SBG STUDY

* Carboxylic acid and derivatives

$R-\overset{O}{\overset{\|}{C}}-OH$	$R-\overset{O}{\overset{\|}{C}}-L$
CA	CAD
	$R-\overset{O}{\overset{\|}{C}}-X$ (Acid halide)
	$R-\overset{O}{\overset{\|}{C}}-OR$ (Ester)
	$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ (Acid anhydride)
	$R-\overset{O}{\overset{\|}{C}}-NH_2$ (Amide).

* Imp (General method of Preparation) of CA :-

- SOA = Acid

(i) By oxidation of aromatic side chain : by SOA (Strong oxidising Agent)

(ii) By oxidation of alkene with SOA

(iii) By " " " with $KMnO_4/OH^{\ominus}/H_2O/\Delta$

(iv) By oxidation of alkene with ozone H_2O without

(v) By " " alkyne " SOA

(vi) " " " 1° alcohol with SOA

(vii) " " " 2° " " Ketone

(8) By oxidation of Aldehyde and Ketone with SOA

9] " " " " by tollen's Reagent

10] " " " " with Fehling and Bendict sol^n.

11] " " " " " Shiff's Reagents.

12] " " " " aq. $HgCl_2$ sol^n

13] " " " " Per acid. [Baeyer vilinger Oxidation]

14] By Perking Condensation Rx^n

15] " Reformatsky Rx^n

16] " Hydrolysis of Nitrile or Cyanide ⇒ CN + H$_2$O → acid

$$R-C\equiv N \xrightarrow[\text{or } H_2O/H^+ \text{ or Dil. } H_2SO_4]{H_3O^+} R-\overset{\ddot{O}}{\overset{\|}{C}}-OH$$

Mech^n:

$$R-C\equiv N: \xrightarrow{H_3O^+ (H^+ + H_2O)} \left[R-C\equiv \overset{\oplus}{N}-N \longleftrightarrow R-\overset{\oplus}{C}=NH\right]$$

$$\| H_2O: \quad R-\overset{OH}{\overset{|}{C}}-\overset{\oplus}{N}H_2 \longleftrightarrow R-\overset{H}{\overset{|}{C}}=\overset{\oplus}{N}H_2 \rightleftharpoons R-C=\ddot{N}H$$

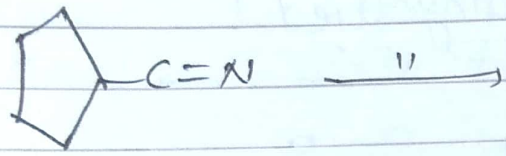
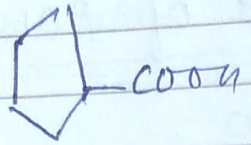
$$\| H_2O: \quad R-\overset{OH}{\overset{|}{C}}-\overset{\oplus}{N}H_2 \rightleftharpoons R-\overset{O-H}{\overset{|}{C}}-NH_3 \xrightleftharpoons{-NH_3} R-\overset{\oplus}{\overset{O-H}{\overset{\|}{C}}} \rightleftharpoons$$

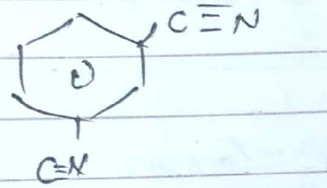
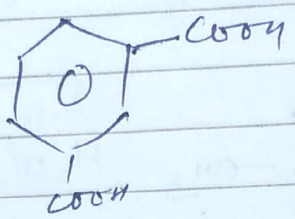
$$R-\overset{OH}{\overset{|}{C}}-\overset{\oplus}{N}H_2 \quad O-H$$

in H_2O/H^+ CN Convert into COOH

$\rightleftharpoons$ $\xrightarrow{-H^+}$ $R-C(=O)-OH$

Q.) $CH_3-C\equiv N \xrightarrow{H_2O/H^+} CH_3-COOH$

2)  $\xrightarrow{''}$ 

3)  $\xrightarrow{''}$ 

Note : Hydrolysis of $(-C\equiv N)$ with H_2O can also be done in the presence of Base.

