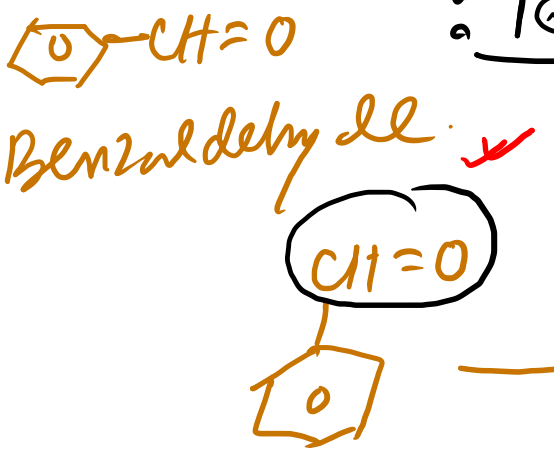
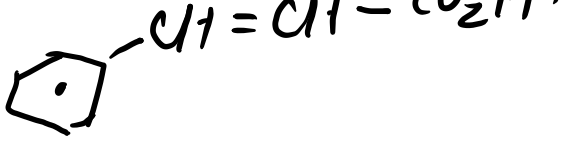
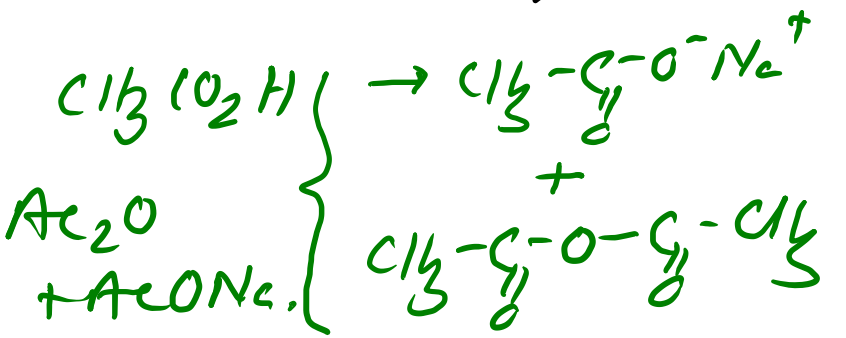
Perkin Reaction: (Applicable for aromatic aldehyde)

