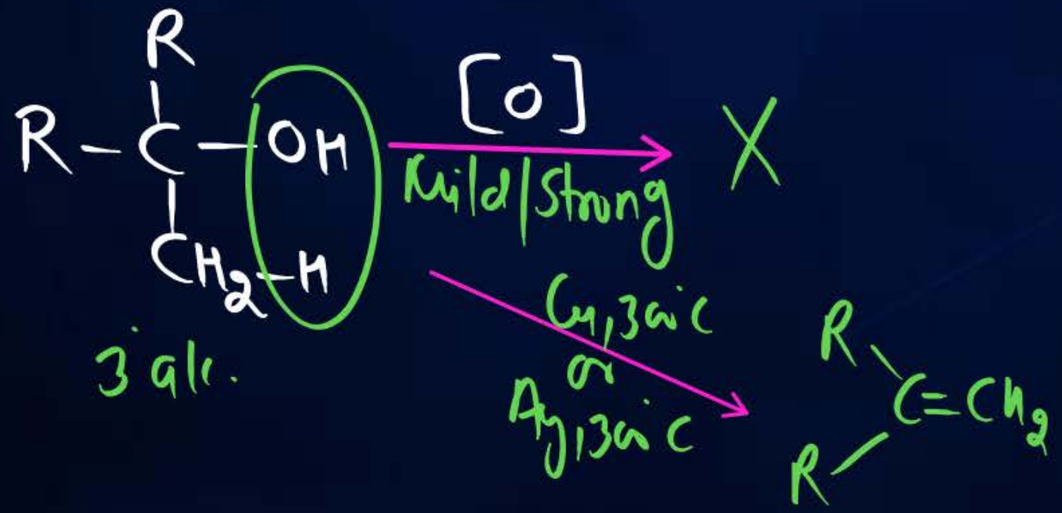
Carbonyl Compounds

Oxidation



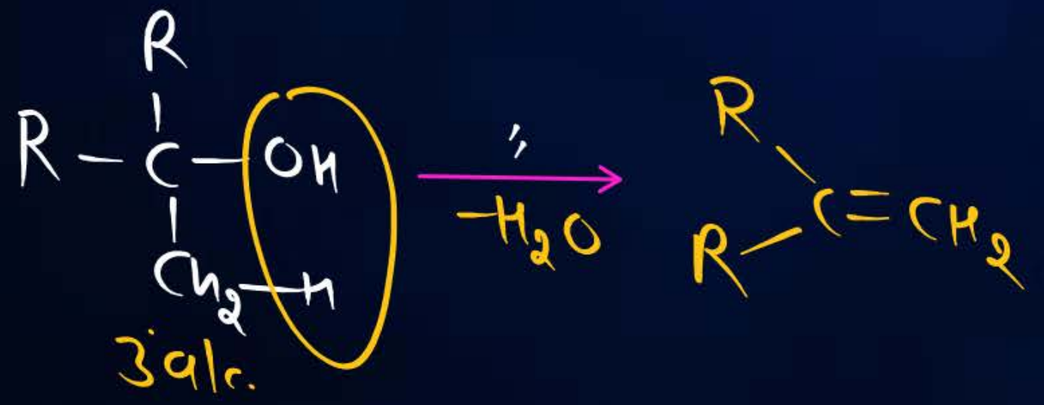
① Oxidation of Alcohol





S.No.	Oxidising Agent		1° R-OH	2° R-OH	3° R-OH
①	$KMnO_4/H^{\oplus}$	Strong O.A.	CARBOXYLIC ACID	KETONE	X
②	$K_2Cr_2O_7/H^{\oplus}$				X
③	Jone's Reagent {$CrO_3 + H_2SO_4$ or $CrO_3 + H_2O$}				X
④	conc^{n} HNO_3				X
⑤	PCC (Pyridiniumchloro chromate)	Mild O.A.	ALDEHYDE		X
⑥	PDC (Pyridiniumdichromate)				X
⑦	CrO_3 + Acetone				X
⑧	Cu/Δ or Ag/Δ Lassaigne				Alkene

② Dehydrogenation of Alcohol:-

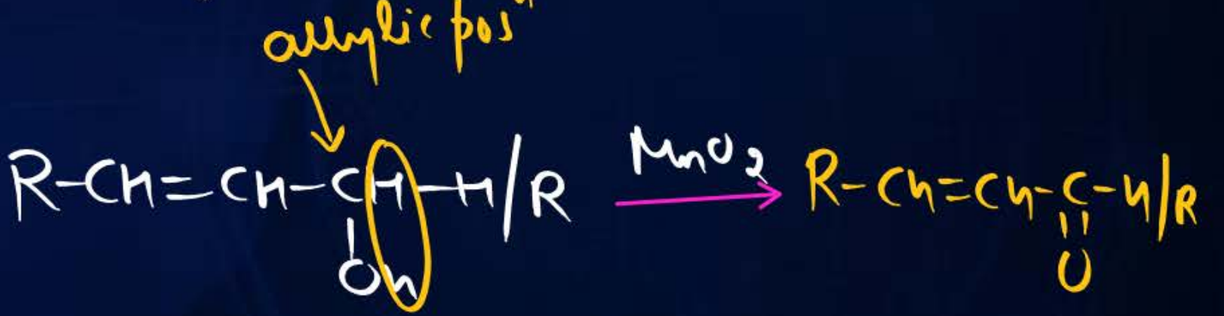


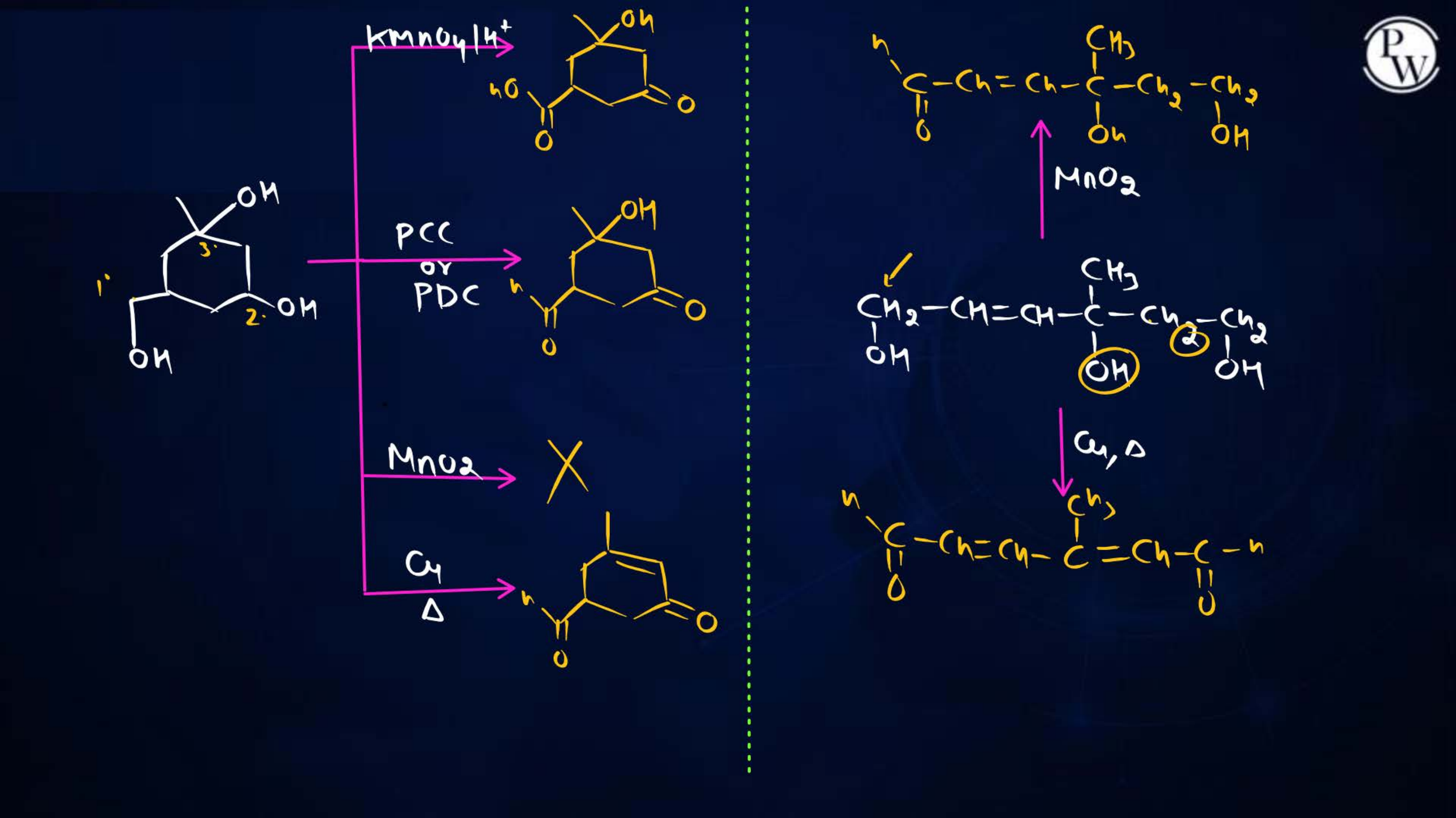
Special O.A. MnO_2 → Mild O.A.

1° allylic or Benzylic R-OH → Ald.

2° allylic or Benzylic R-OH → Ketone

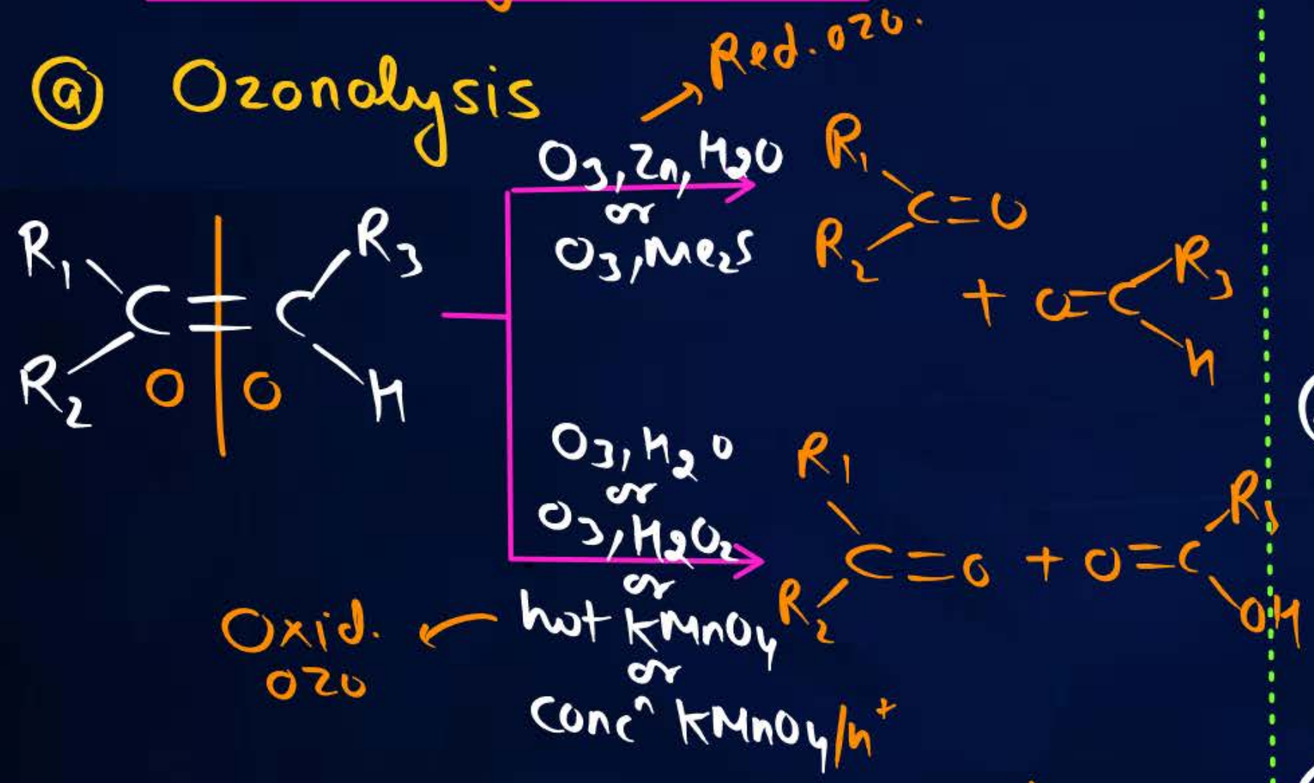
3° allylic or Benzylic R-OH → ✗

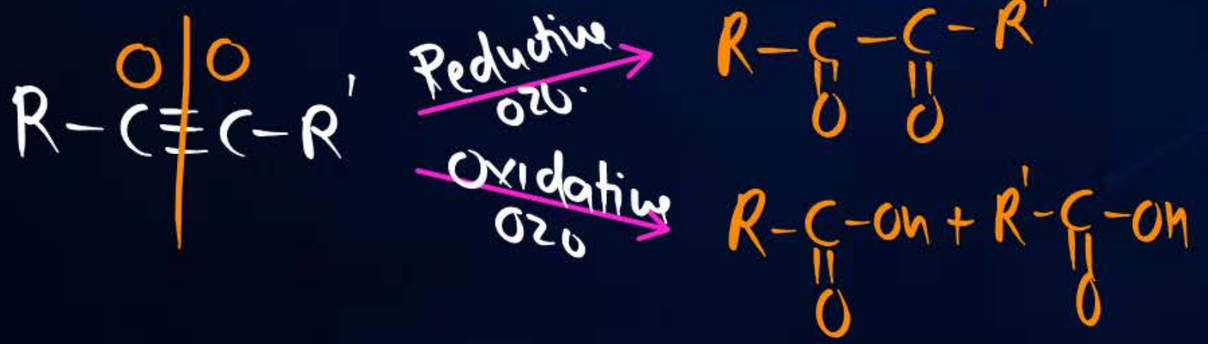



KMnO4/H+
PCC
or
PDC
MnO2
X
Cu
Δ
MnO2
Cu, Δ

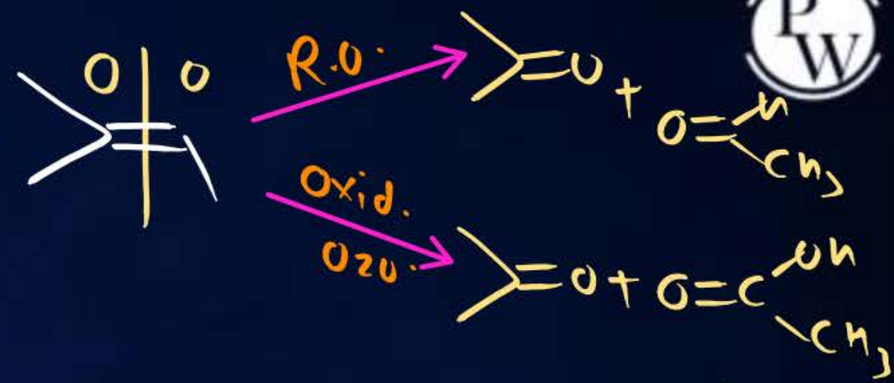
③ From Hydrocarbon

ⓐ Ozonolysis

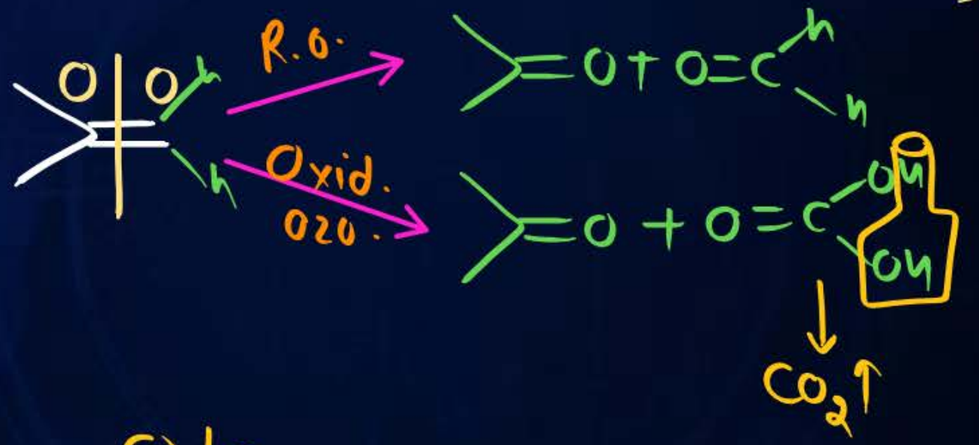




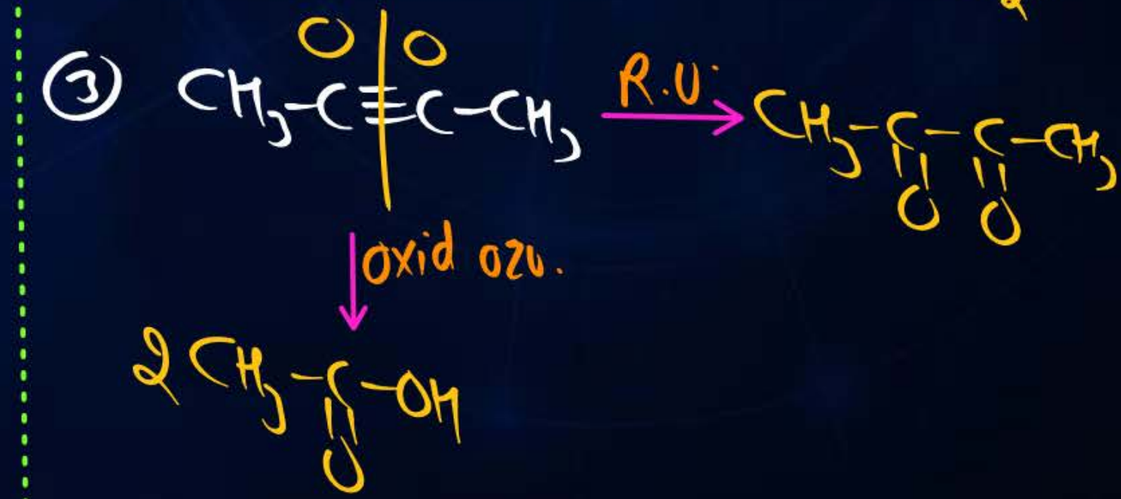
Ex:- ①



②



③



③ From Hydrocarbon

ⓑ Kucherov Rxn :- (M w/o R) (Addⁿ of H_2O)

$$R-C\equiv CH \xrightarrow[\text{or } Hg^{2+}/\text{dil. } H_2SO_4 \text{ or } Hg^{2+}/H^{\oplus}]{HgSO_4/\text{dil. } H_2SO_4} R-\underset{\underset{O}{\|}}{C}-CH_3$$

(via $R-C(OH)=CH_2$ ⇌ tauto)

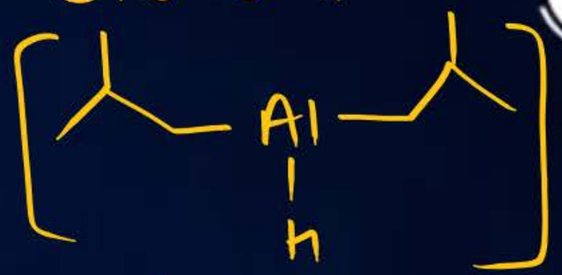
Ex:- ① $CH_3-C\equiv CH \xrightarrow{''} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ (via $CH_3-C(OH)=CH_2$ ⇌ tauto)

② $Ph-C\equiv CH \xrightarrow{''} Ph-\underset{\underset{O}{\|}}{C}-CH_3$ (via $Ph-C(OH)=CH_2$ ⇌ tauto)

MOP of ALDEHYDES

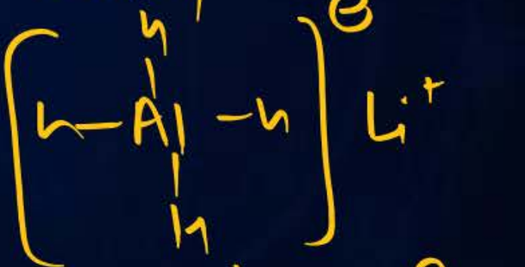
(N-bar)