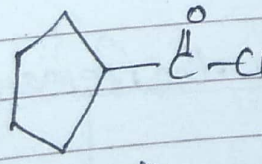
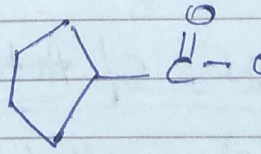
$$CH_3-C\equiv N \xrightarrow{H_2O/OH^-} CH_3-COO^-$$

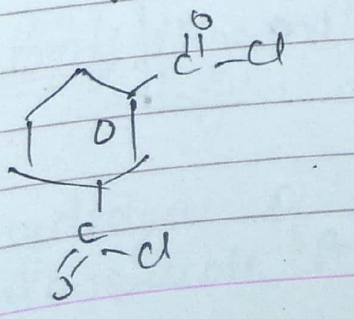
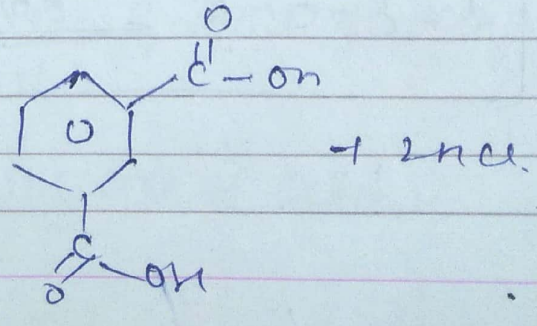
(17) **By Hydrolysis of acid halide :**

$$R-\overset{O}{\overset{\|}{C}}-X \xrightarrow{H_2O/H^+} R-\overset{O}{\overset{\|}{C}}-OH + HX$$

Acid halide

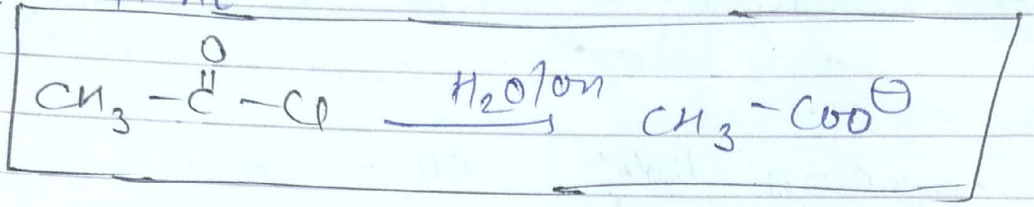
Q - $CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{H_2O/H^+} CH_3-\overset{O}{\overset{\|}{C}}-OH + HCl$