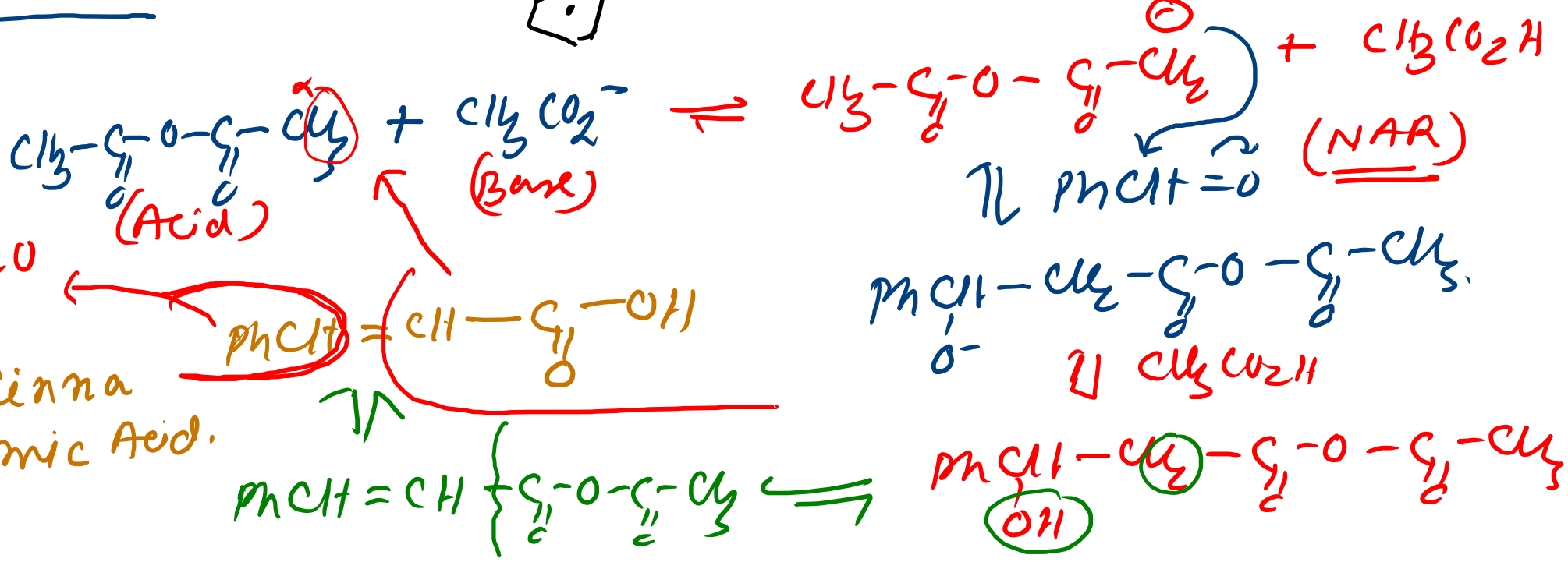


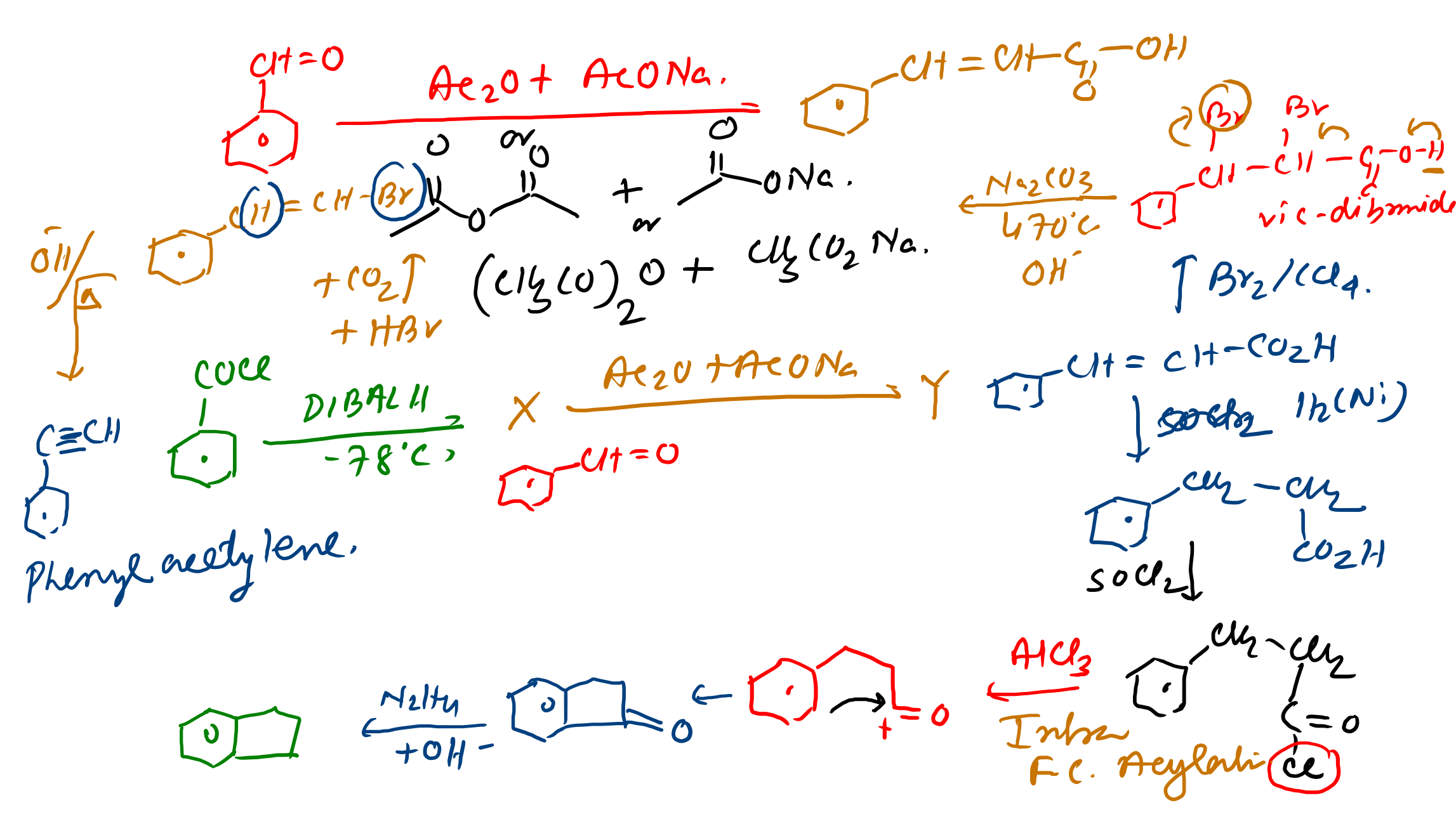
$Ac_2O + AcONa.$

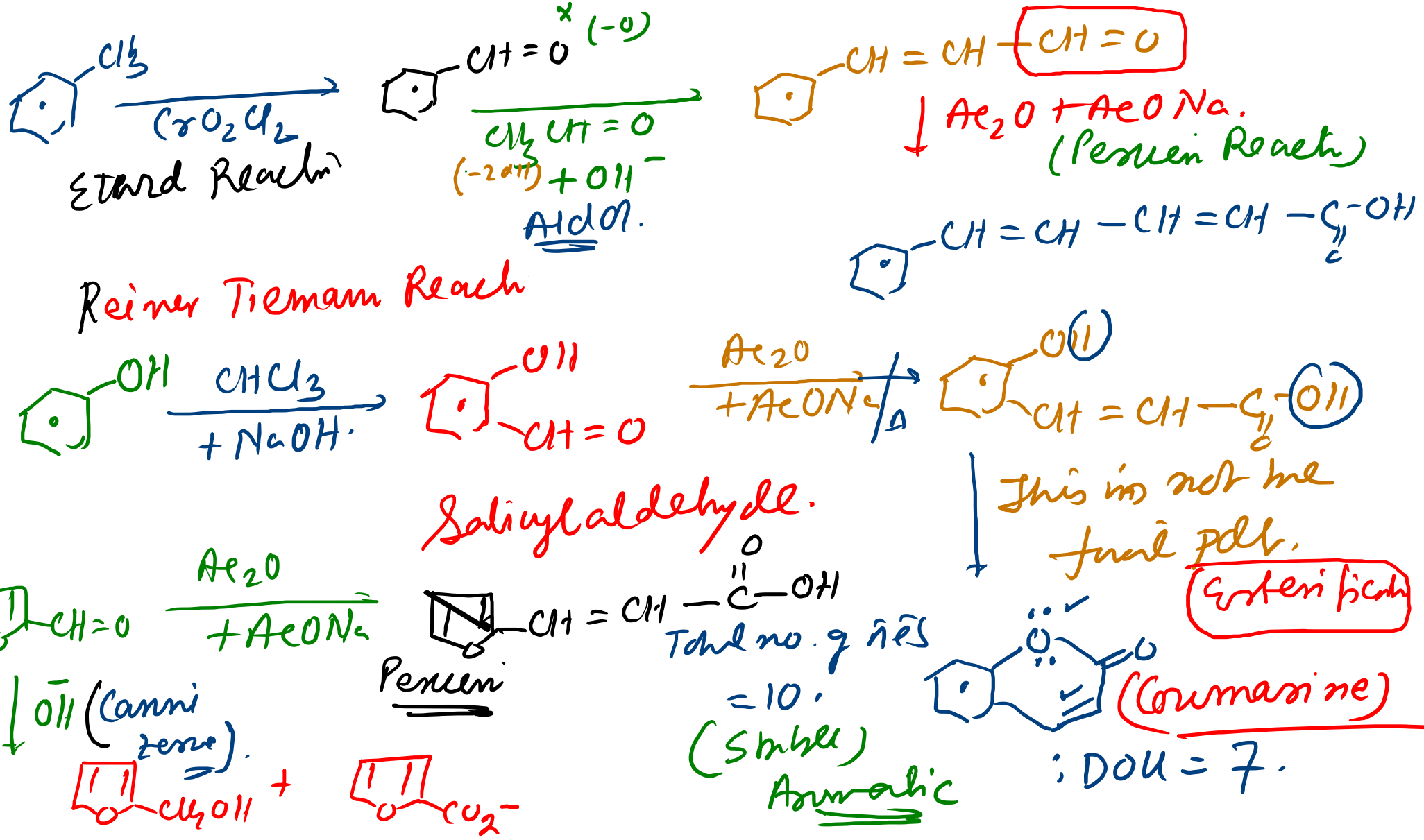




Mechanism:




CH=O
Ac2O + AcONa.
CH=CH-CO2H
CH=CH-Br
+ CO2↑
+ HBr
(CH3CO)2O + CH3CO2Na.
Na2CO3
470°C
OH⁻
Br2/CCl4.
vic-dibromide
OH
COCl
DIBAL H
-78°C
X
Ac2O + AcONa
Y
CH=O
C≡CH
Phenyl acetylene.
CH=CH-CO2H
SOCl2
H2(Ni)
CH2-CH2
CO2H
SOCl2
N2H4
+OH⁻
O
AlCl3
Intra
F.C. Acylation


CH3
CrO2Cl2
Etard Reaction
CH=O
(-O)
CH3CH=O
(-2H)
+OH⁻
Aldol.
CH=CH-CH=O
Ac2O + AcONa.
(Perkin Reaction)
CH=CH-CH=CH-C(=O)-OH
Reimer Tiemann Reach
OH
CHCl3
+NaOH.
OH
CH=O
Salicylaldehyde.
Ac2O
+AcONa/Δ
OH
CH=CH-C(=O)-OH
This is not the final pdt.
Esterification
CH=O
Ac2O
+AcONa
CH=CH-C(=O)-OH
Perkin
OH⁻ (Cannizzaro)
CH2OH
+
CO2⁻
Total no. of πes = 10.
(Stable)
Aromatic
(Coumarine)
; DOU = 7.

: Claisen Condensation :

This is the reaction of ester having α-hydrogen.

i) $CH_3-\overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-OEt$

ii) $CH_3-\overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-OEt$

iii) $Ph\overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-OCH_3$

Base used can be
$OMe^- / OEt^- / RO^- / \Delta$.

$CH_3-\overset{O}{\overset{\|}{C}}-OEt + \overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-OEt$

$\downarrow -EtOH.$

$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\beta}{CH_2}-\overset{O}{\overset{\|}{C}}-OEt.$

(β keto ester)

$\downarrow H_3O^+$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$ β keto acid

$\downarrow \Delta$ undergoes decarboxylation.

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$.