DIBAL-H



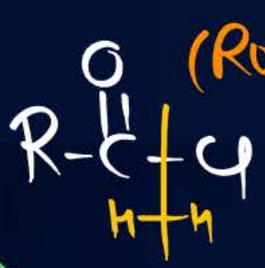
↳only one $H^{\ominus}$ donor

LiAlH$_4$

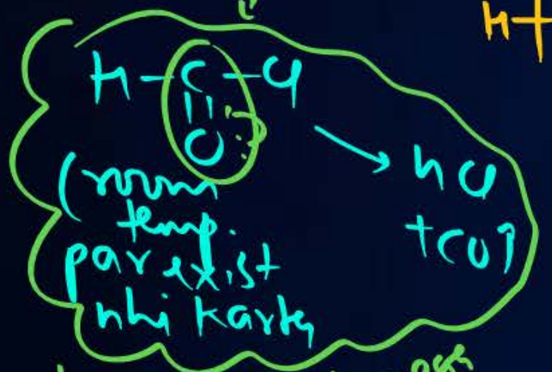


↳4 $H^{\ominus}$ donors

(Rosenmund Red^n)



H_2/Pd-BaSO$_4$ + Quinoline



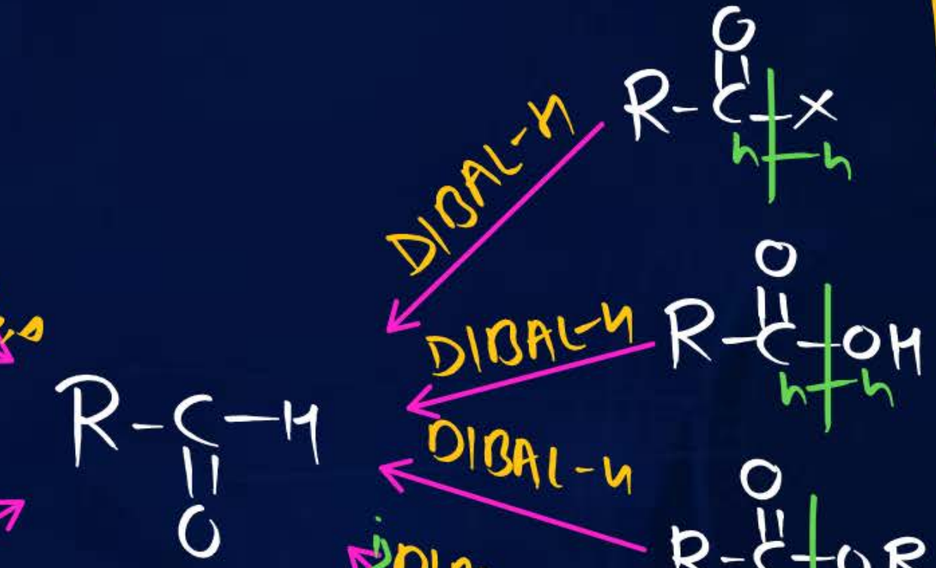
(room temp pr exist nhi krta)

$H-\underset{\underset{O}{\|}}{C}-H$ nhi bnega

ketone X

i) $SnCl_2$ + HCl

ii) H_2O



DIBAL-H

DIBAL-H

DIBAL-H

i) DIBAL-H

ii) H_2O

(Stephen Red^n)

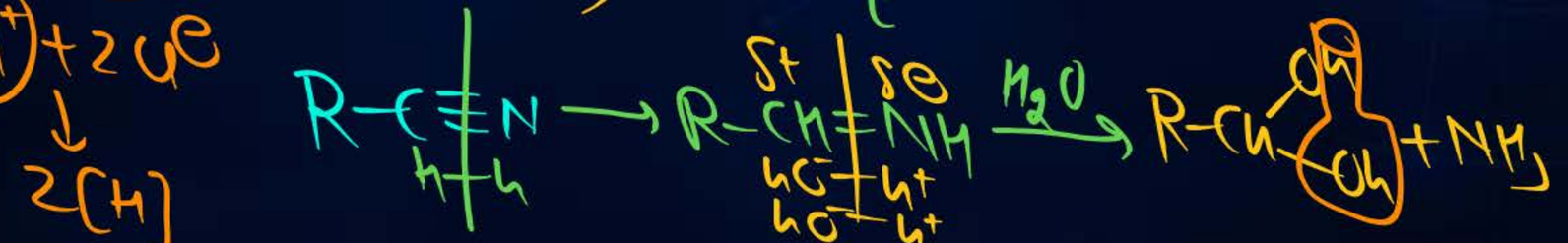
(ketone X)

$Sn^{+2} \rightarrow Sn^{+4} + 2e^{\ominus}$

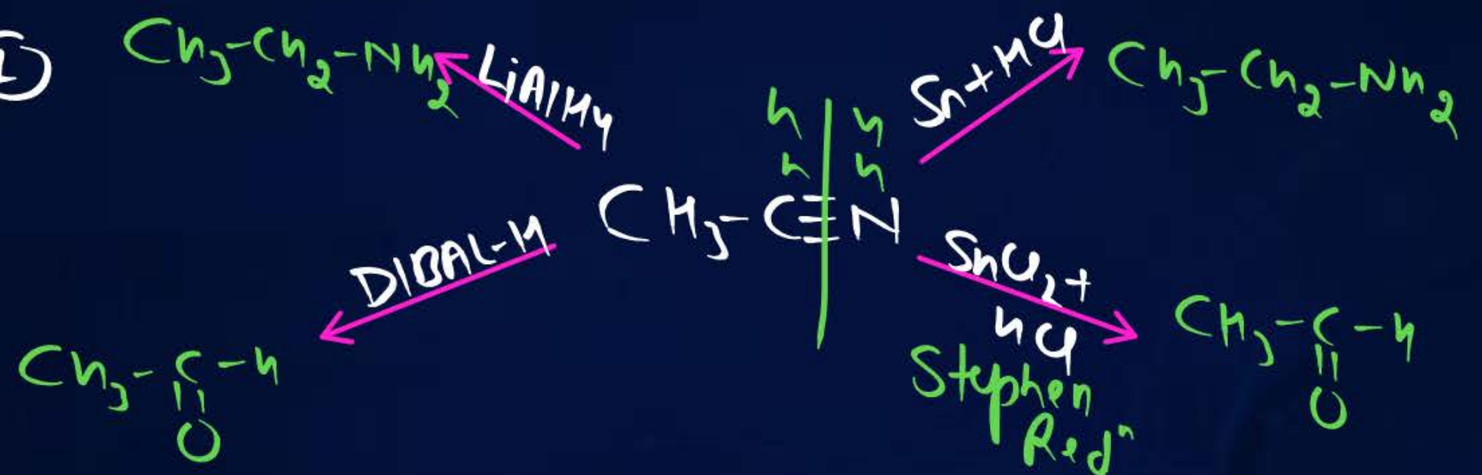
$2HCl \rightarrow 2H^{+} + 2Cl^{\ominus}$

$\downarrow$

$2[H]$



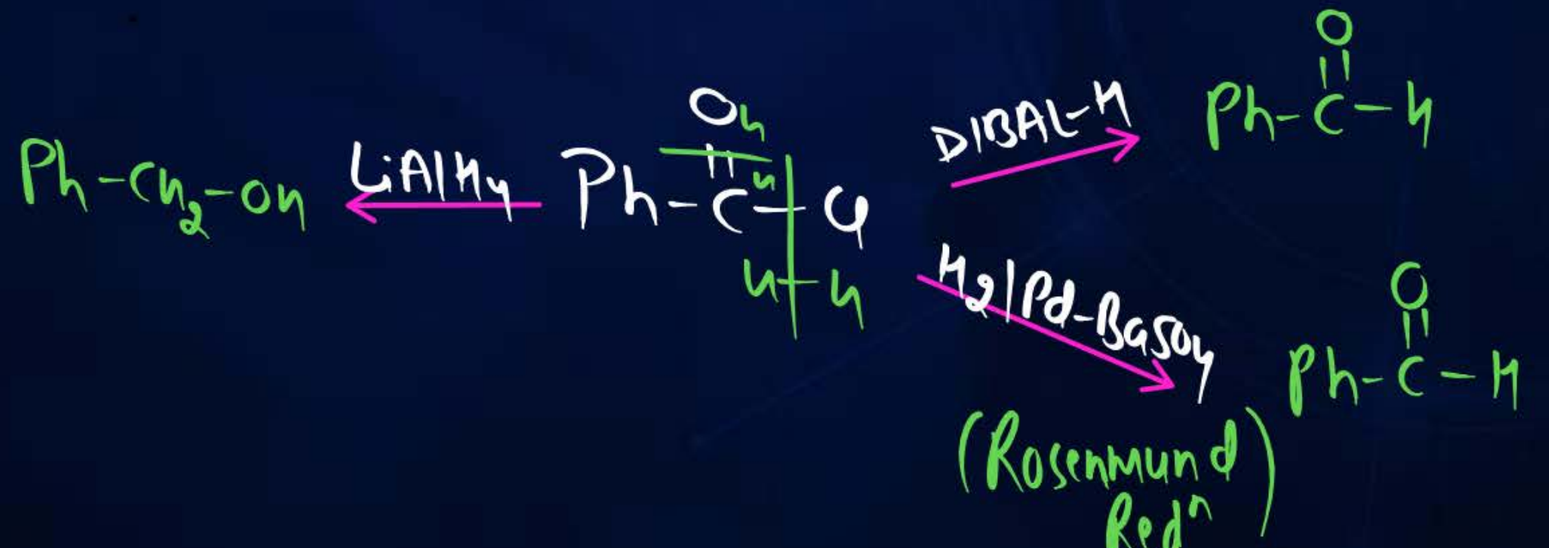
Ex:→ (1)

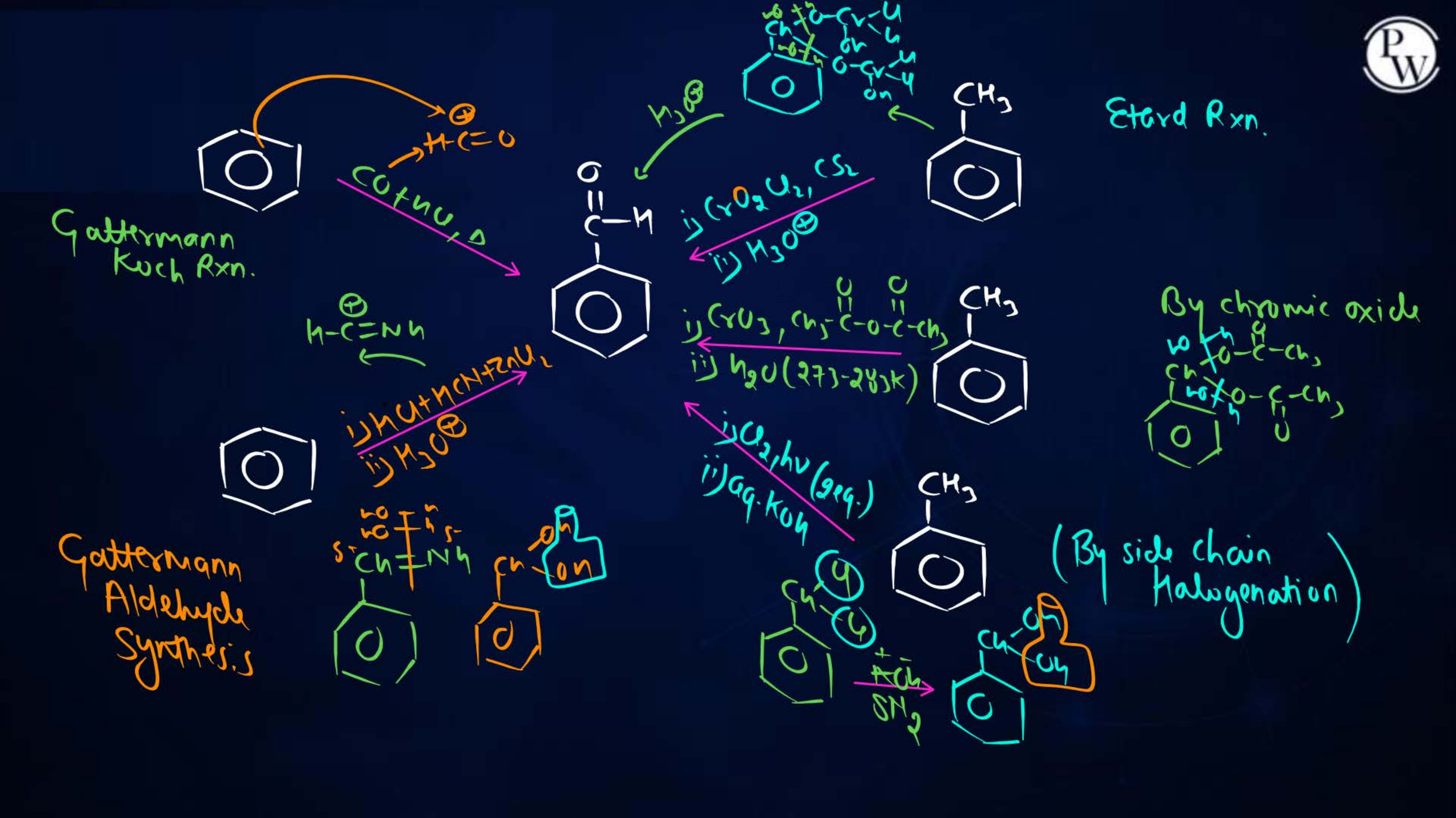


$Sn \rightarrow Sn^{+4} + 4e^{\ominus}$

$4HCl \rightarrow 4H^{\oplus}$ → $4(H)$

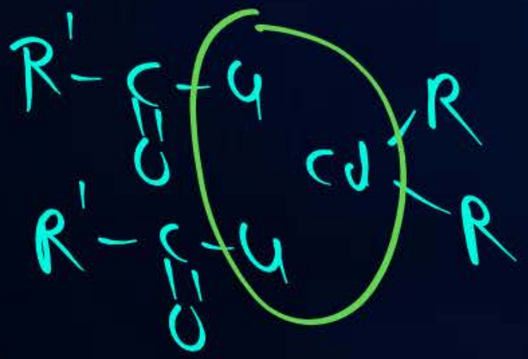
(2)

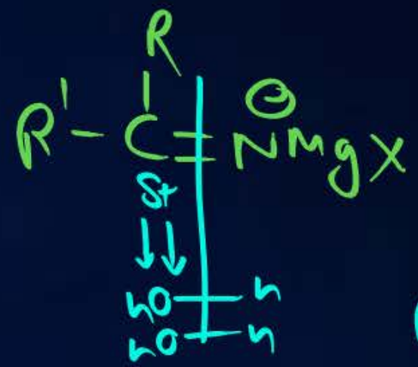



Gattermann Koch Rxn.
Etard Rxn.
By chromic oxide
Gattermann Aldehyde Synthesis
(By side chain Halogenation)

MOP of ketones

(C ka δ⊕ par G.R. ka R jod dijiye)

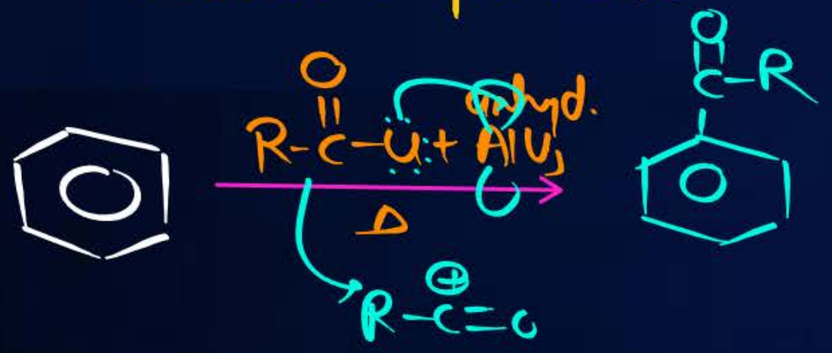




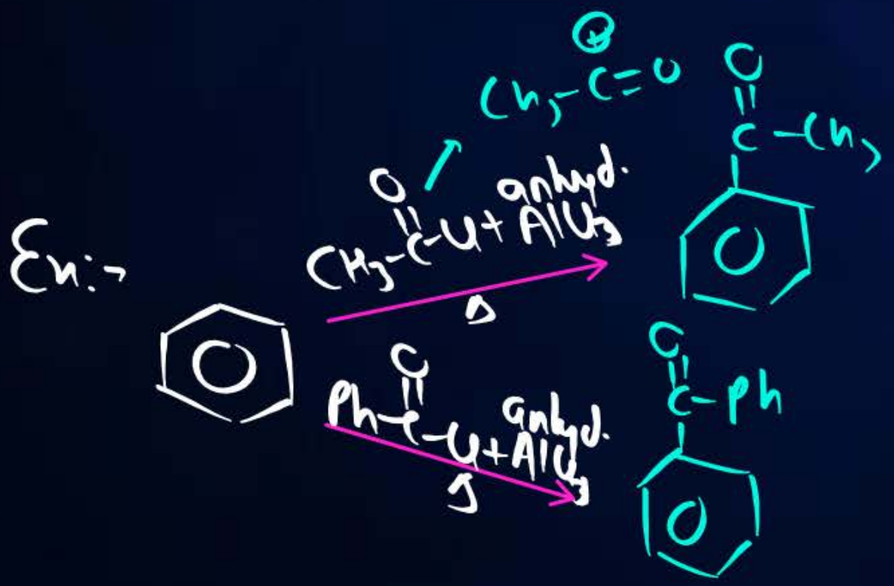
{Cyanide k saath kitna bhi G.R. lelo hamesha Ketone he banega}

MOP of ketones

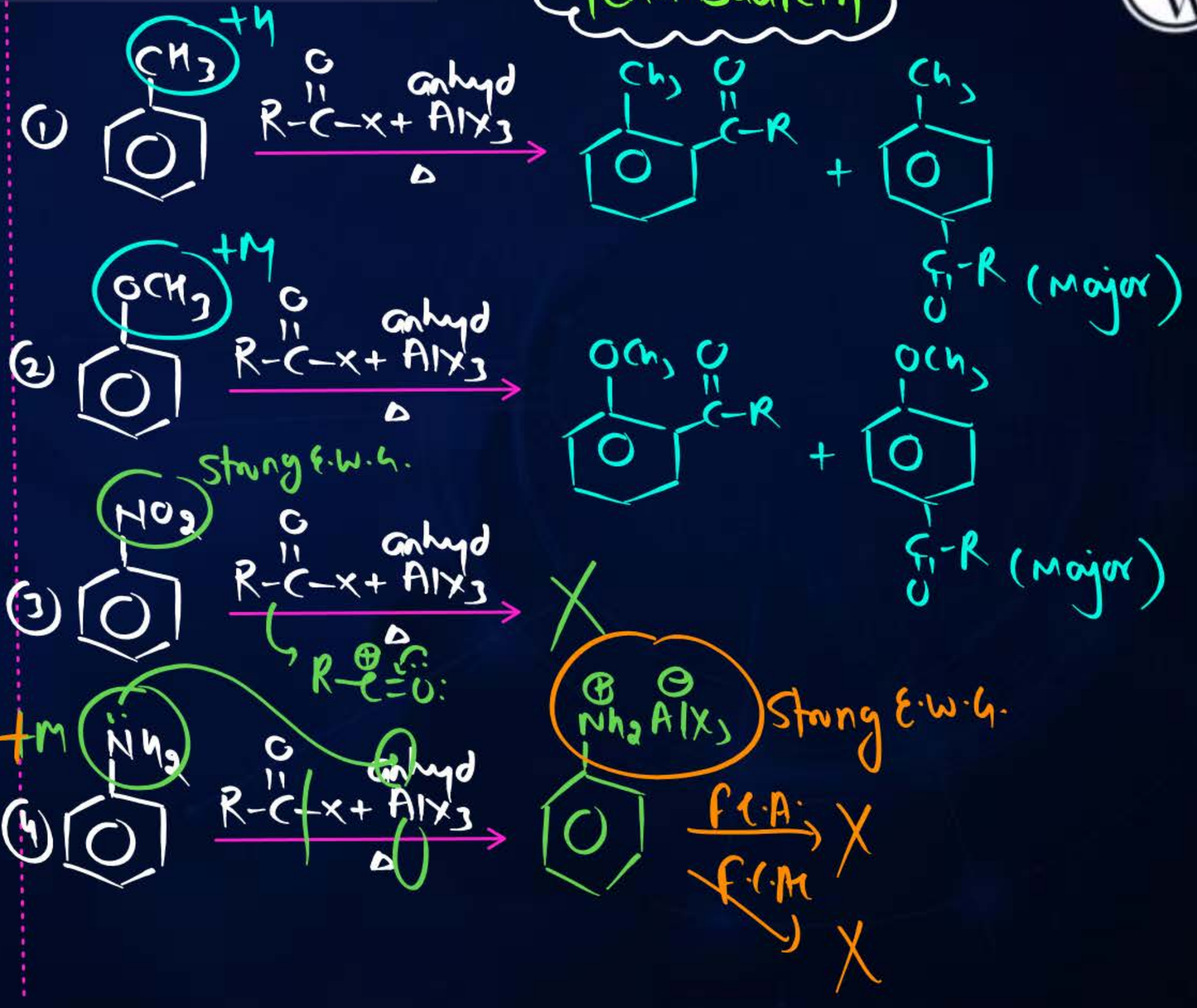
Friedal Craft Rxn:-



Ex:-



Gehri Baatein



Chemical properties of

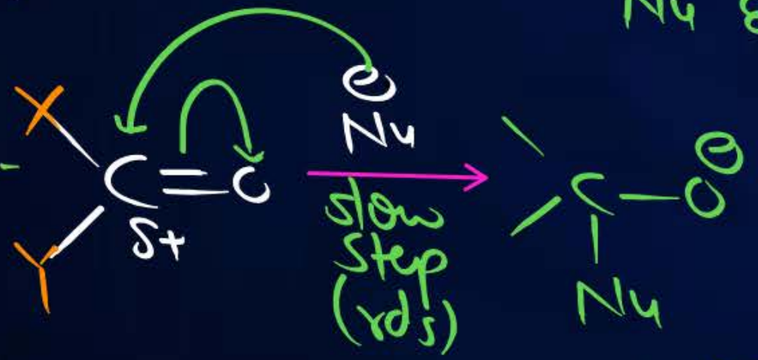
Carbonyl Compounds

Nucleophilic Addition Rxn:- (NAR)