System loosing ROH (alcohol)

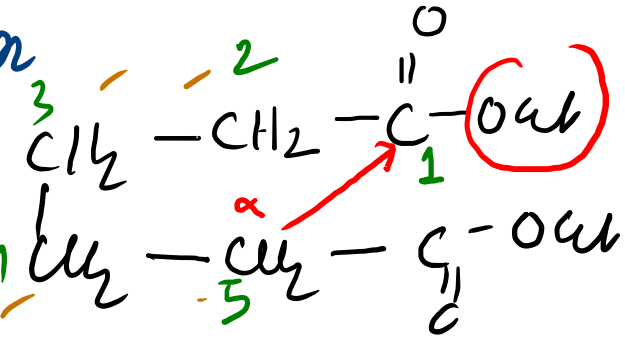
$Ph-CH_2-\overset{O}{\overset{\|}{C}}-OCH_3 + \overset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-OCH_3$
(Ph)

$PhCH_2-\overset{O}{\overset{\|}{C}}-CH(Ph)-\overset{O}{\overset{\|}{C}}-OCH_3 + CH_3OH$

$\downarrow H_3O^+$

$PhCH_2-\overset{O}{\overset{\|}{C}}-CH(Ph)-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} PhCH_2COCH_2Ph$

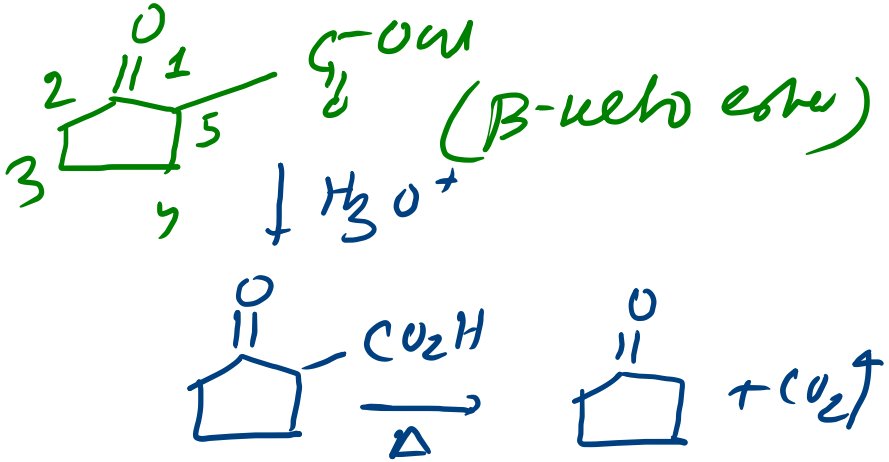
Dieckmann Condensation



Diethyl adipate

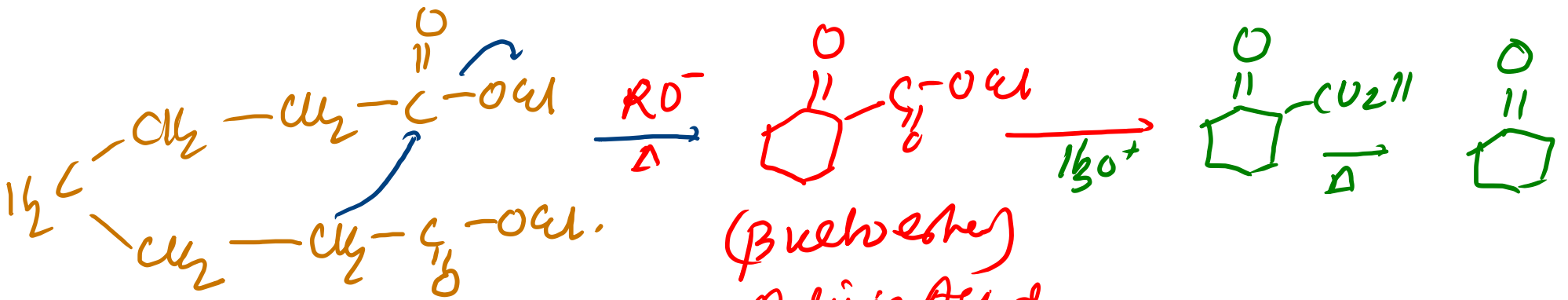
OR / Δ.

Intramolecular



(β-keto ester)

: Criteria: 5/6 membered ring is formed.