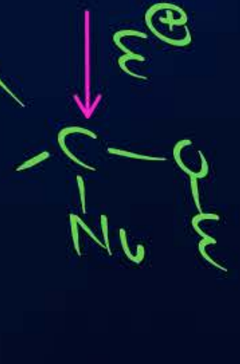
* First attack of $\overset{\ominus}{Nu}$
* Overall addn (1 π-bond break 2 strong σ-bond form)

Rxn:-

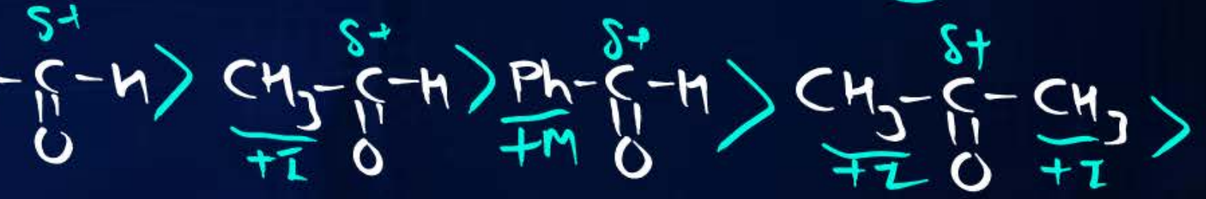
Mech:-



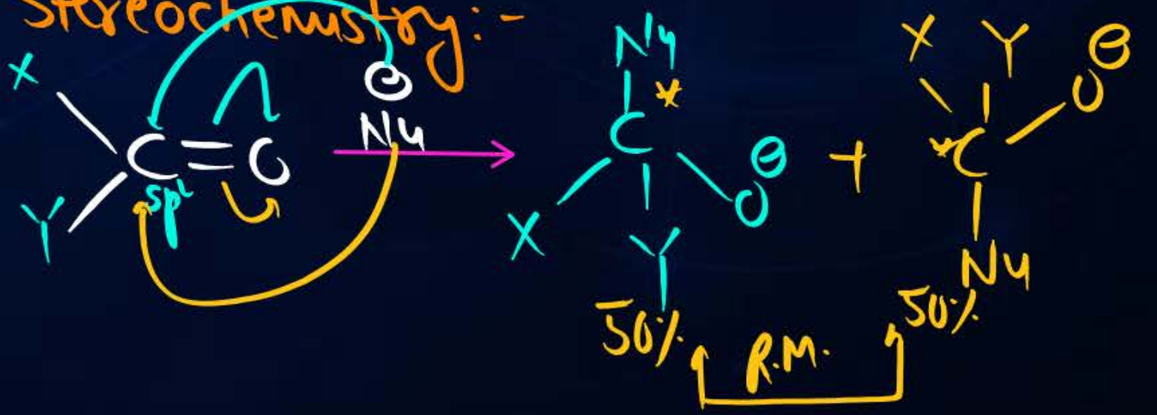
Rate of NAR $\propto$ $\frac{1}{\text{Steric hindrance at } C=O}$ & $\delta\oplus$ ve at $C=O$

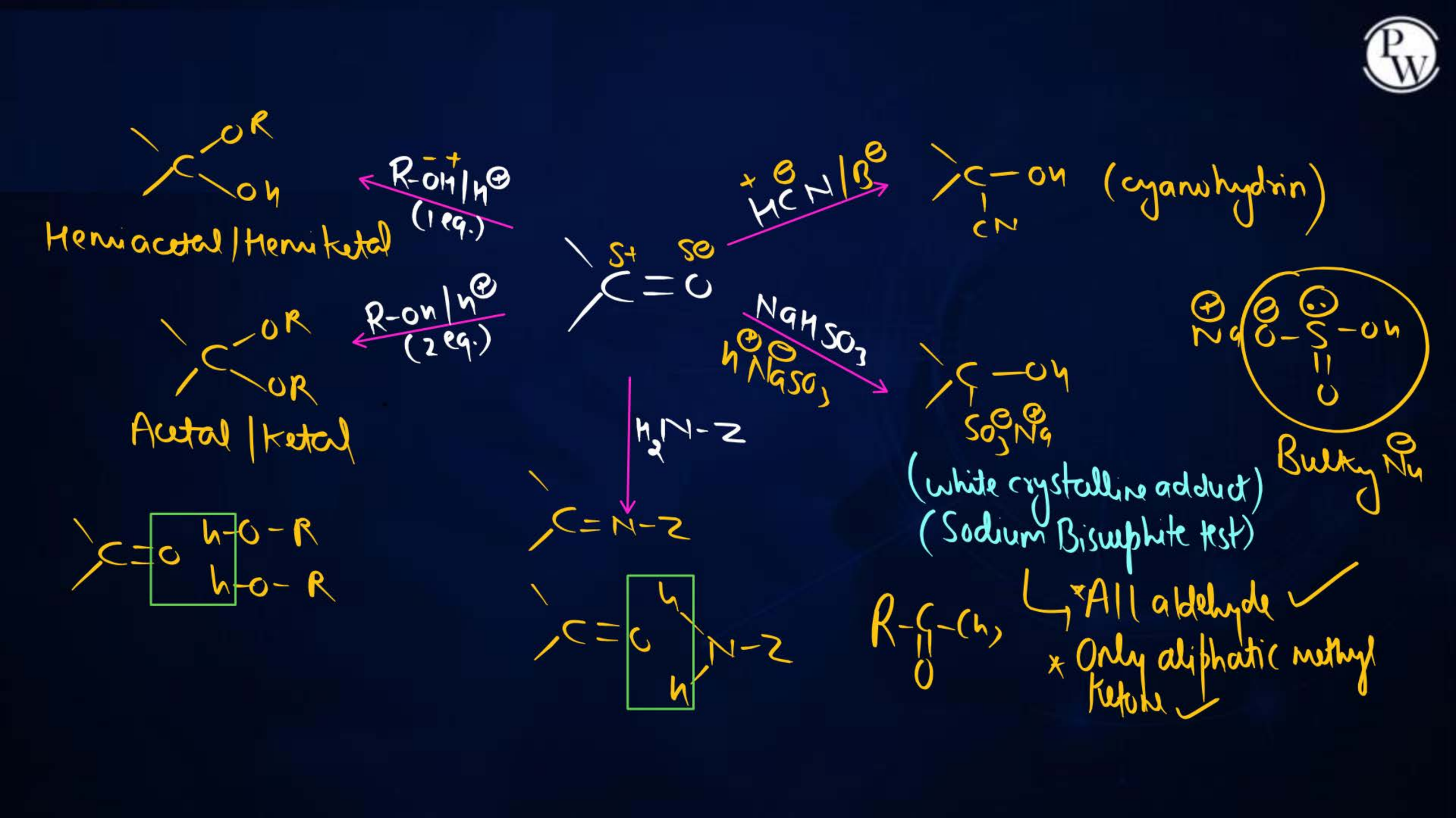


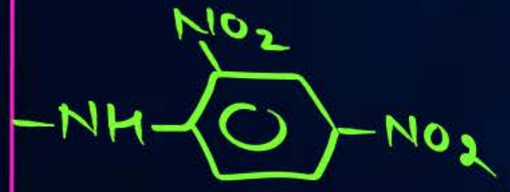
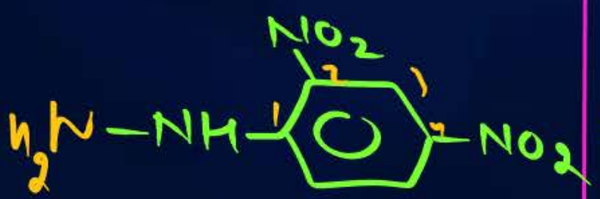
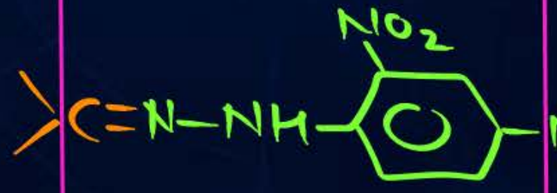
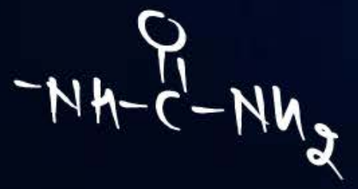
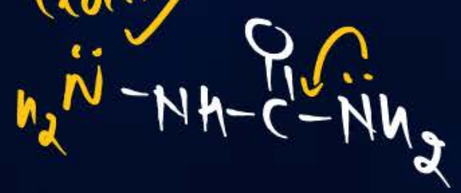
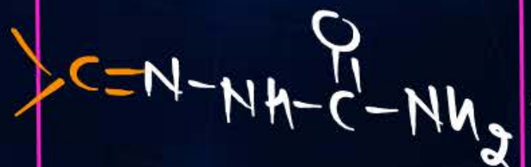
Rate of NAR:- Ald > Ketone



Stereochemistry:-




Hemiacetal / Hemiketal
R-OH / H⊕ (1 eq.)
Acetal / Ketal
R-OH / H⊕ (2 eq.)
HCN / B⊖
(cyanohydrin)
NaHSO3
(white crystalline adduct)
(Sodium Bisulphite test)
Bulky Nu
H2N-Z
All aldehyde
Only aliphatic methyl ketone

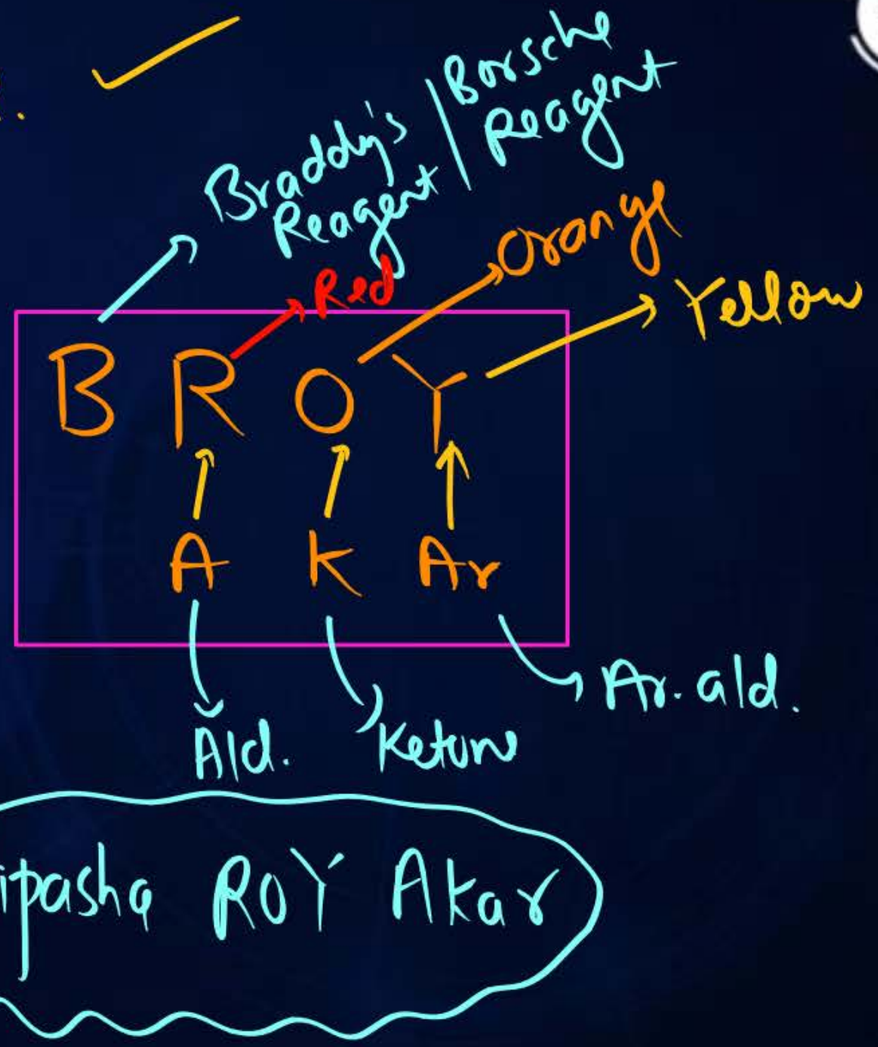
S.No.	$-Z$	NH_2-Z	Name	$>C=N-Z$	Product
①	$-H$	H_2N-H	Ammonia	$>C=N-H$	Imine
②	$-R$	H_2N-R	Alkylamine	$>C=N-R$	N-alkylimine (Schiff's Base)
③	$-OH$	H_2N-OH	Hydroxylamine	$>C=N-OH$	Oxime
④	$-NH_2$	H_2N-NH_2	Hydrazine	$>C=N-NH_2$	Hydrazone
⑤	$-NH-Ph$	$H_2N-NH-Ph$	N-phenyl Hydrazine	$>C=N-NH-Ph$	N-phenyl hydrazone
⑥			2,4-dinitro phenyl hydrazine (2,4-DNP)		2,4-DNP hydrazone
⑦			Semicarbazide		Semicarbazone

* 2,4-DNP is used in Poc of carbonyl.

Aldehyde $\xrightarrow{2,4\text{-DNP}}$ Red colour

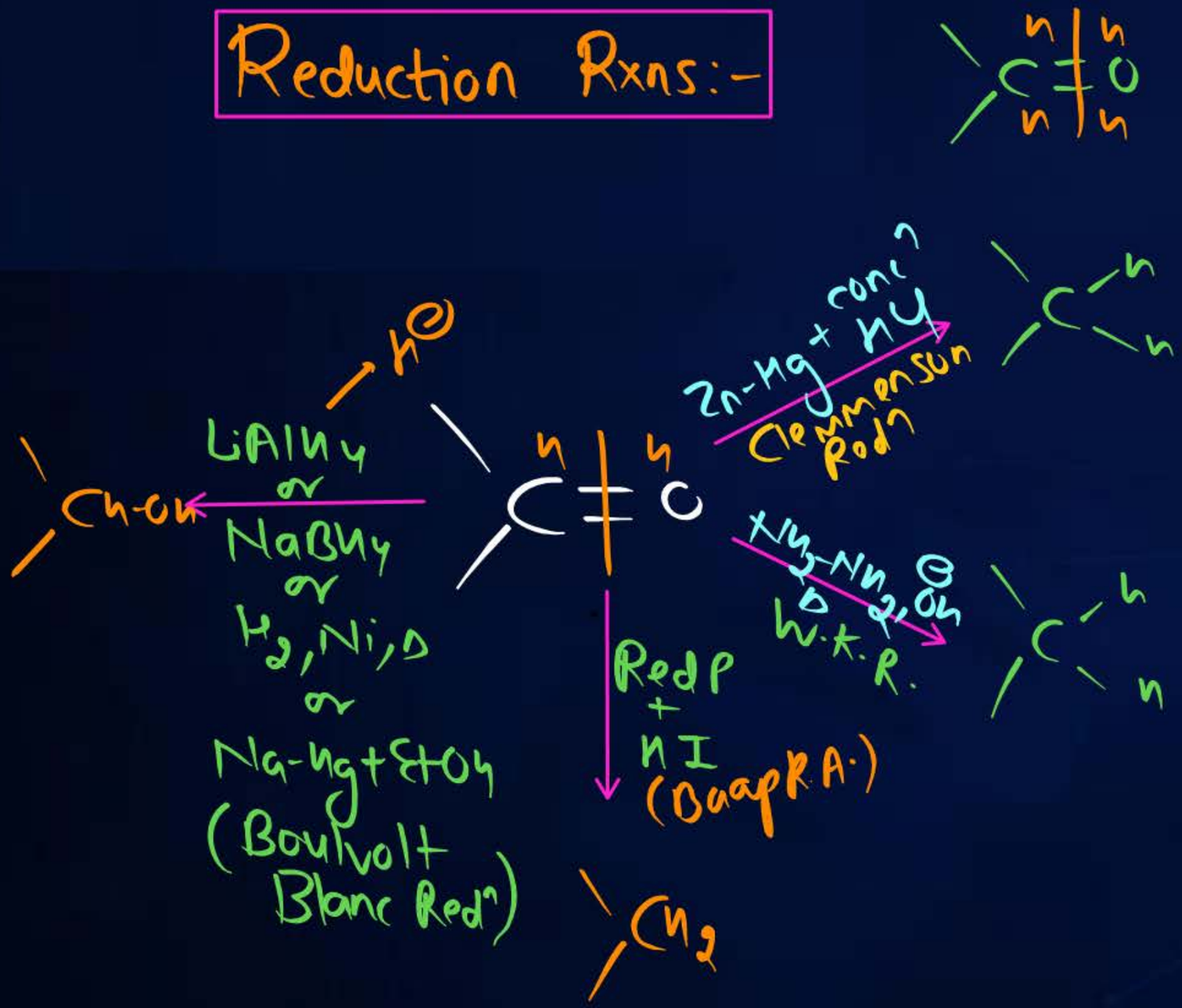
Ar. ald. $\xrightarrow{\text{"}}$ Yellow colour

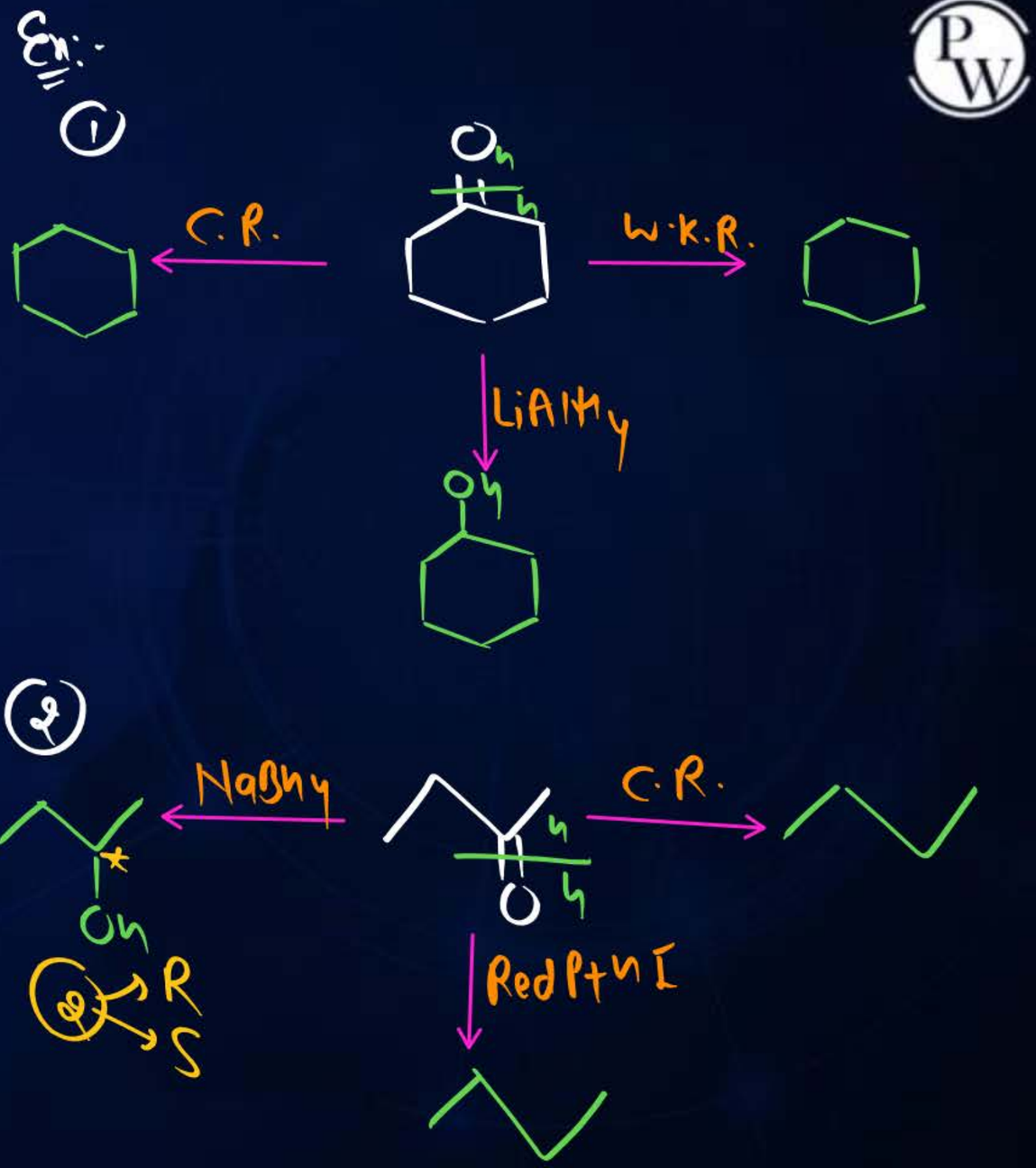
Ketone $\xrightarrow{\text{"}}$ Orange colour



Bipasha ROY Akar

Reduction Rxns:-





Oxidation Reactions

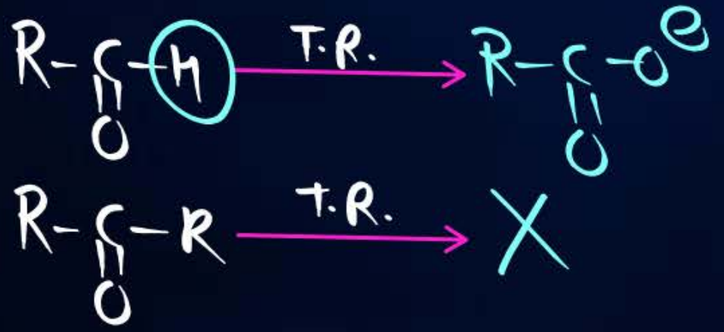
$Ag^{+} > Cu^{+2}$ {Oxidising Power}

Tollen's Test

Tollen's Reagent :- $AgNO_3 + NH_4OH$ or $Ag^{+}(NH_3)_2\ OH^{\ominus}$

Reacting Specie :- Ag_2O

① Aldehyde ✓
② Ar. ald. ✓
③ ketone ✗

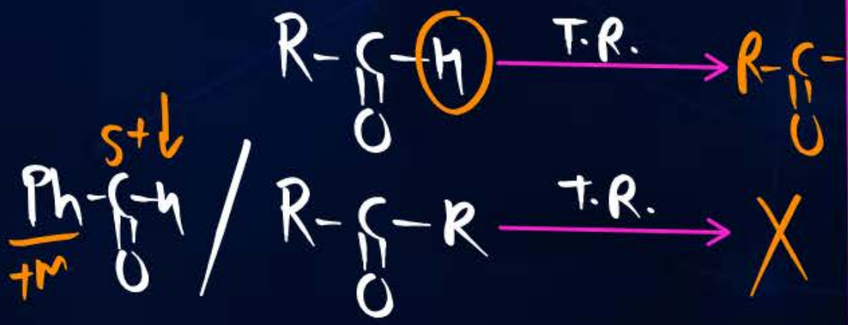


Fehling Test

Fehling Reagent :- Fehling sol^{n} (A) aq. $CuSO_4$
Fehling sol^{n} (B) Na-K tartarate (Roschelle Salt)

Reacting Specie :- Cu_2O
Cu^{+2} (Blue) $\longrightarrow$ Cu^{+1} (Brick Red)

① Aldehyde ✓
② Ar. ald. ✗
③ ketone ✗



Benedict Test

Benedict Reagent :- aq. $CuSO_4$ + $NaOH$ + Sodium citrate

Reacting Specie :- Cu_2O
Cu^{+2} (Blue) $\longrightarrow$ Cu^{+1} (Brick Red)

① Aldehyde ✓
② Ar. ald. ✗
③ ketone ✗

Oxidation Reactions

Schiff's Test

Schiff's Reagent → p-ROS aniliniumhydrochloride

Schiff's Reagent (Magenta dye / pink dye) $\xrightarrow{SO_2}$ Colourless

- Ald. → pink colour regenerate
- ketone → colourless

Mercuric Chloride Test

$$R-\underset{\underset{O}{\|}}{C}-H + \overset{+2}{Hg}Cl_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-OH + \overset{+1}{Hg_2}Cl_2\downarrow$$

(white ppt.)

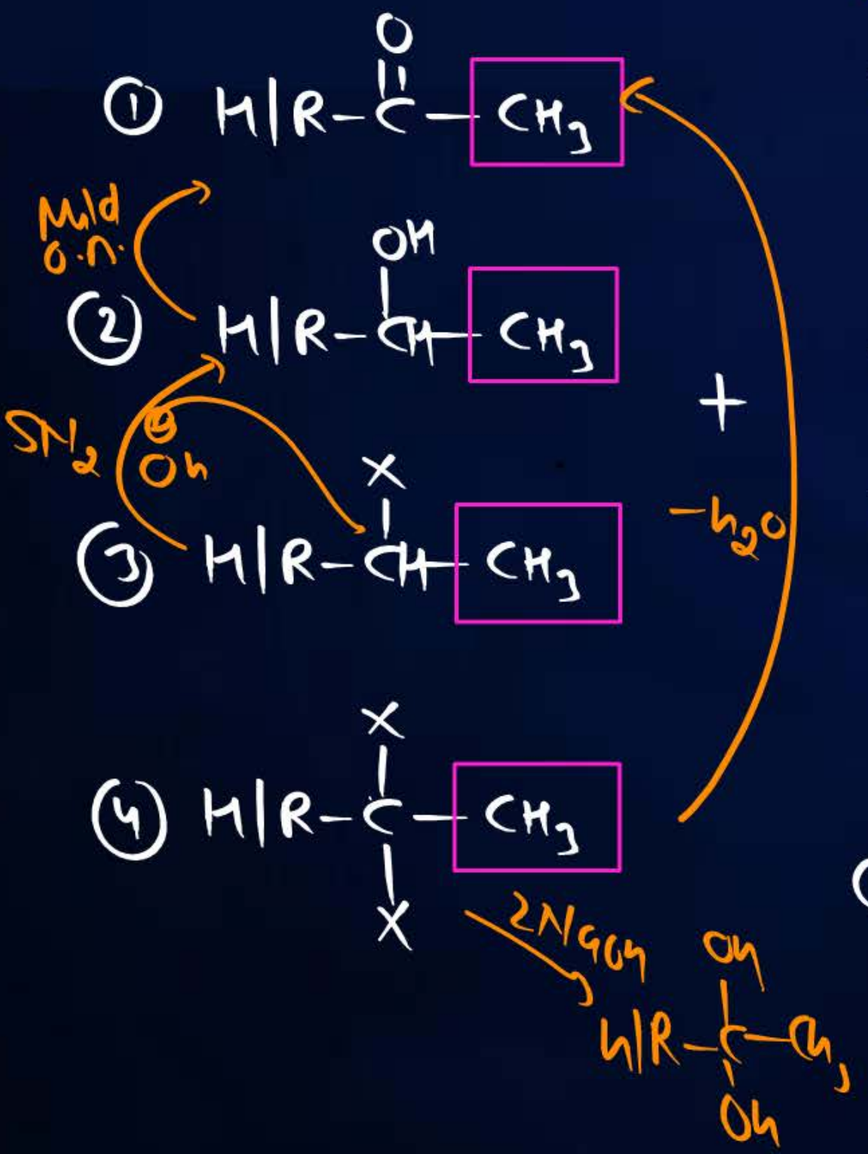
$$R-\underset{\underset{O}{\|}}{C}-H + \overset{+1}{Hg_2}Cl_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-OH + \overset{0}{Hg}\downarrow$$

(greyish black)

Oxidation Reactions

Haloform Test

Substrate



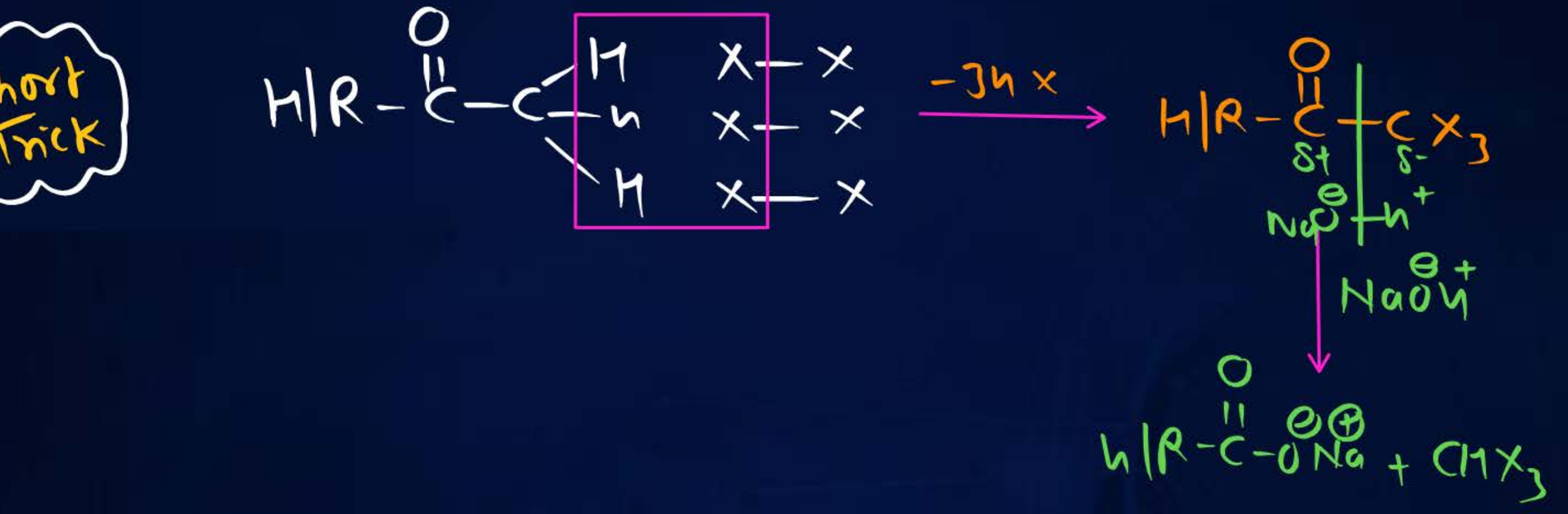
Reagent (Mild O.N.)

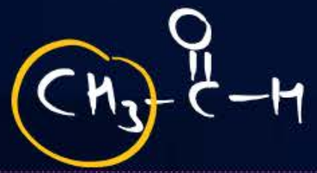
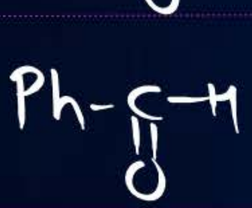
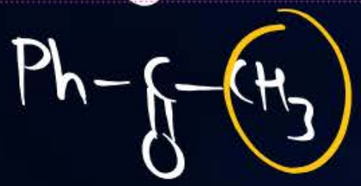
X_2 + Base
or
X_2 + NaOH
or
X_2 + KOH
or
$X_2 + Ca(OH)_2$
or
$NaOX \rightarrow NaOH + X_2$
or
$CaOCl_2 \cdot 2H_2O$

$\longrightarrow$ $CHX_3 + H/R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus}$

CHI_3 (yellow colour)
(Iodoform)

Short Trick



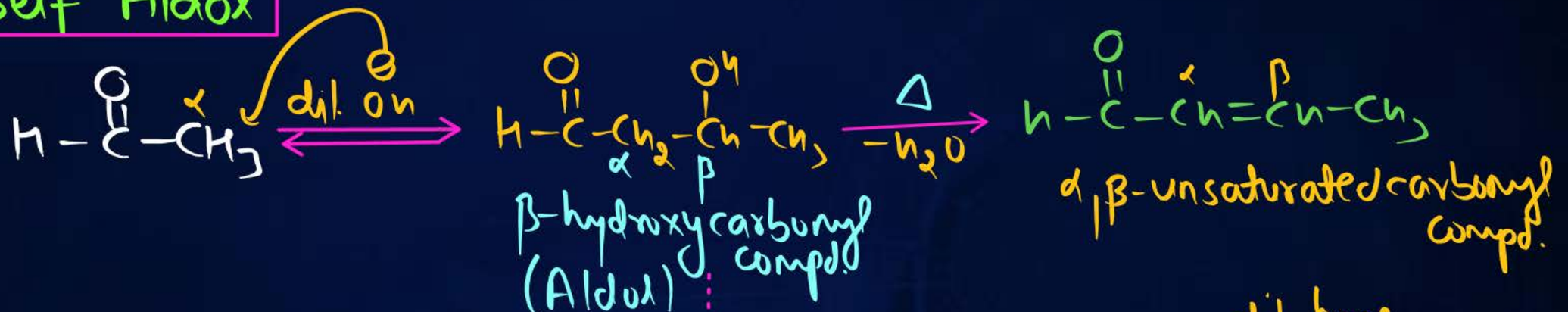
S.No.	Substrate	Tollen	Fehling	Iodoform	$NaHSO_3$ test
①		✓	✓	✗	✓
②		✓	✓	✓	✓
③		✓	✓	✗	✓
④		✓	✗	✗	✓
⑤		✗	✗	✓	✓
⑥		✗	✗	✓	✓
⑦		✗	✗	✓	✗

Aldol Rxn:-

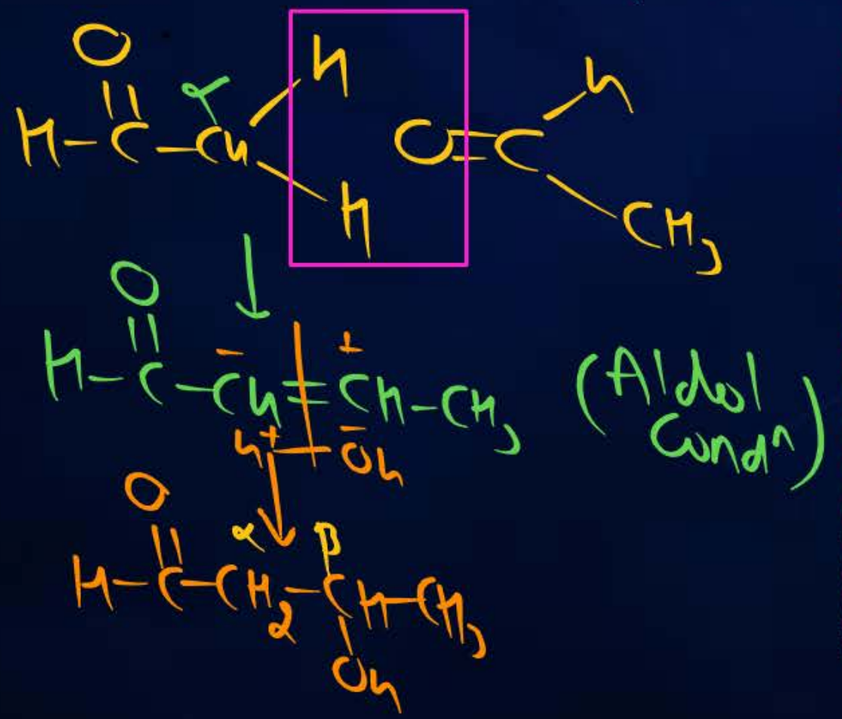
NaOH, KOH, $Ba(OH)_2$, Na_2CO_3 etc.

① Self Aldol

Rxn:-



Short Trick :-



* Condⁿ for Aldol → dil. base, α-H ✓
* Int → $C^{\ominus}$
* New C–C bond
* Rate of NAR:- Ald > Ketone

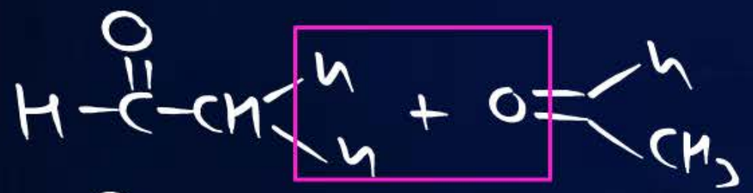
② Cross or Mixed Aldol

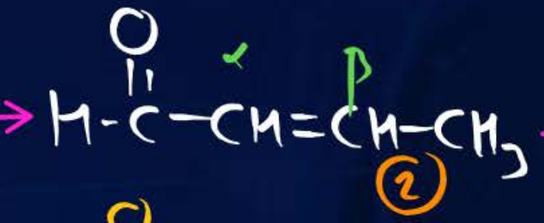
Rxn:- $H-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightleftharpoons{dil.\ \overset{\ominus}{O}H}$

(A) $H-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2$ (B) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2$

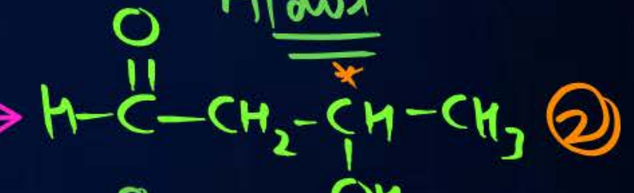
	Aldol	Aldol condⁿ
No. of struct. product =	4	4
No. of possible product =	6	6

(A)-(A)

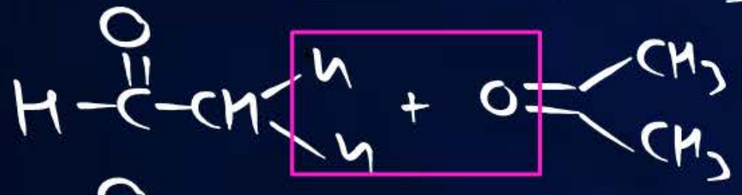


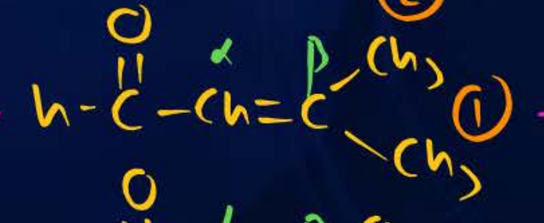


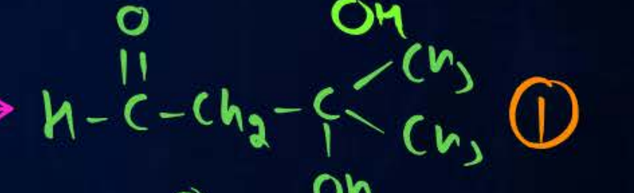
Aldol



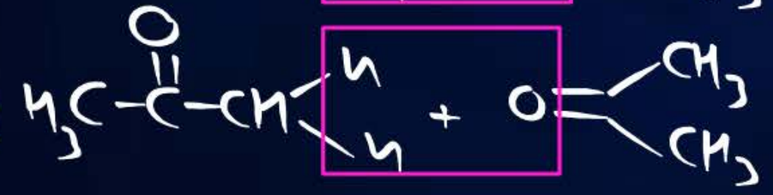
(A)-(B)