Diethyl pimelate

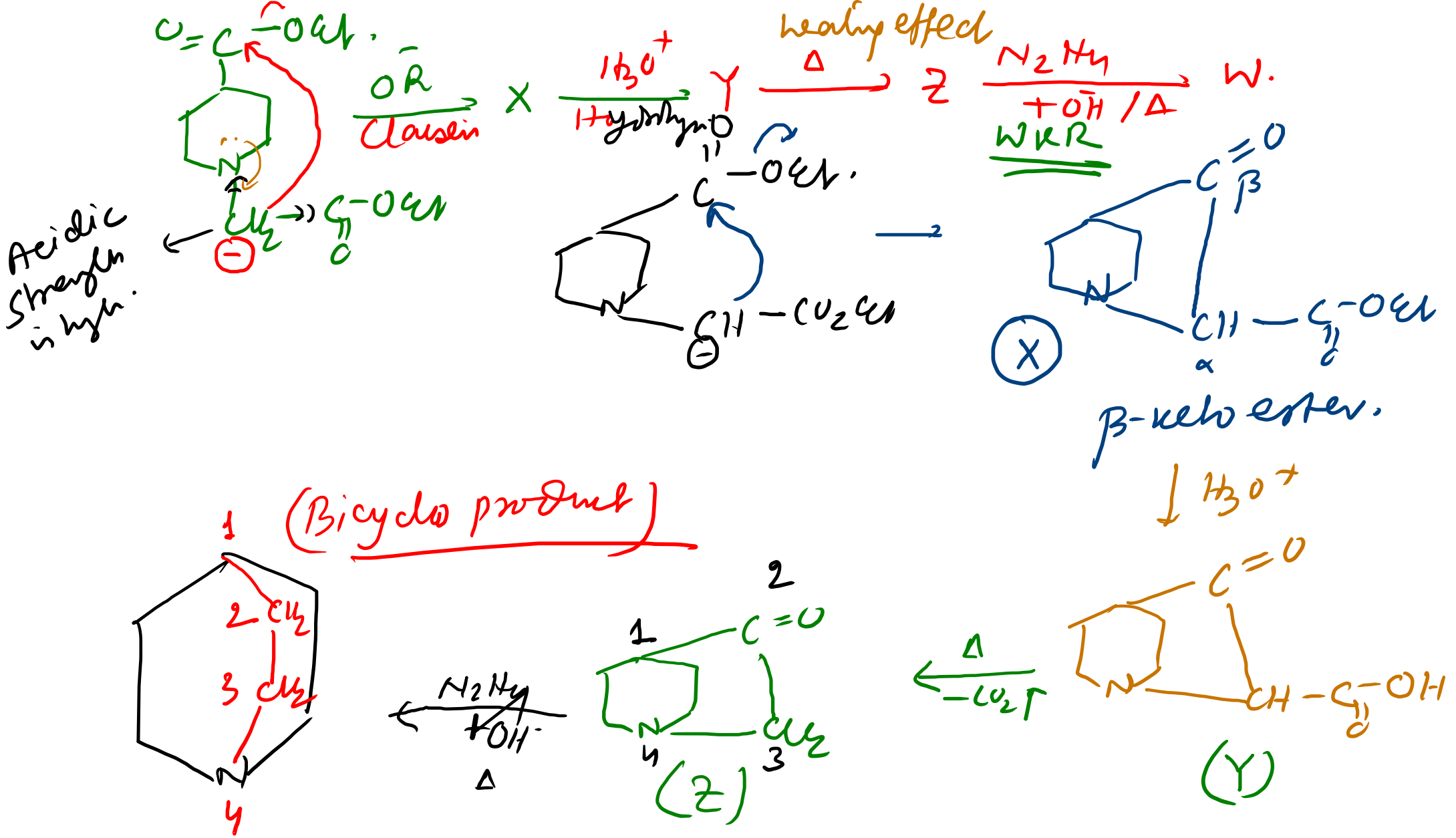
(Pimelic Acid)

(β-keto ester)

Adipic Acid.

OMSG APSA

Pimelic Acid.


Acidic strength is high.
OR
Claisen
Heating effect
Hydrolysis
WKR
β-keto ester.
(Bicyclo product)
(Z)
(Y)
(X)

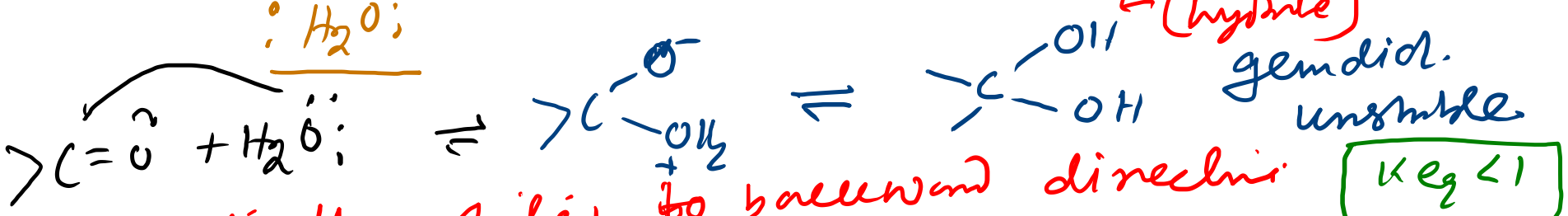
: Nucleophilic Addition:

$>C=\ddot{O} + Nu^{\ominus}$ ⇌ $>C(-O^{-})-Nu.$ (sp^2 → sp^3)

carbonyl cpds is very susceptible towards nucleophilic attack.

Examples of nucleophile

Donor atom	Example
i) Oxygen:	$\overset{\ominus}{O}H$ (cannizzaro); H_2O; ROH
ii) Nitrogen:	NH_3; NH_2-NH_2; NH_2-OH, NH_2-NH–(2,4-D.N.P)–NO_2 (NO_2) (Brady's reagent)
iii) Carbon:	CH_3MgX; $\overset{\ominus}{C}N$; $CH_2-CH=O$ (Aldol); $CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$; (Perkin) $\overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-OCH_3$ (claisen)
iv) Sulphur:	$RS\ddot{H}$; $CH_2\ddot{S}H$ / $CH_2\ddot{S}H$; $NaHSO_3$ = Sodium hydrogen bisulphite
v) $H^{\ominus}$:	$LiAlH_4$; $NaBH_4$;