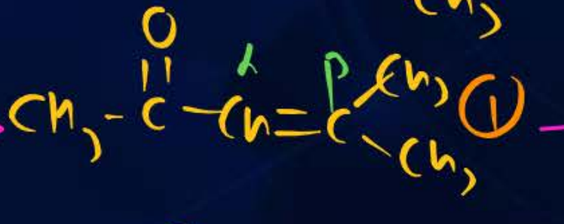


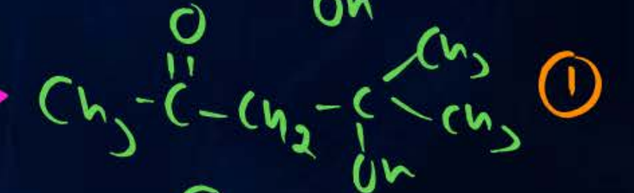




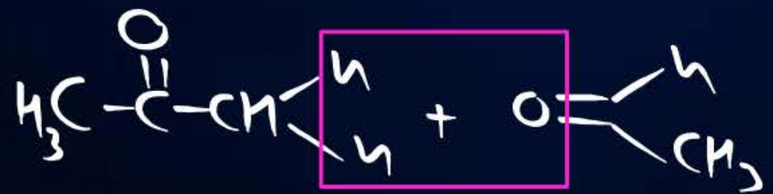
(B)-(B)

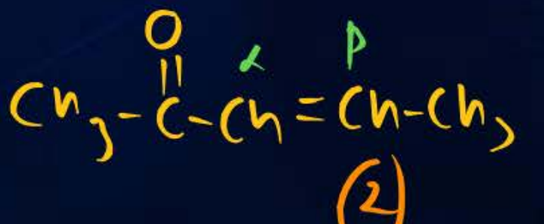


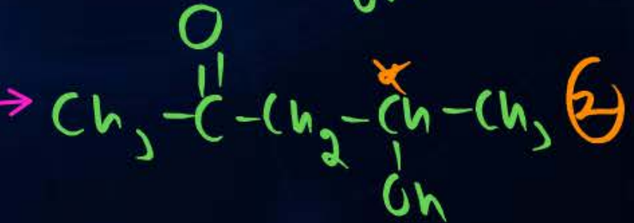




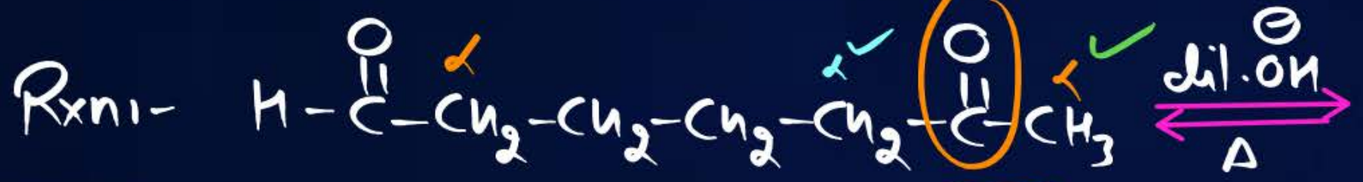
(B)-(A)





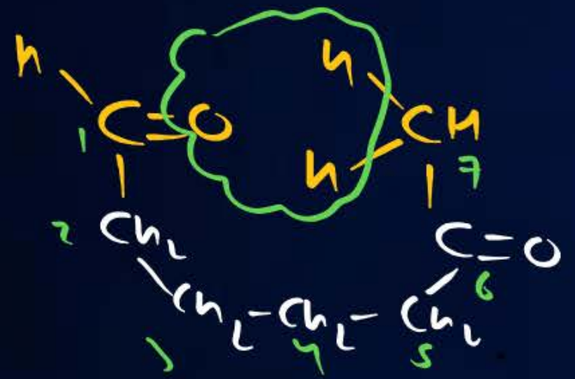


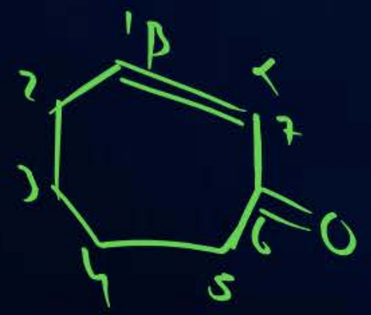
③ Intramolecular Aldol

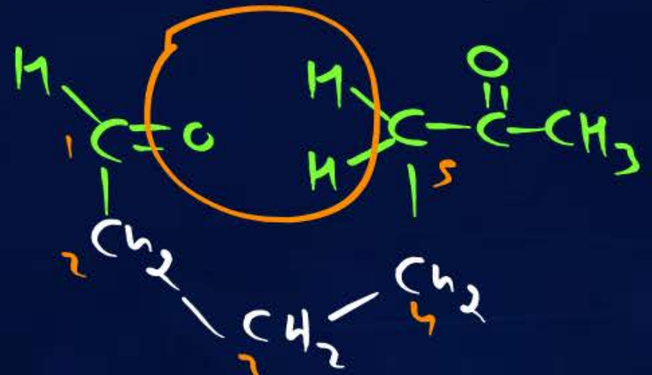
Rxn :- 

Ring stability order :→ 6 > 5 = 7 > 4 > 3

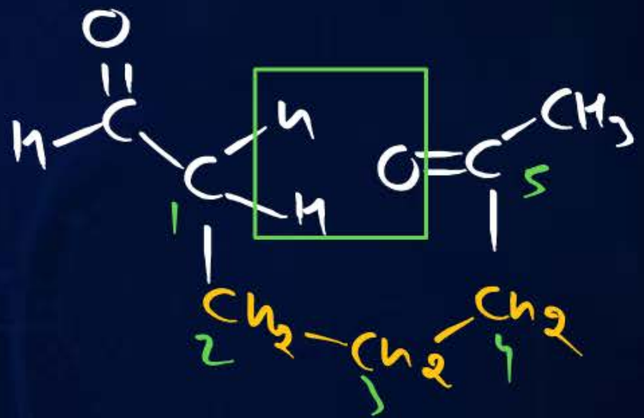
Rate y NAR :→ Ald > Ketone

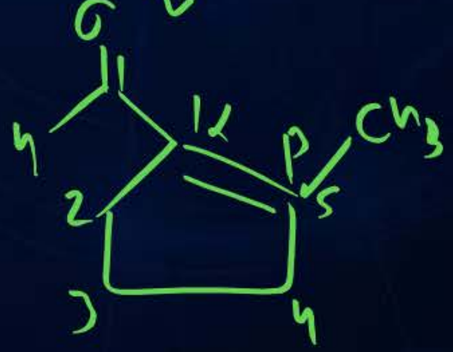






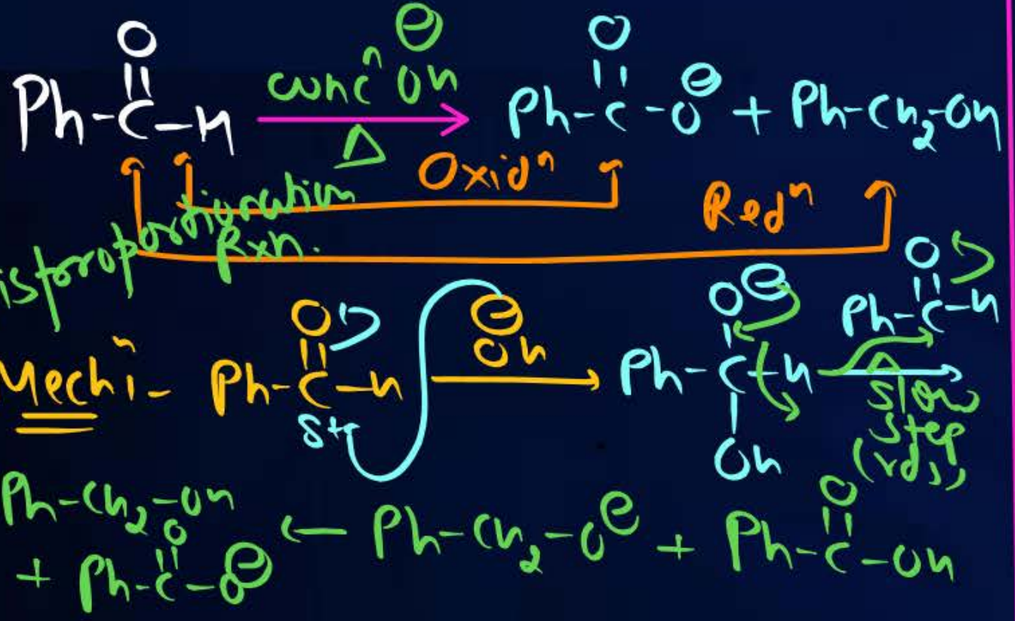
(Major)





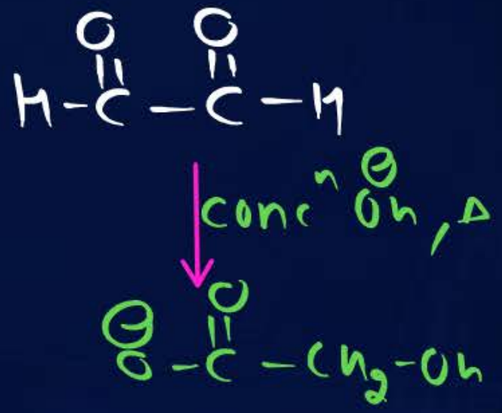
Cannizaro Rxn :- ($\alpha H = 0$)

① Self Cannizaro

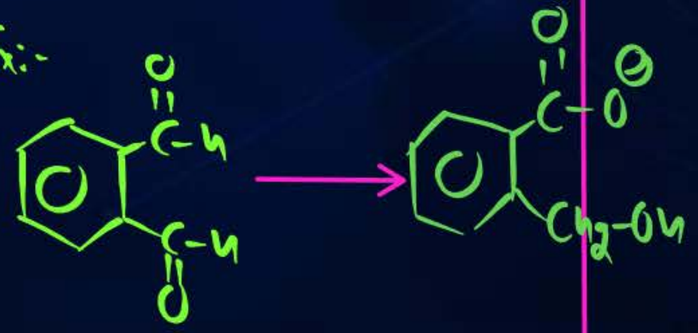


* Cond^n → Conc^n base
  → $\alpha H = 0$ ($H-CHO$, $Ph-CHO$, CH_3-CHO ✗)
* High temp.
* Transfer of Hydride is RDS.

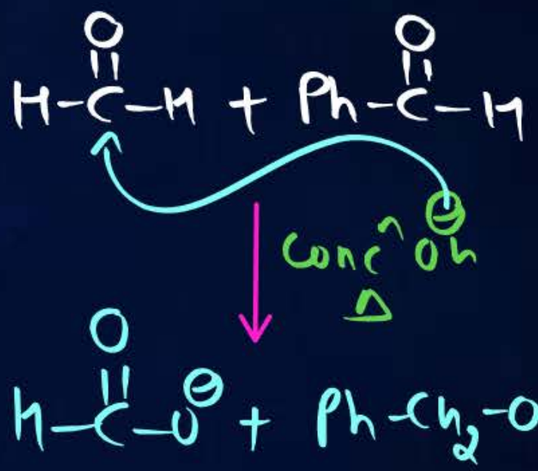
② Intramolecular Cannizaro



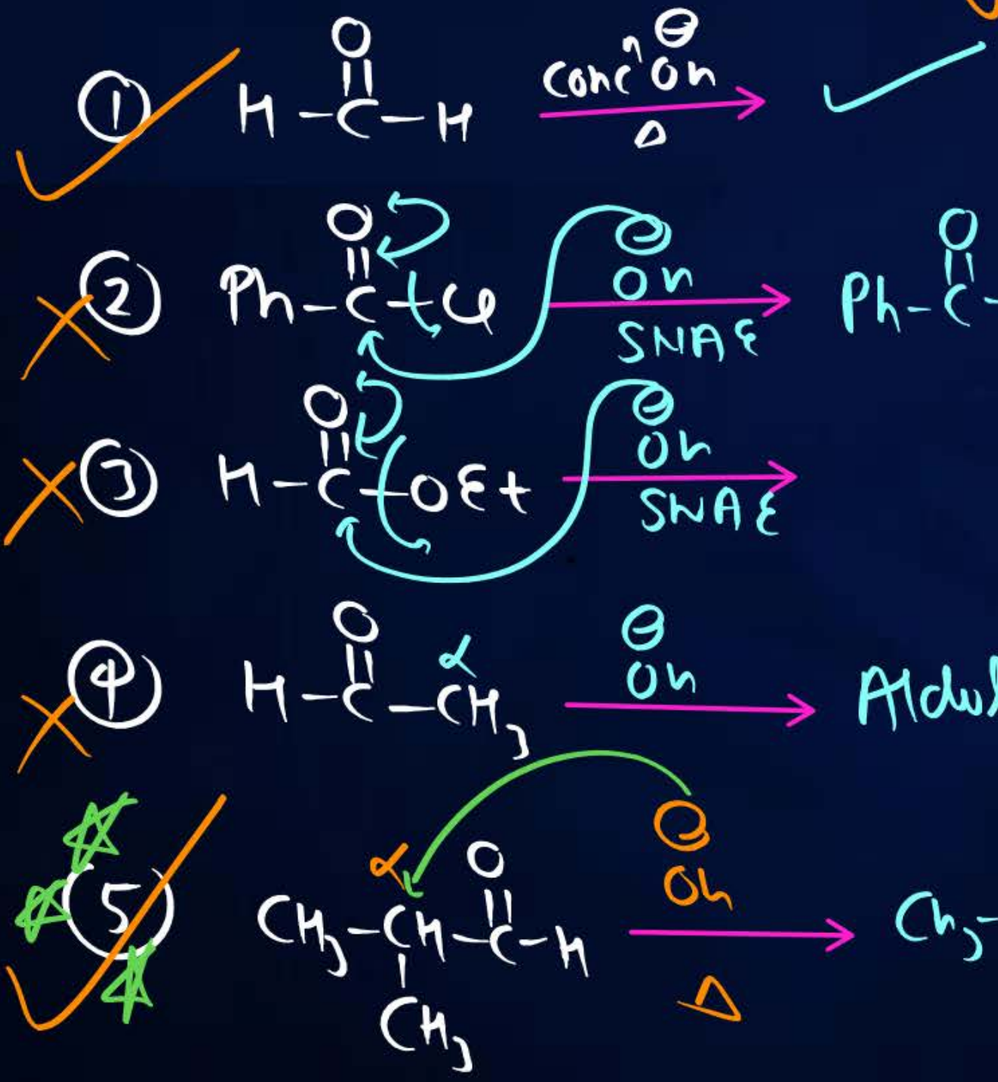
Ex:-

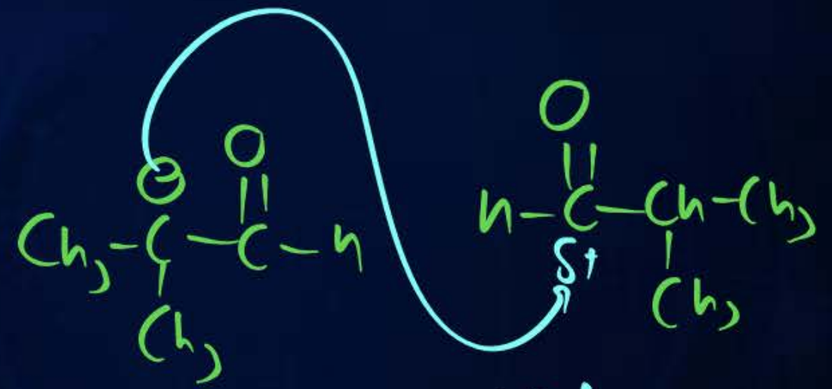


③ Cross or Mixed Cannizaro (Redox Rxn.)