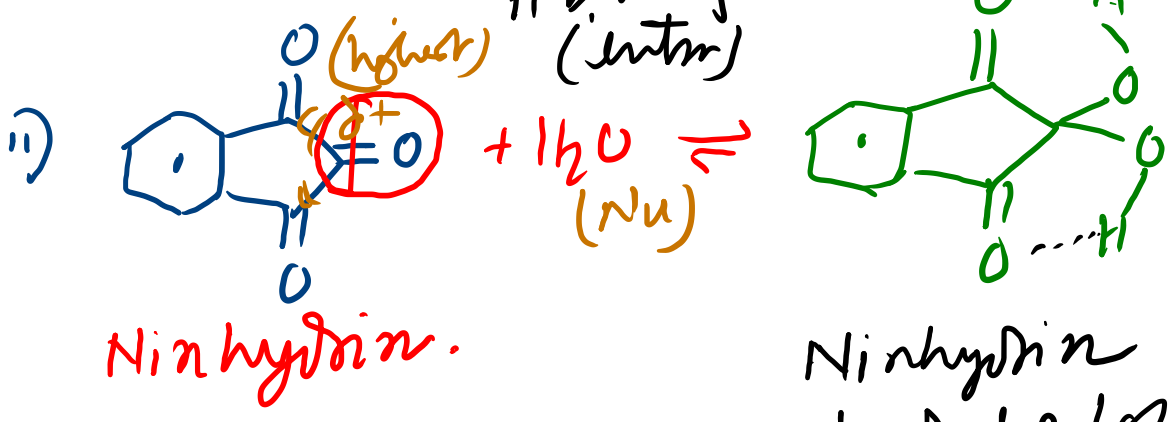


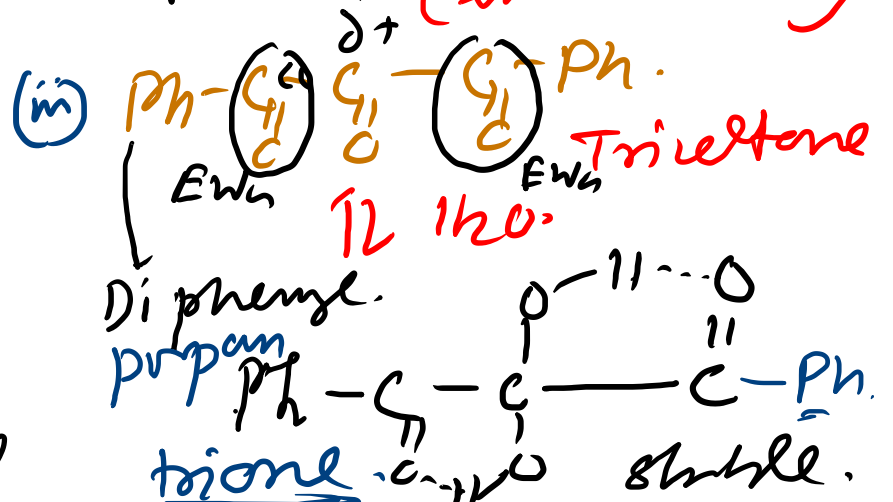
Exceptions: For the following cpds. gemdiol is stable; $K_{eq} > 1$.

i) $Cl_3C-CH=O$ ⇌ (H_2O) → $Cl_3C-CH(OH)_2$ (chloral hydrate) extremely stable

3 chlorine. H bonding (intra)

Inductive ↪ (electron withdrawing)



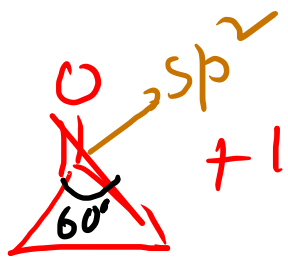


i) $H_2C=O + H_2O \rightleftharpoons$ $K_{eq} > 1$

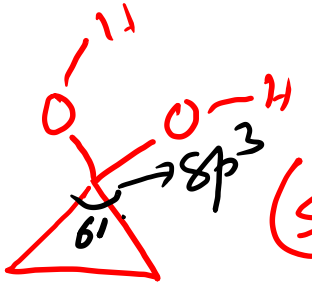
(most reactive carbonyl cpd)

$H_2C(OH)_2$

Ninhydrin is used for amino acid detection

ii) 

$+ H_2O \rightleftharpoons$



(stable) (carbonyl)

(cyclopropane)

Angle strain $= (120° - 60°)$
$= (60°)$

Angle strain $= (109°28' - 60°)$
$= 49°28'$

~~sp^3~~ Bulky gem diol formation angle strain is reduced. Ppts can be isolated. $K_{eq} > 1$

a) $H_2C=O$ > $CH_3\overset{\delta+}{C}H=O$ > $CH_3-\overset{\delta+\text{(lowest)}}{\underset{O}{\overset{\|}{C}}}-CH_3$

b) $CH_3-\underset{O}{\overset{\|}{C}}-CH_3$ > $Ph-\underset{O}{\overset{\|}{C}}-CH_3$ > $Ph-\underset{O}{\overset{\|}{C}}-Ph$ (+R)

Reactivity towards K_{eq} order

Reaction with $CN^{\ominus}$ is HCN + Base or NaCN / KCN.