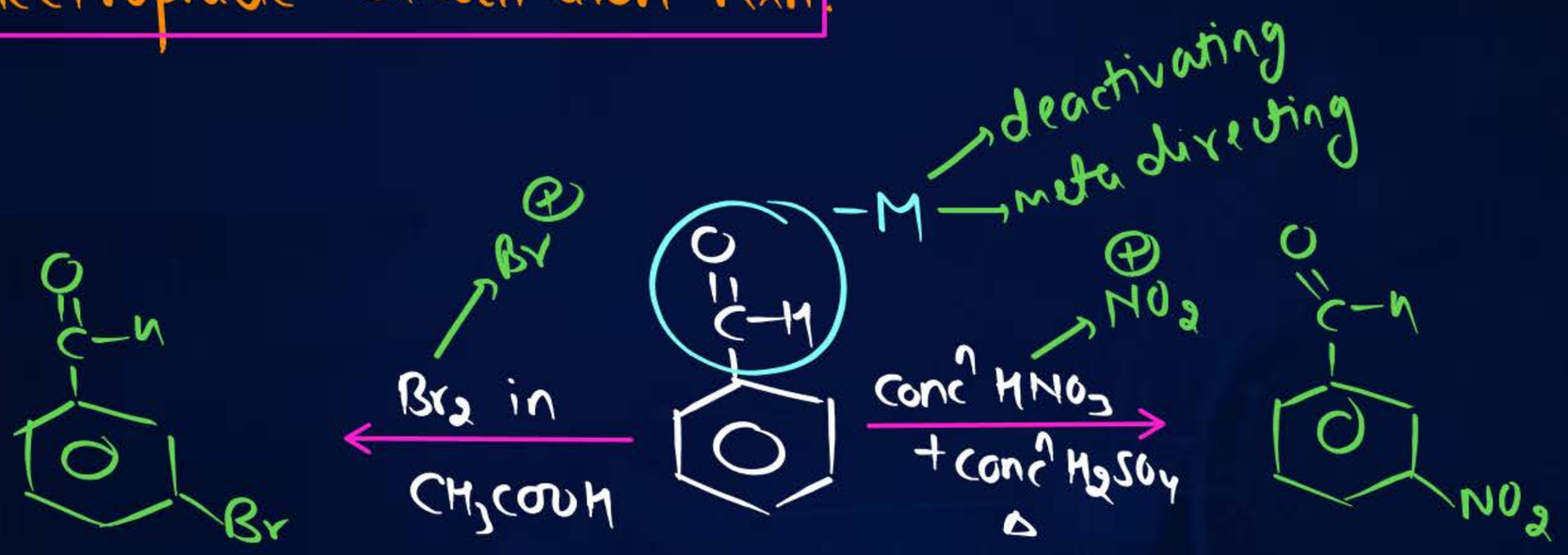


Que. Which of the following gives Cannizaro's-



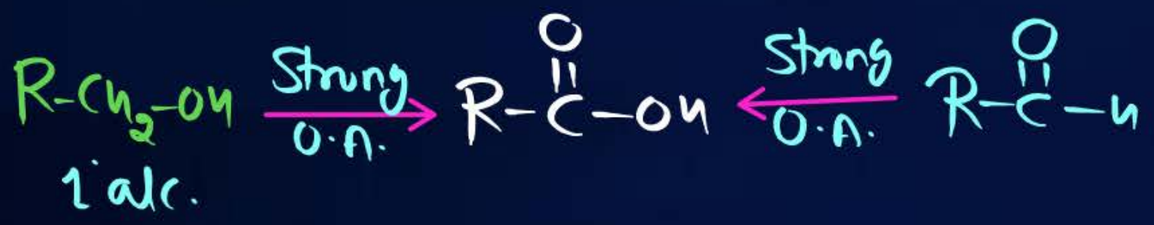


Electrophilic Substitution Rxn :-



MOP of Carboxylic Acid

① From oxidation of Alcohols, Aldehyde & Ketones



Strong O.A:-

① $KMnO_4, H^{\oplus}$

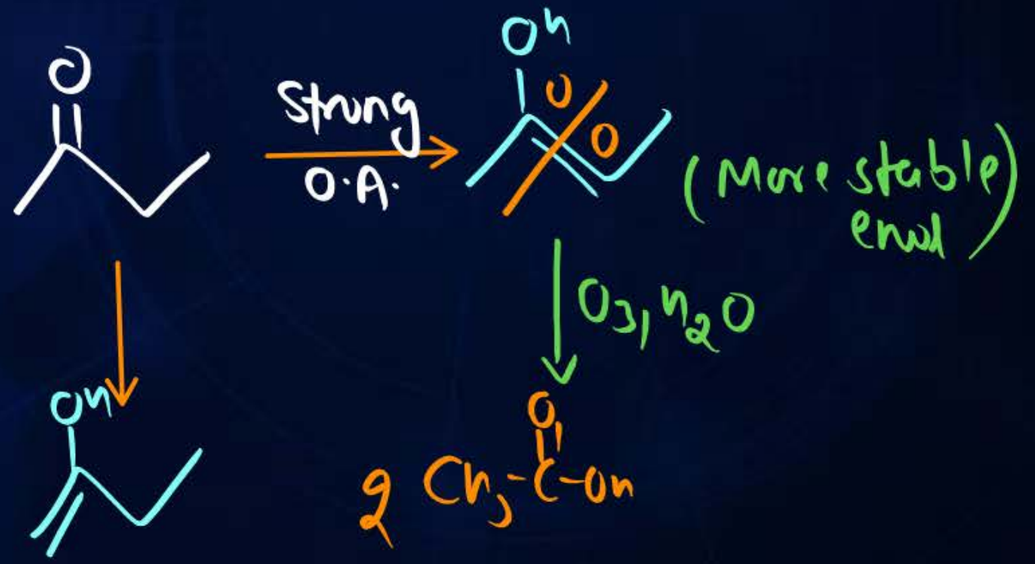
② $K_2Cr_2O_7, H^{\oplus}$

③ Jone's Reagent

④ conc^n HNO_3

Popoff's Rule

Draw stable enol then oxidative ozonolysis



② Tollen's test ✓

③ Fehling test ✓

④ Benedict test ✓

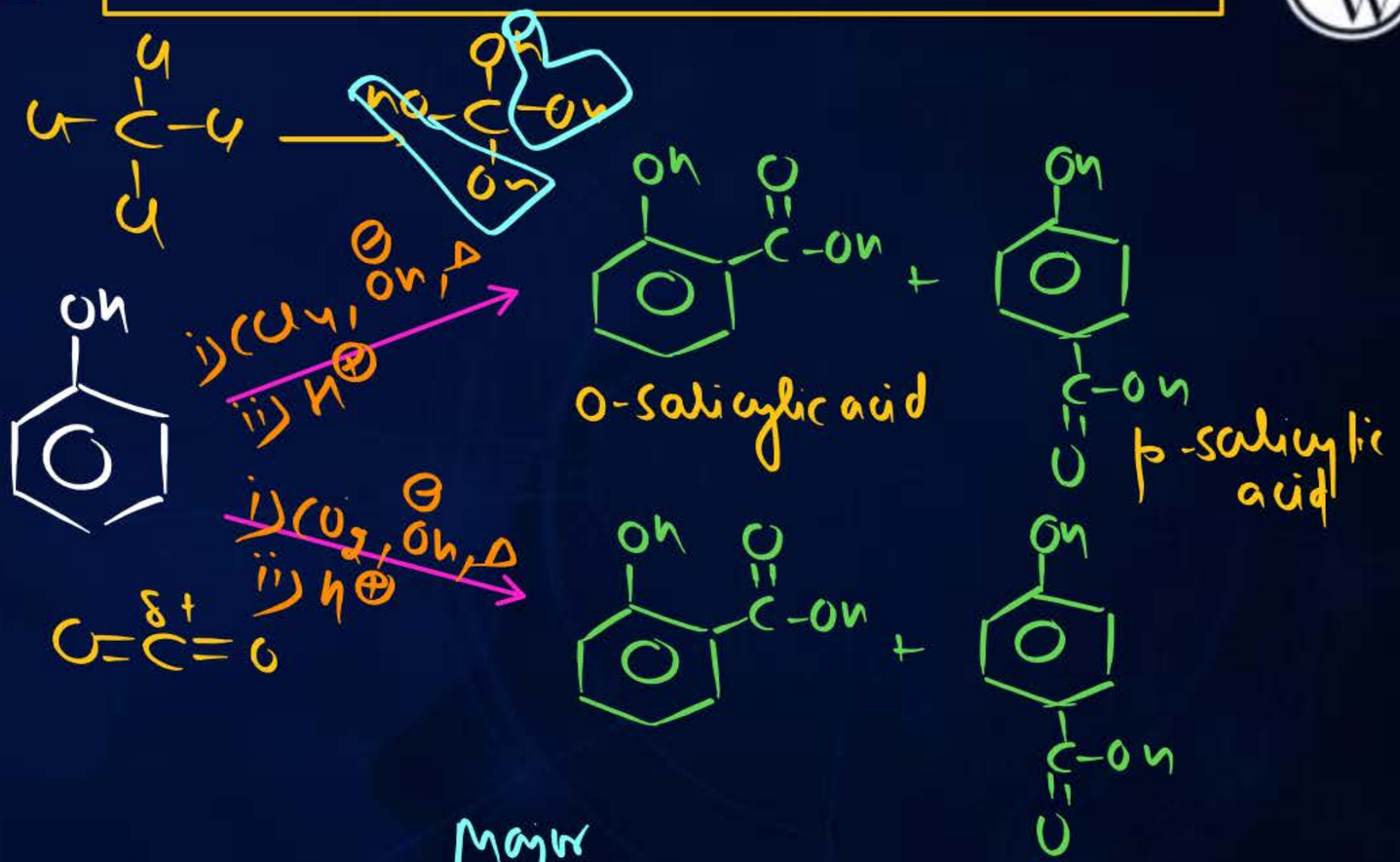
⑤ Mercuric Chloride Test ✓

⑥ Haloform test ✓

⑦ Cannizaro Rxn. ✓

⑧ Oxidative ozonolysis ✓

⑨ Reimer Teimann Rxn: & Kolbe Rxn:-

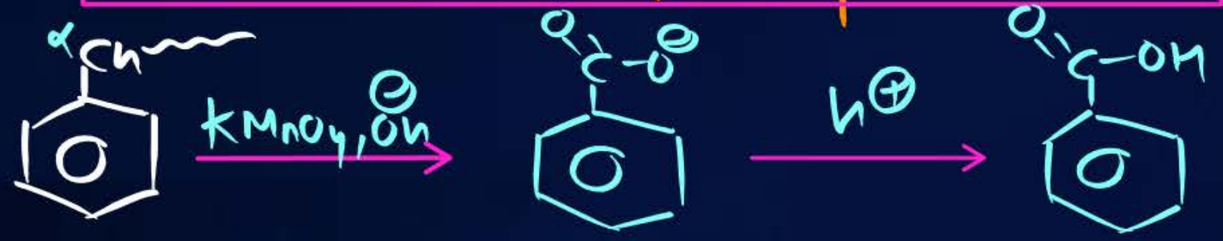


NaOH → Major ortho ✓

KOH → para ✓

(10) From oxidation of Alkylated Benzene:-

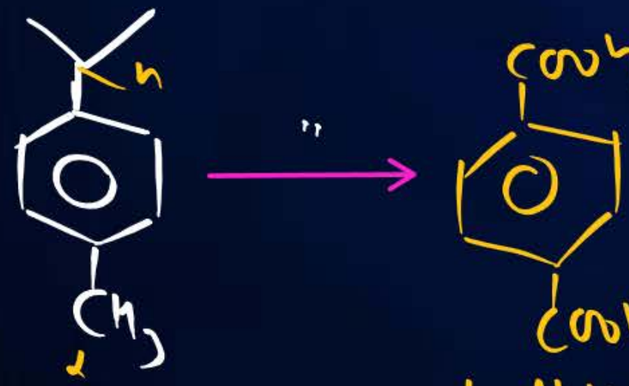
Rxn:-



Ex:- (1)

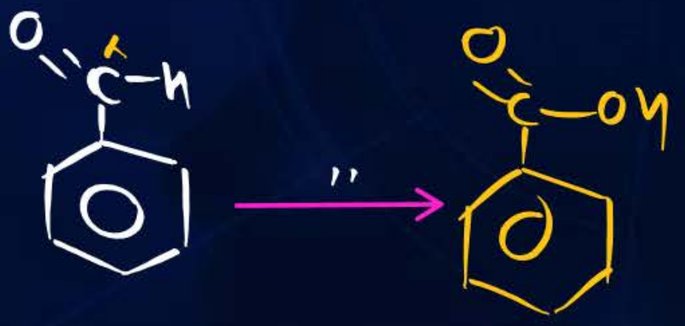
(3)

(2)



terephthalic acid

(4)



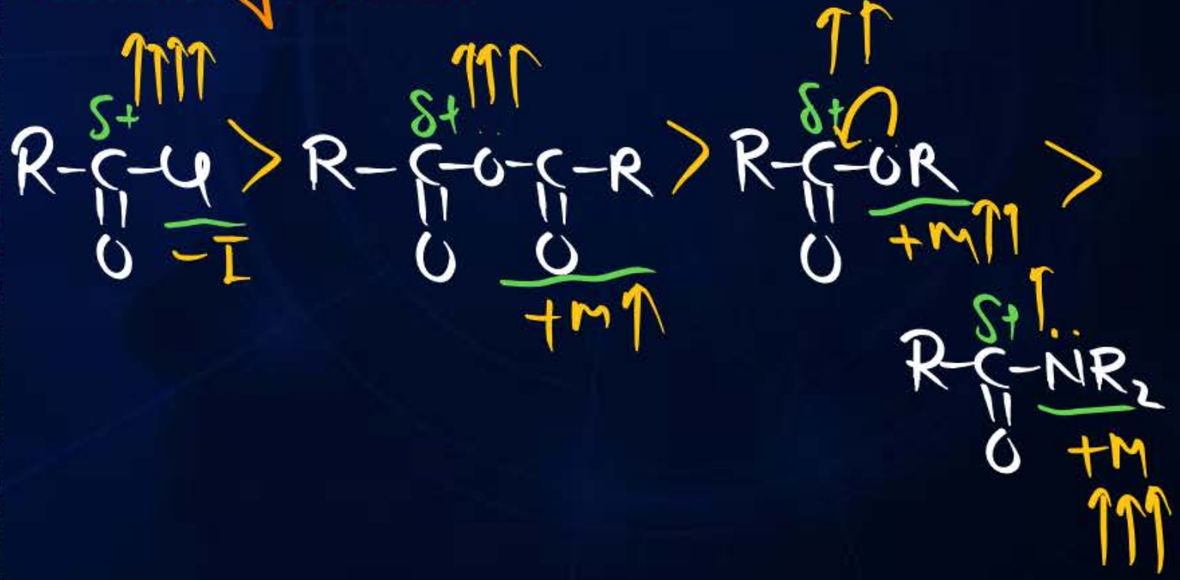
SNAE Rxn:-

- $-X$
- $-O-\overset{\overset{O}{\|}}{C}-R$
- $-OR$
- $-NR_2$

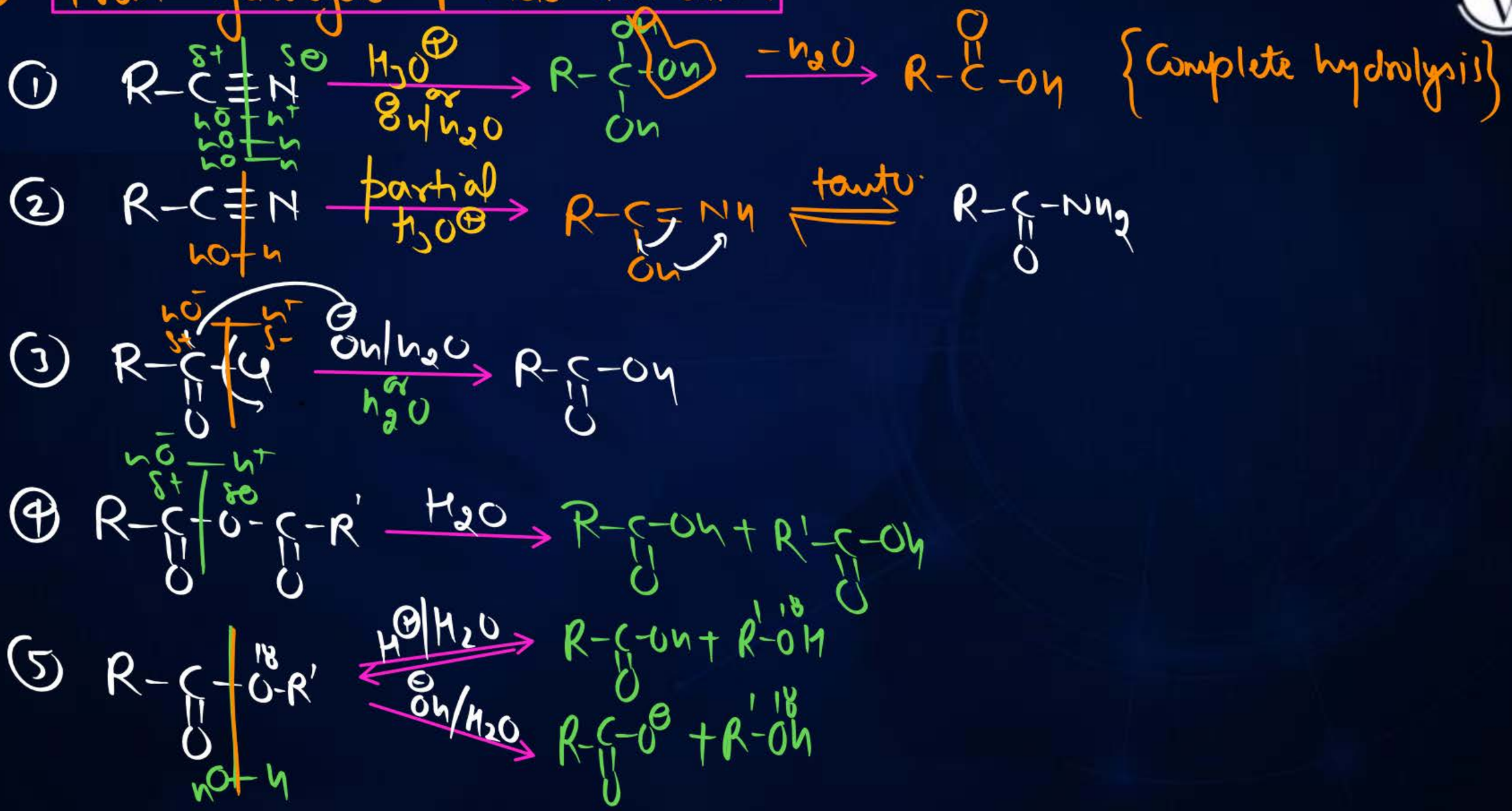
B.E.: C=O > C-O

Rate of SNAE ∝ δ⊕ on at carbonyl grp

Rate of SNAE:-



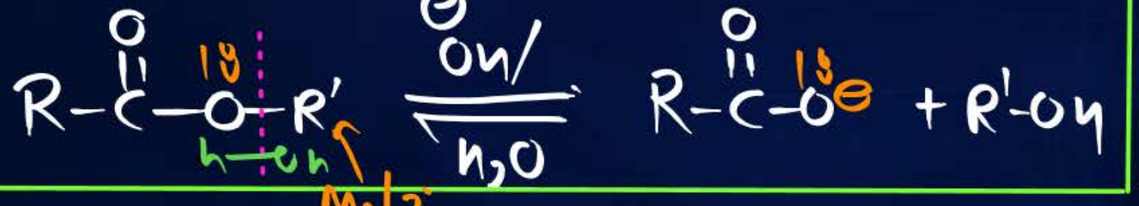
(11) From hydrolysis of Acid derivative



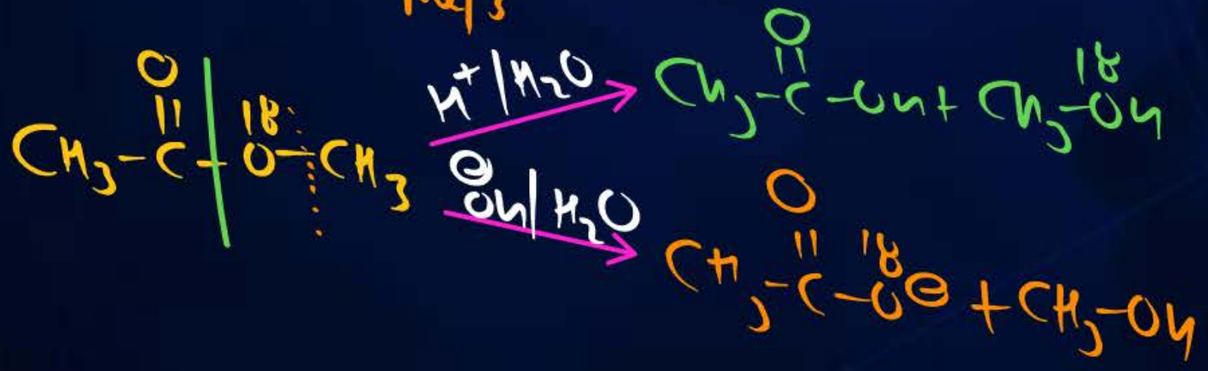
Gehri Baat

Acidic Medium

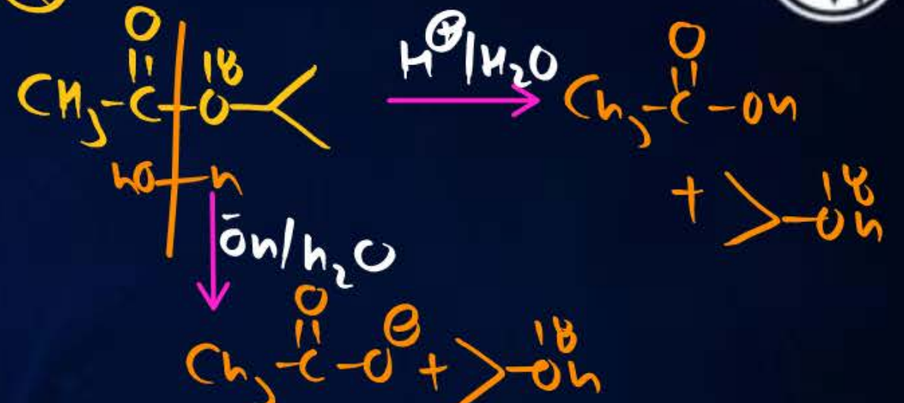
Basic Medium



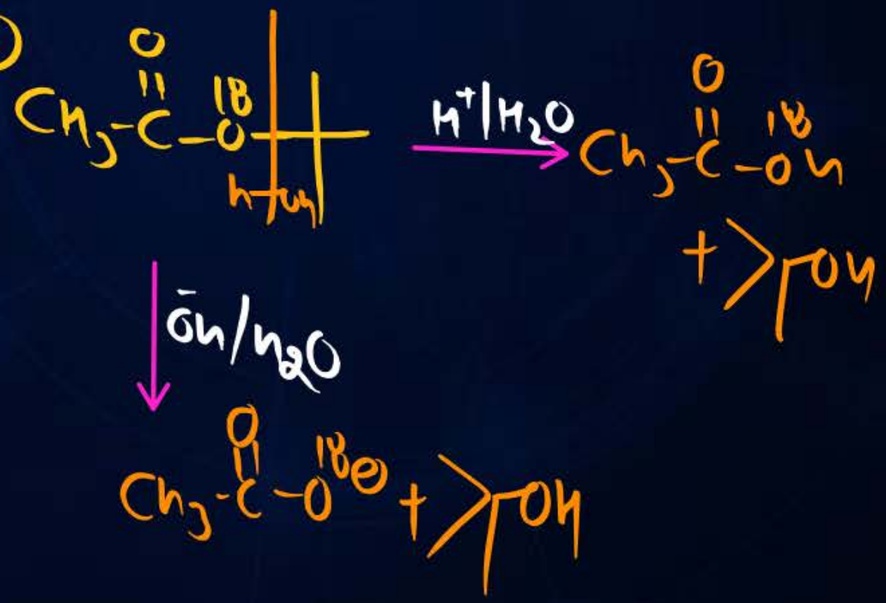
Ex:- ①



②



③



(12) From Grignard Reagent

Rxn:- $RMgX \xrightarrow[ii)\ H_2O]{i)\ CO_2} R-\overset{O}{\overset{\|}{C}}-OH + Mg\begin{<}X\\OH\end{>}$