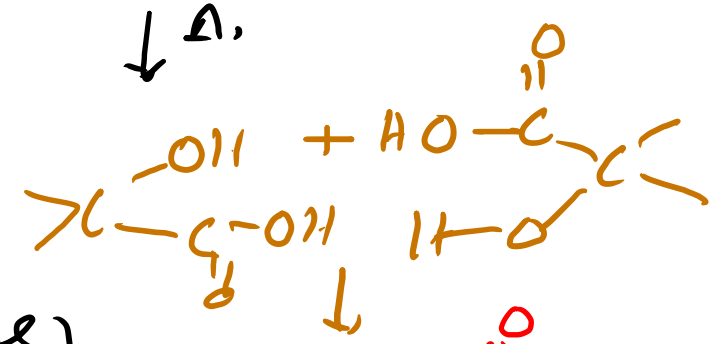
$R-C\equiv N + H_3O^+ \longrightarrow RCO_2H + NH_4^+$

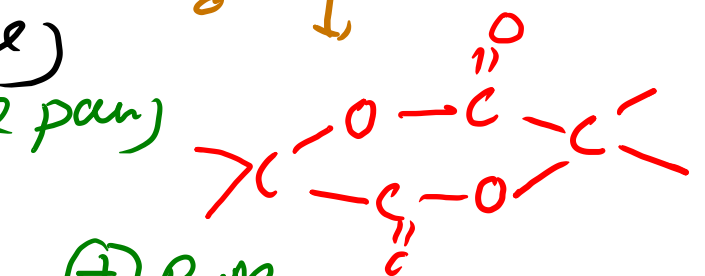
$>C=O + CN^- \rightleftharpoons >C(O^-)-C\equiv N$

$\xrightarrow{H^+}$ $>C(OH)-C\equiv N$ (cyanohydrin) $\xrightarrow{H_3O^+}$ $>C(OH)-CO_2H$

α-hydroxy acid.

$\downarrow \Delta$.





Lactide (Cyclic diester)

$CH_3CH=O + NaCN$ (followed by H^+) $\rightarrow$ $CH_3CH(OH)-C\equiv N$

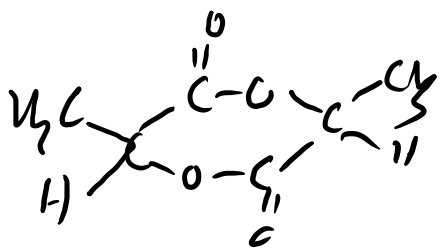
50% R + 50% S

$\pm$ (Racemic mixture)

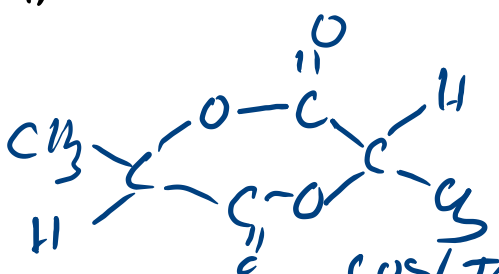
H_3O^+

(d/l pair)

$\pm$ R.M



TWM + 3 pdts. (A)



COS/Trans pdt

$\xleftarrow{\Delta}$ $CH_3-CH(OH)-CO_2H$

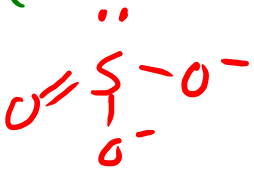
Lactic Acid

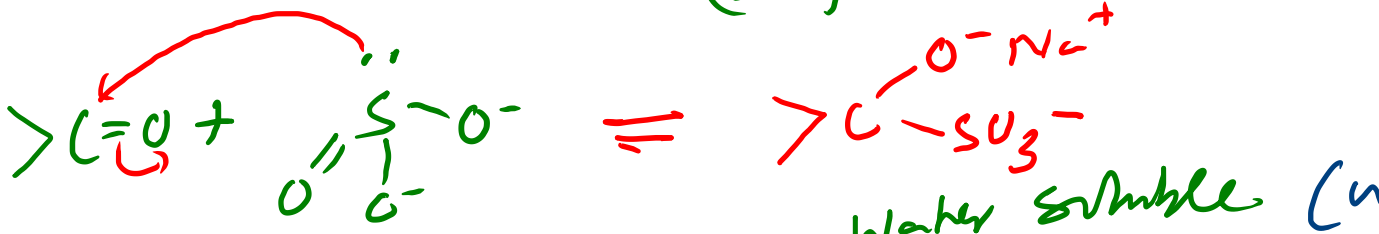
: Reaction with $NaHSO_3$:

$$Na(HSO_3) + OH^- \longrightarrow SO_3^{2-} + H_2O + 2Na^+$$

($NaHSO_3$ = sodium bisulphite ion; SO_3^{2-} = sulphite ion)

(donor atom)





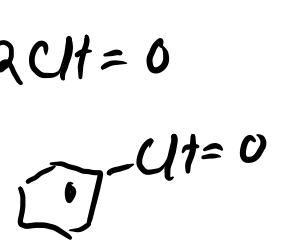
Water soluble (white crystalline ppt)

This reaction is for carbonyl system.