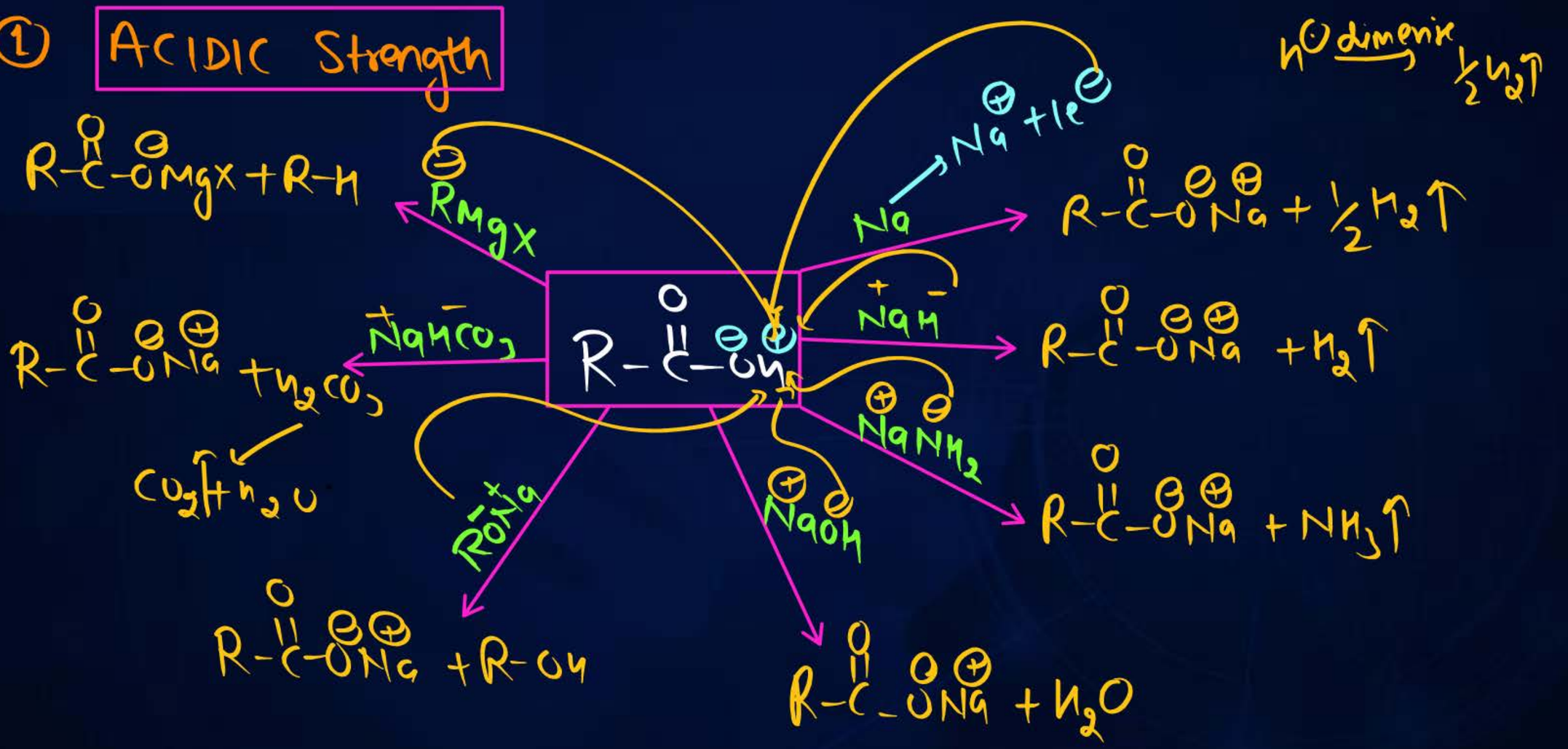
Mech^n:- $R\overset{\ominus}{M}gX$ attacks $O=\overset{\delta+}{C}=O$ $\rightarrow R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}MgX \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-OH + Mg\begin{<}X\\OH\end{>}$

Ex:- (1) $PhMgBr \xrightarrow[ii)\ H_3O^{\oplus}]{i)\ CO_2} Ph-\overset{O}{\overset{\|}{C}}-OH$

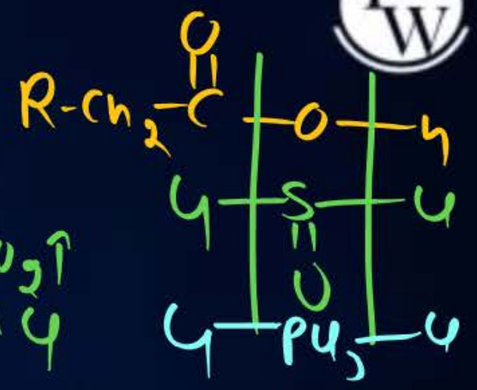
(2) $CH_3MgBr \xrightarrow[ii)\ H_3O^{\oplus}]{i)\ CO_2} CH_3-\overset{O}{\overset{\|}{C}}-OH$

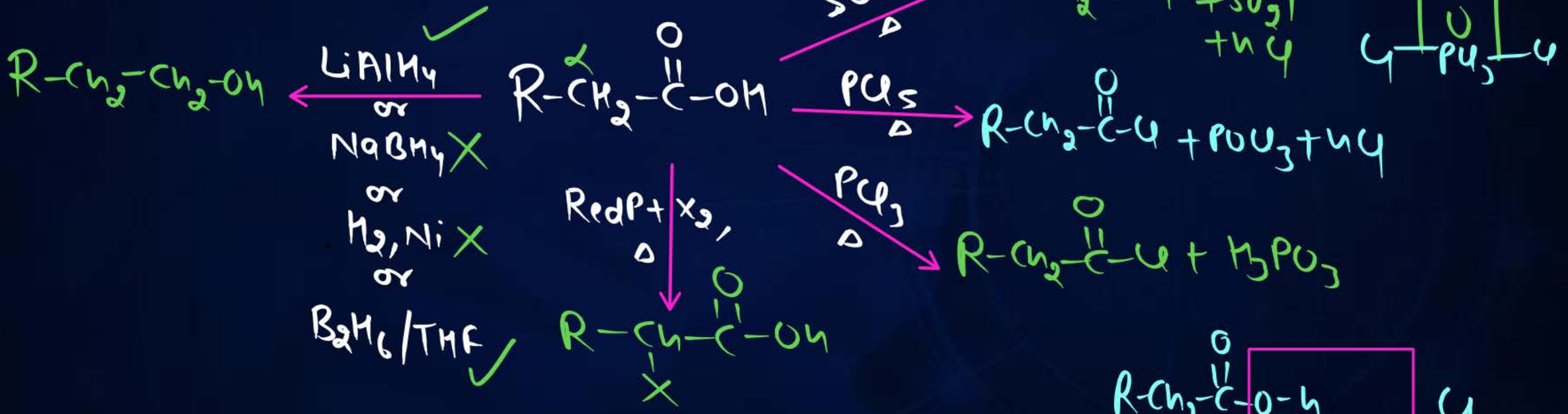
Chemical properties of Carboxylic Acid

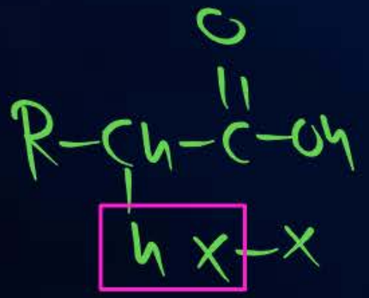
① ACIDIC Strength



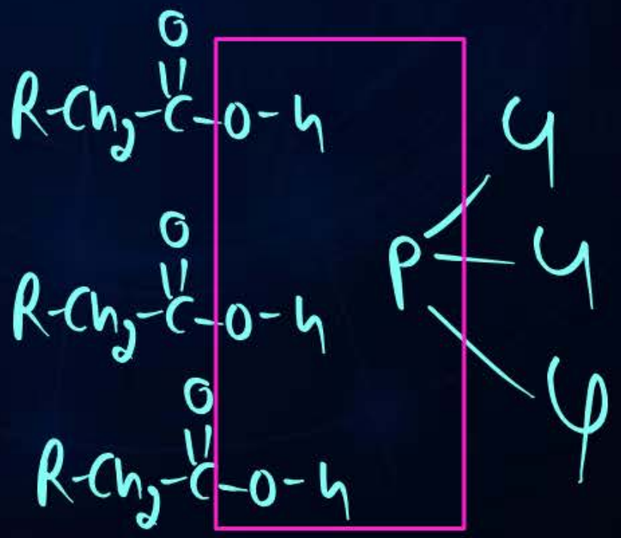
$NaBH_4$ → ① Ald ② Ketone ③ Acid halide ④ R–X (To S_N2 detach)

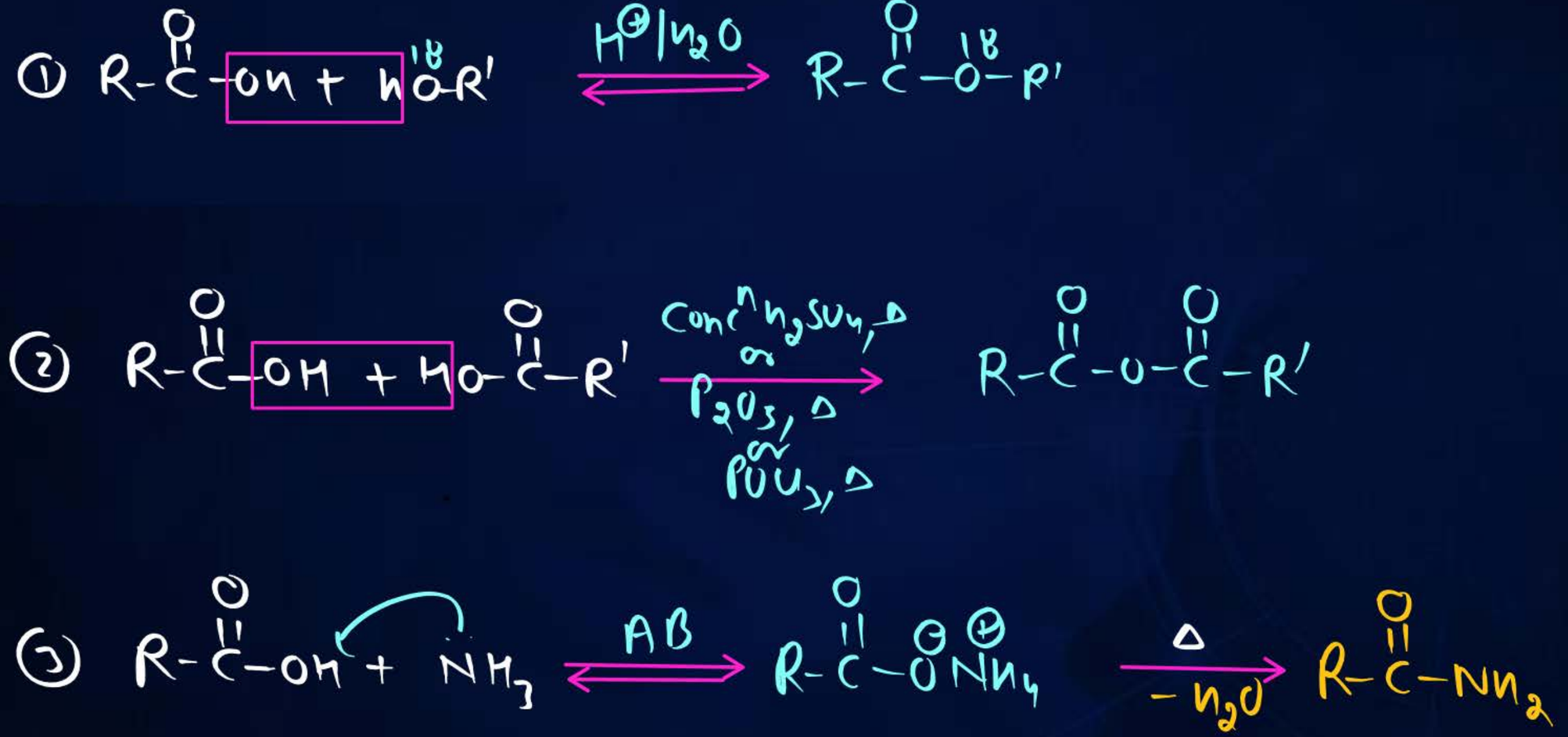






Hell Volhard Zelenskei (HVZ Rxn.)



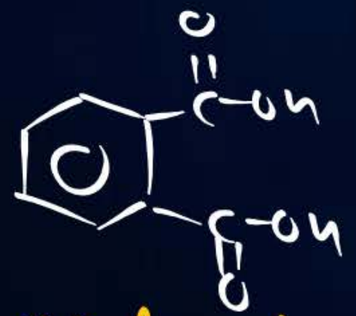

① R-C(=O)-OH + H¹⁸O-R' ⇌ (H⊕/H₂O) R-C(=O)-¹⁸O-R'
② R-C(=O)-OH + HO-C(=O)-R' → (Conc^n H₂SO₄, Δ or P₂O₅, Δ or POCl₃, Δ) R-C(=O)-O-C(=O)-R'
③ R-C(=O)-OH + NH₃ ⇌ (AB) R-C(=O)-O⊖ NH₄⊕ → (Δ, −H₂O) R-C(=O)-NH₂

Ex:

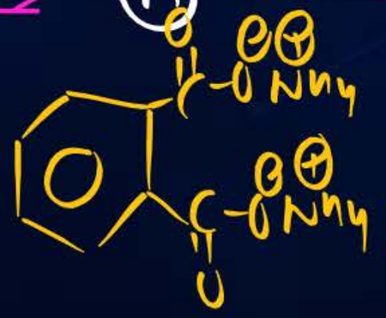
① $CH_3-C(=O)-OH + H^{18}O-R' \rightleftharpoons[H^{\oplus}/H_2O]{} CH_3-C(=O)-{}^{18}O-R'$

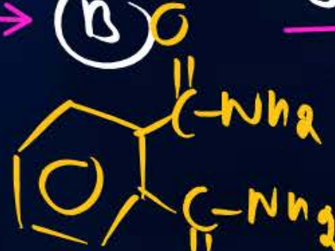
② $CH_3-C(=O)-OH + HO-C(=O)-Ph \xrightarrow{P_2O_5,\Delta} CH_3-C(=O)-O-C(=O)-Ph$

③ $CH_3-C(=O)-OH + NH_3 \rightleftharpoons[\Delta]{} CH_3-C(=O)-O^{\ominus}NH_4^{\oplus} \xrightarrow{\Delta} CH_3-C(=O)-NH_2$ Acetamide

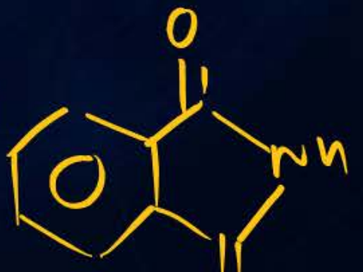
④  + $NH_3 \rightleftharpoons[\Delta]{}$ (A) $\xrightarrow{\Delta}$ (B) $\xrightarrow[\Delta]{Strong}$ (C)

phthalic acid

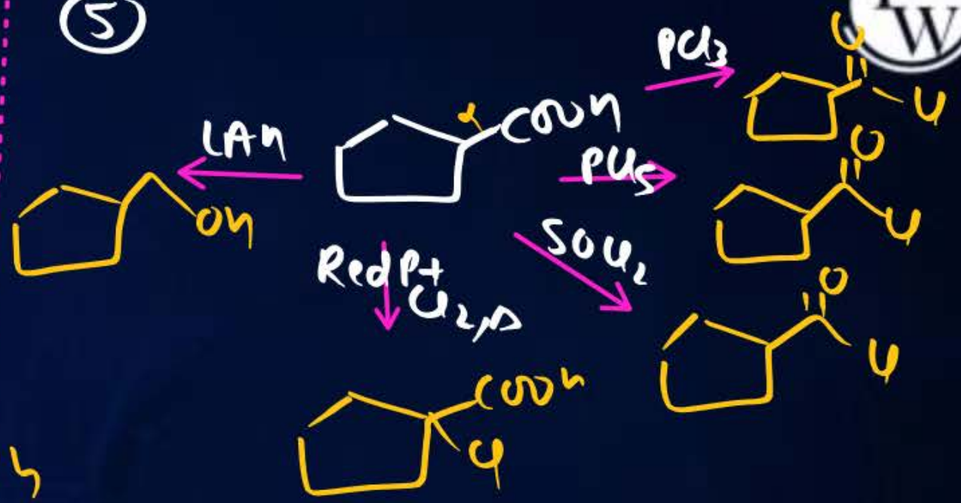


(B) 

phthalamide

(C) 

phthalimide

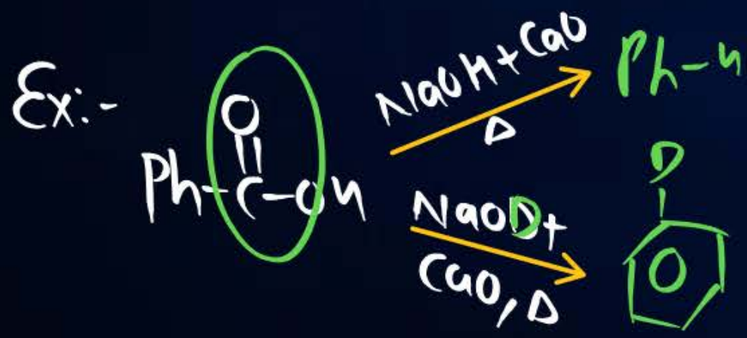
⑤ 

Decarboxylation Reaction

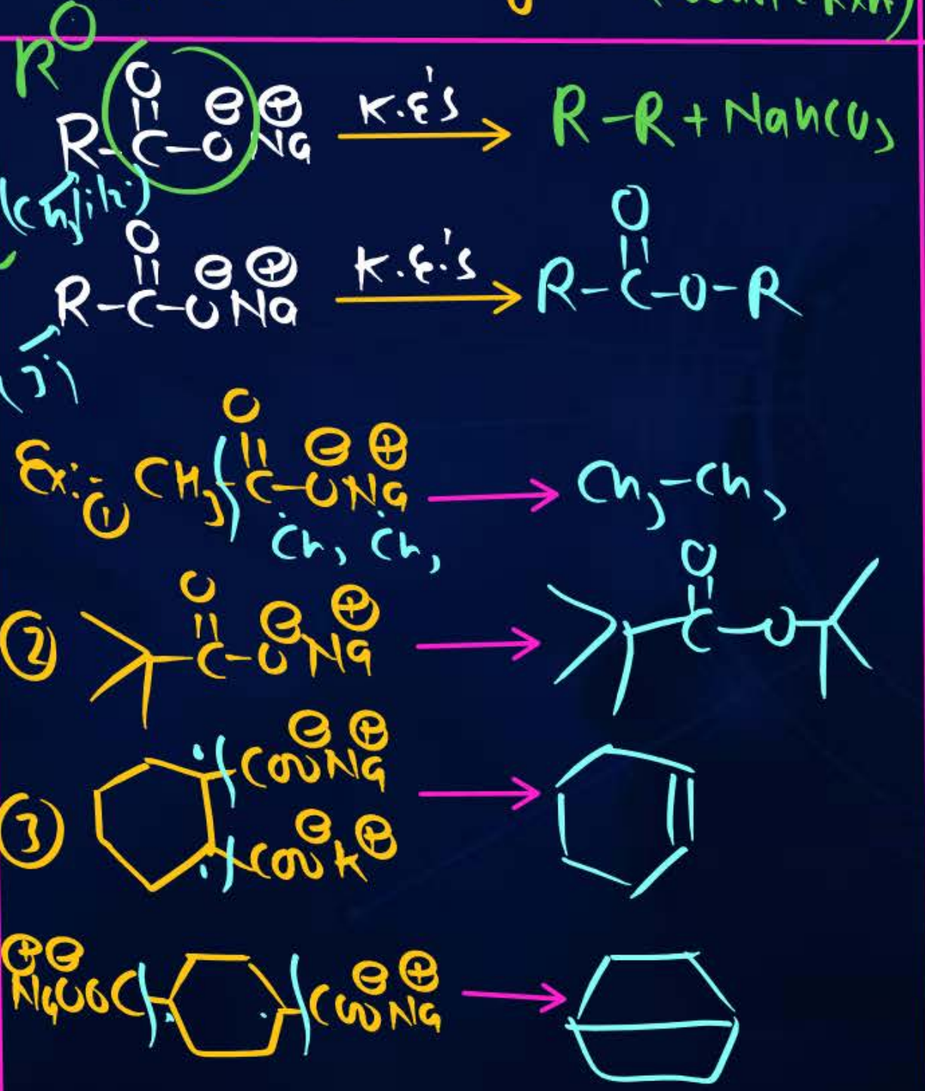
Decarboxylation by Soda Lime

Rate of Decarboxylation $\propto$ St. of $C^{\ominus}$

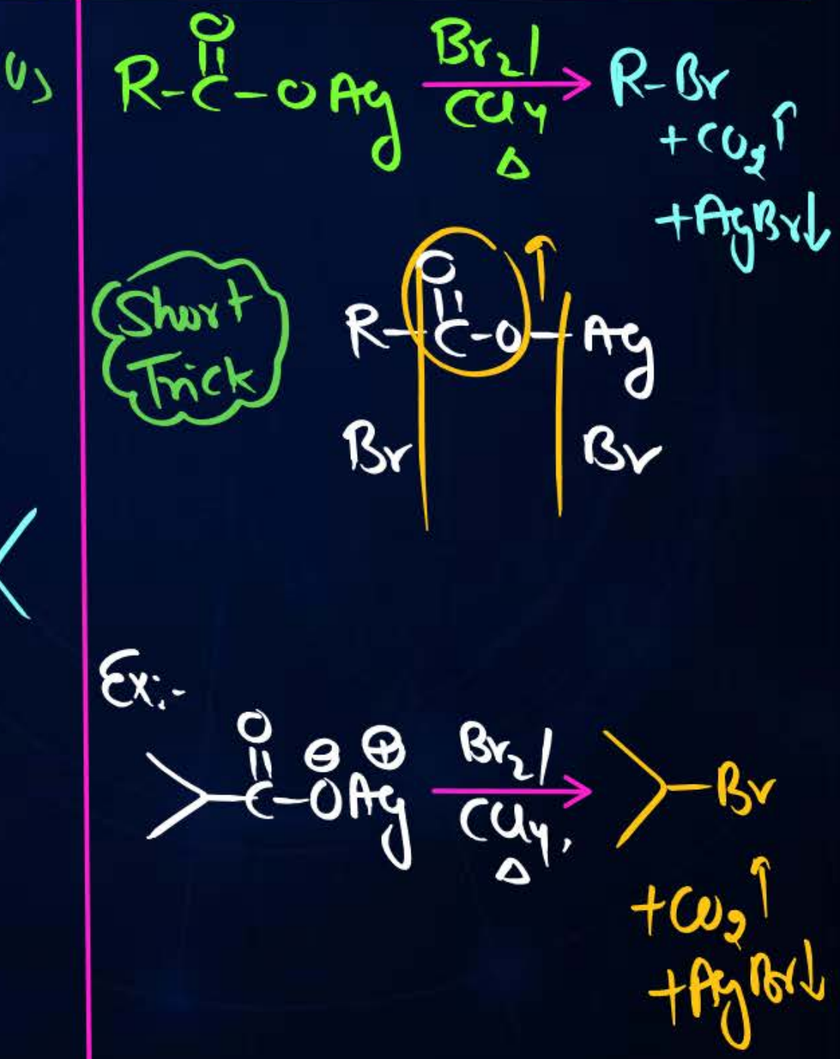
Ex:-



Kolbe Electrolysis (Just like Wurtz Rxn)