⇒ All aldehydes give +ve test, ketone having $-\overset{O}{\overset{\|}{C}}-CH_3$ grp gives +ve test.

cyclic ketone gives also +ve test.

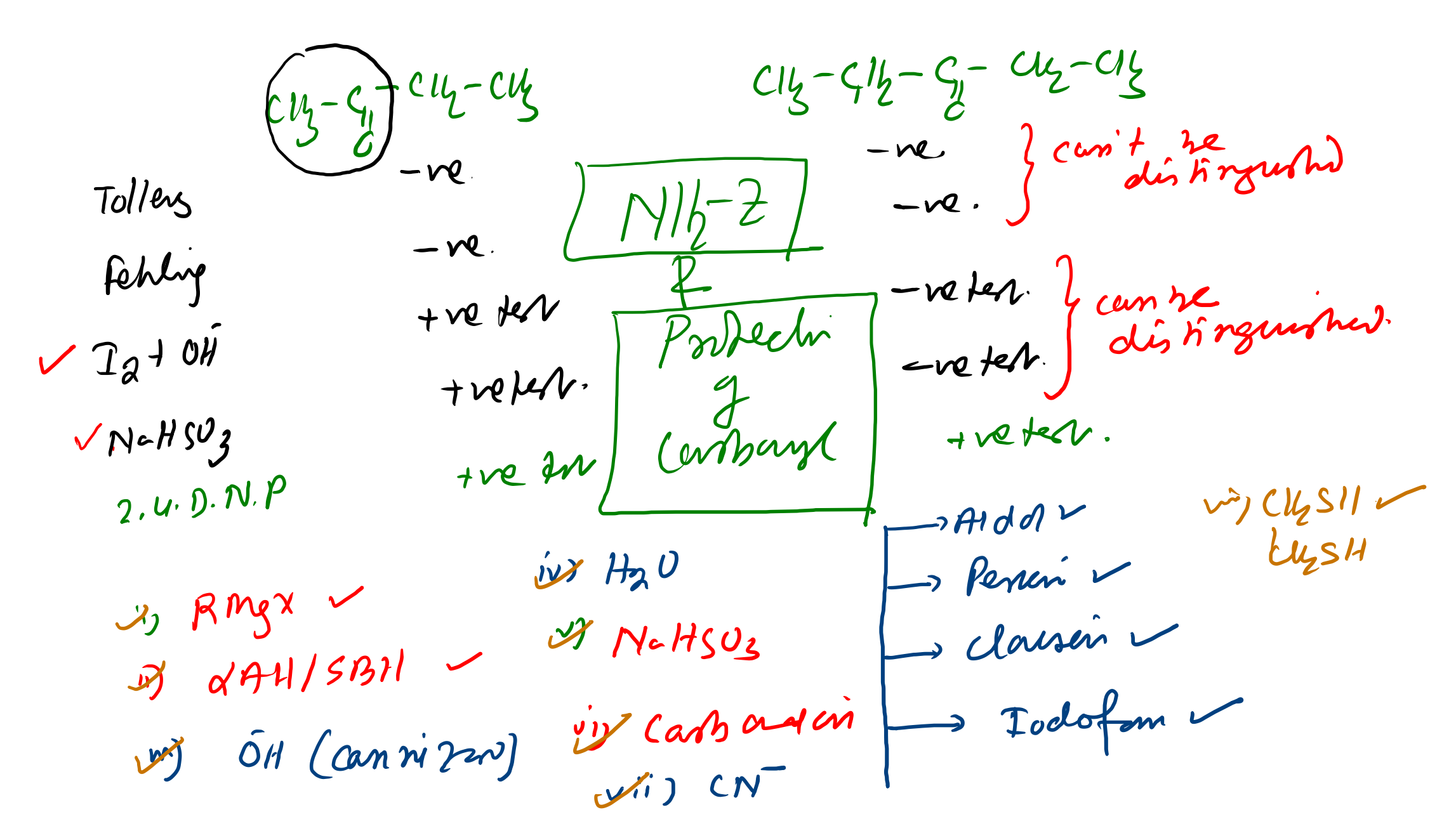
i) $RCH=O$

ii) 

iii) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

v) $CH_3-\overset{O}{\overset{\|}{C}}-C-C-C$

m) $H_3C-\overset{O}{\overset{\|}{C}}-CH_3$. (i) to (v) gives +ve test. [white crystalline ppt.]


CH3-CO-CH2-CH3
-ve
-ve.
+ve ter
+ve ter.
+ve 2n
Tollens
Fehling
✓ I2 + OH
✓ NaHSO3
2,4-D.N.P
NH2-Z
&
Phenol
&
Carbonyl
CH3-CH2-CO-CH2-CH3
-ve
-ve.
can't be distinguished
-ve ter.
-ve ter.
can be distinguished.
+ve ter.
i) RMgX ✓
ii) LAH/SBH ✓
iii) OH (cannizzaro)
iv) H2O
v) NaHSO3
vi) Carbanol
vii) CN
Aldol ✓
Perkin ✓
claisen ✓
Iodoform ✓
viii) CH2SH
CH2SH