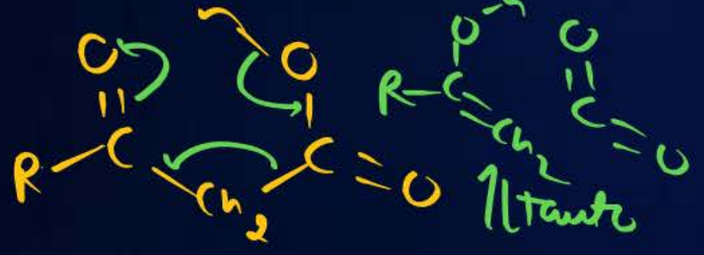
Hundsdiecker Rxn.



Decarboxylation Reaction (Heating effect)

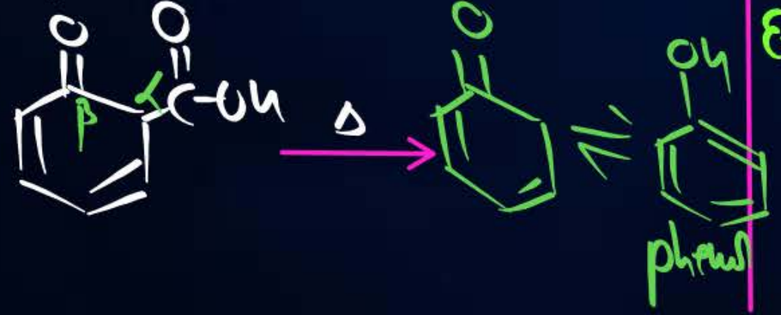
Heating of β-keto acid

Mech:-

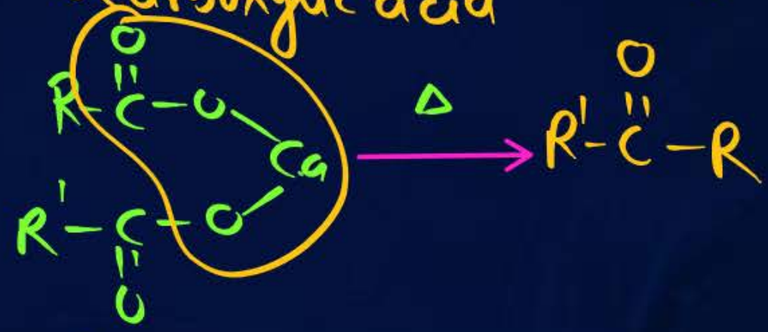


Ex:- ①

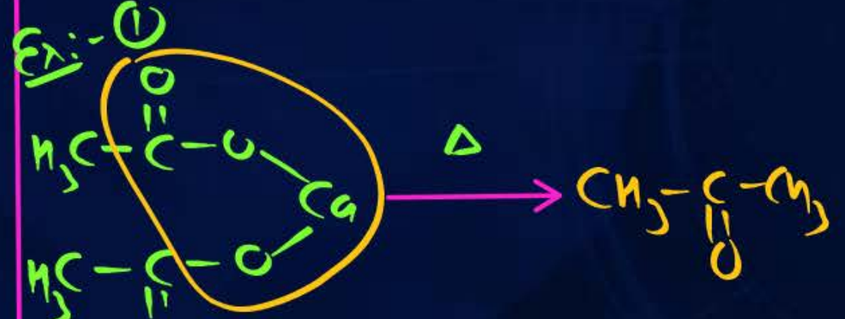
② 

③ 

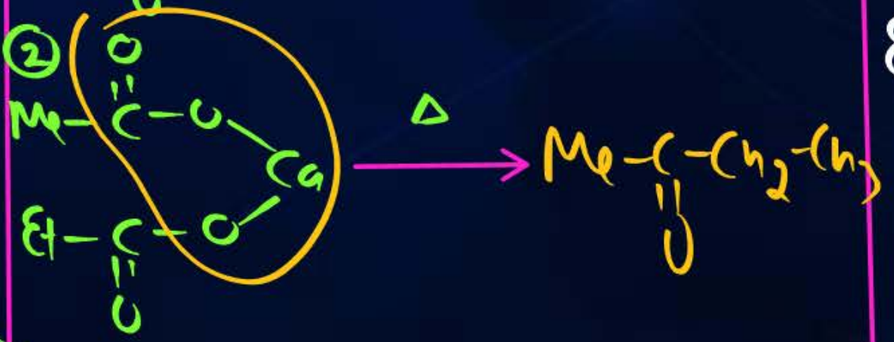
Dry distillation of Ca Salt of Carboxylic acid



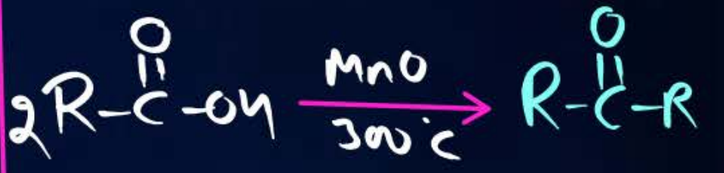
Ex:- ①



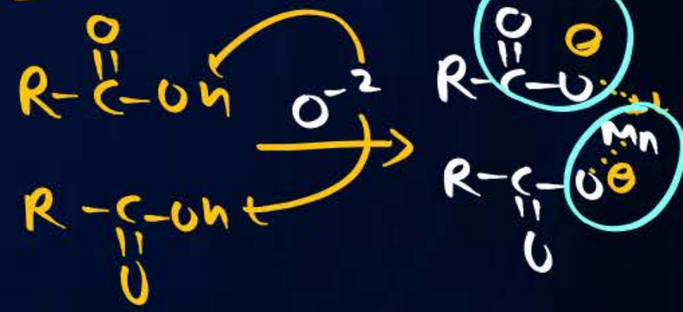
②



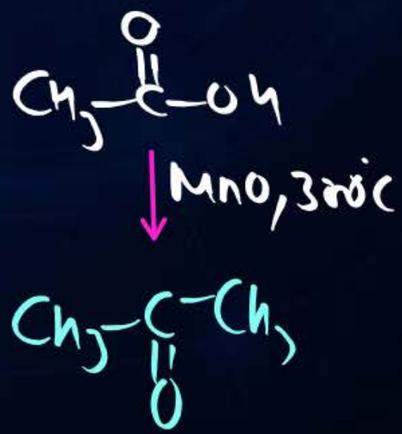
Rxn. with MnO at 300°C



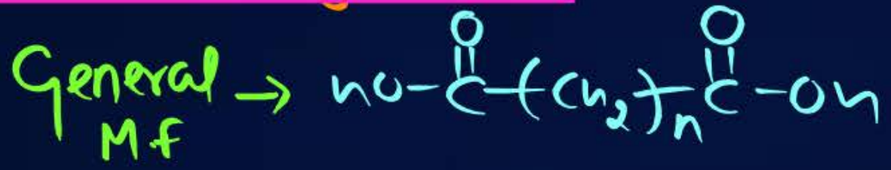
Mech^{n} $MnO \rightarrow Mn^{+2} + O^{-2}$



Ex:→



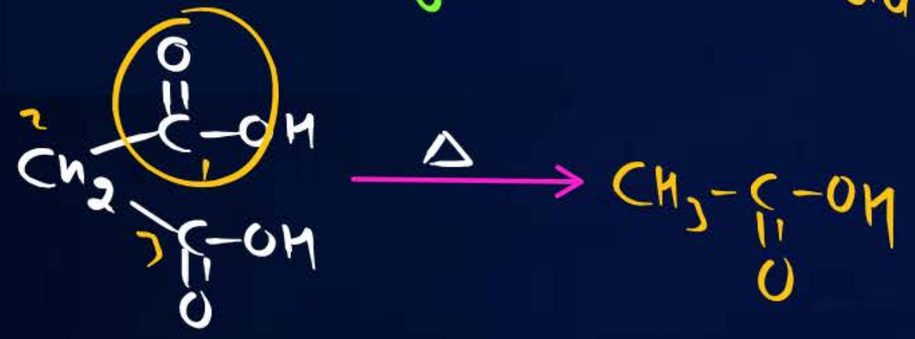
Heating of Dicarboxylic Acid

General Mf → 

n=	0	1	2	3	4	5	6
	O	M	S	G	A	P	S
	Oxalic Acid	Malonic acid	Succinic Acid	Glutaric acid	Adipic acid	Pimelic acid	Suberic acid

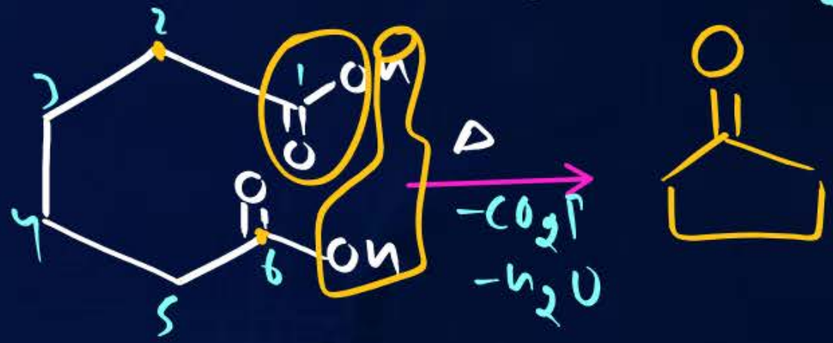
Case-1 1,2-dicarboxylic acid / 1,3-dicarboxylic acid $\xrightarrow[-CO_2\uparrow]{\Delta}$ Mono Carboxylic acid

Ex:-



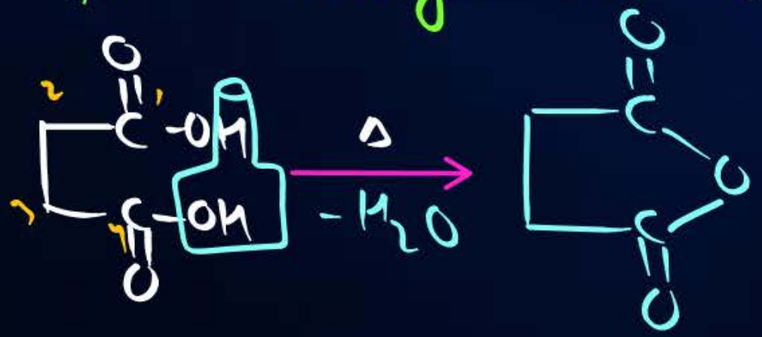
$\xrightarrow{\Delta}$ $CH_3-C(=O)-OH$

Case-3 1,6-dicarboxylic acid / 1,7-dicarboxylic acid $\xrightarrow[-CO_2\uparrow\ -H_2O]{\Delta}$ Cyclic ketone



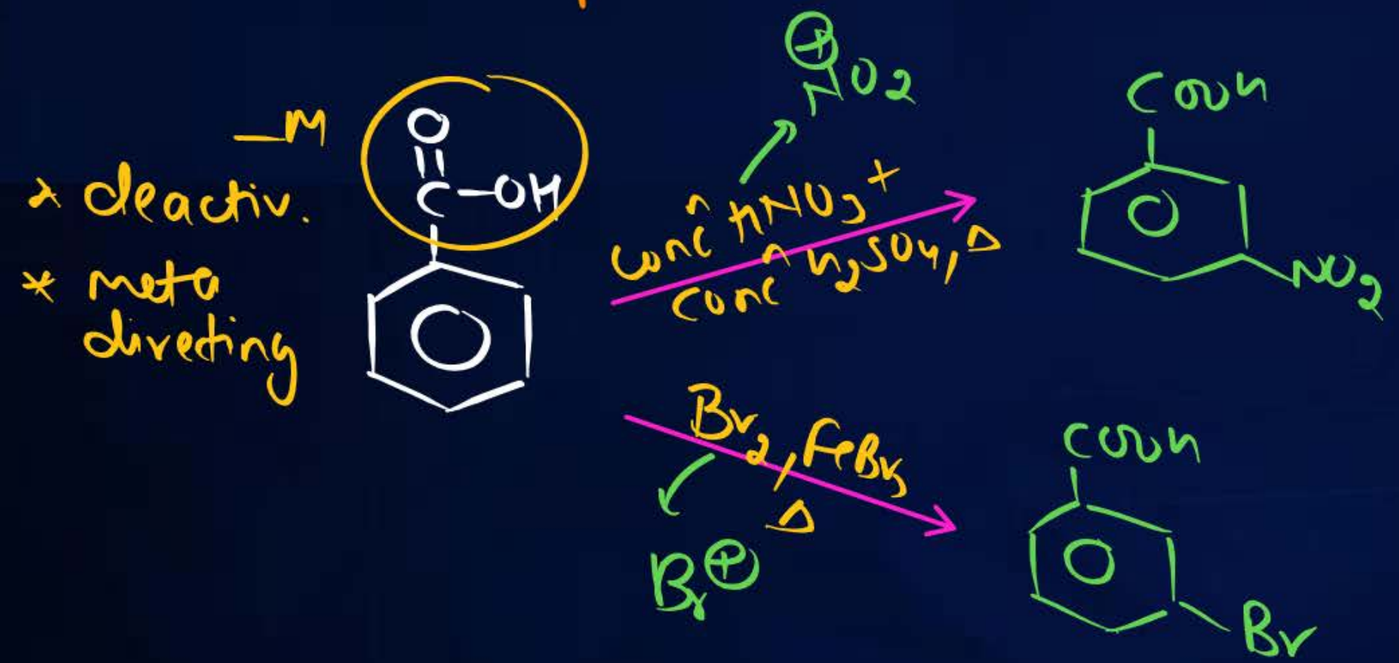
Case-2 1,4-dicarboxylic acid / 1,5-dicarboxylic acid $\xrightarrow[-H_2O]{\Delta}$ cyclic anhydride

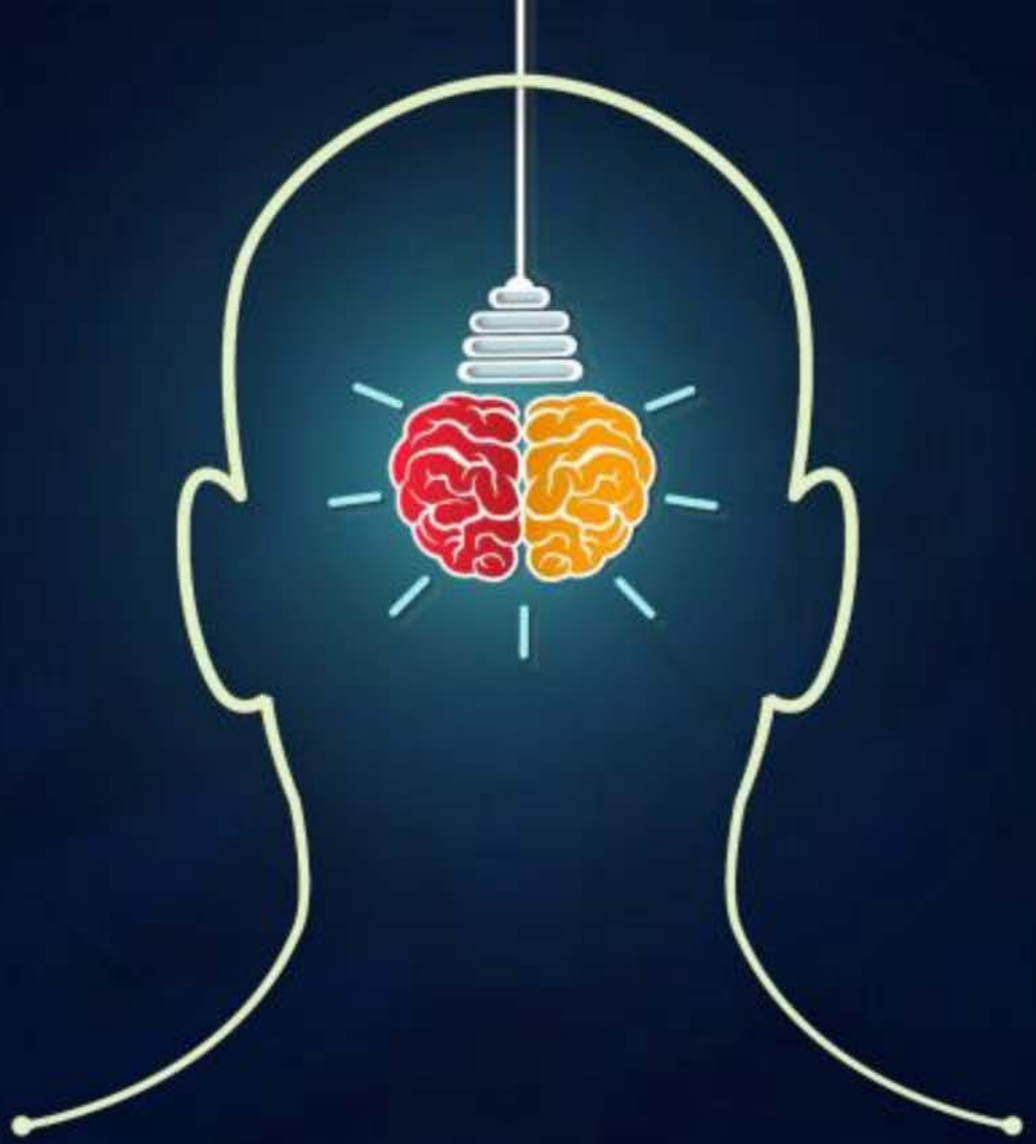
Ex:-



Case-4 1,6-dicarboxylic acid or onwards $\xrightarrow[-H_2O]{\Delta}$ polymerisation

Electrophilic Substitution Rxn:-





THANK YOU