2)  $\xrightarrow{''}$ 

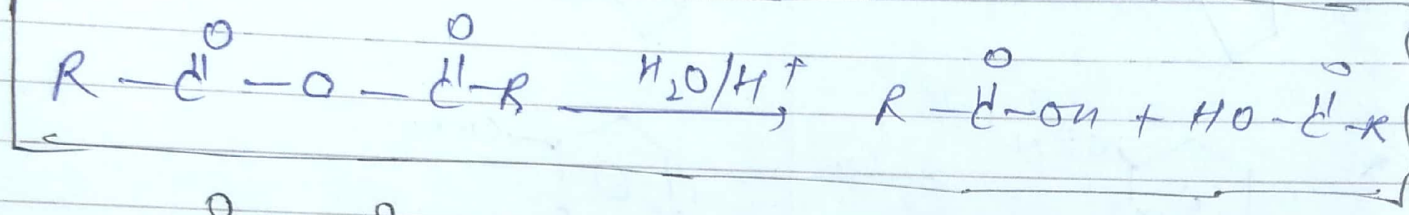
(3)  $\xrightarrow{''}$ 

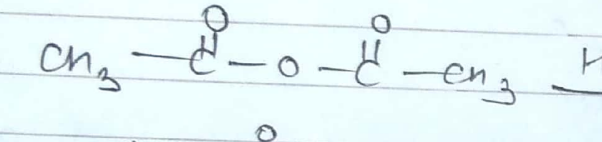
Mechm :- S_NAE

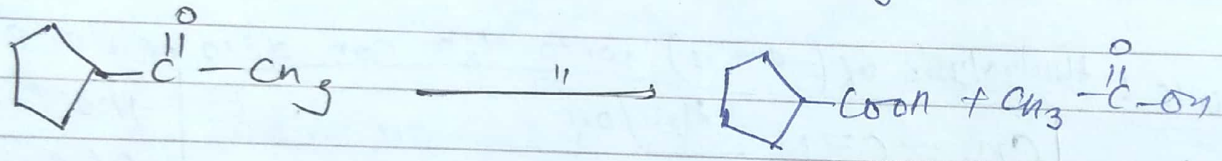
* Note :

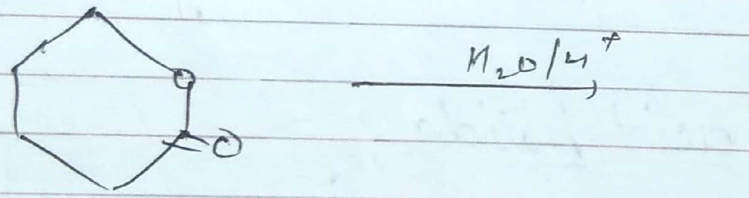


* By hydrolysis of Acid Anhydried :

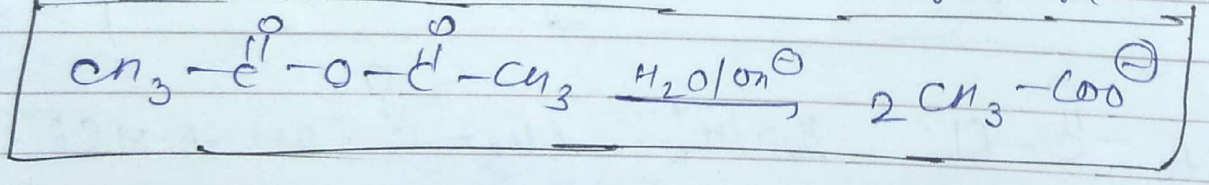


Q. 

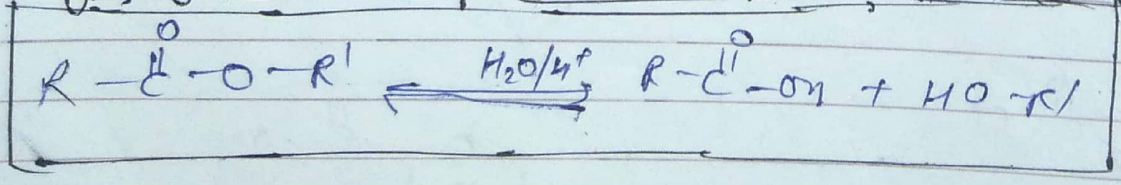
2) 

(3) 

Note : Hydrolysis of (Anhydride) with H_2O can be done in the presence of Base

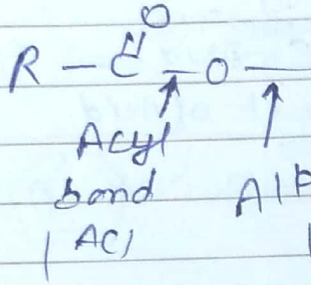


* By hydrolysis of ~~Acid~~ Aesters :- In the Presence of Acid

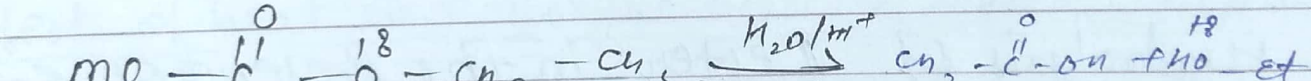


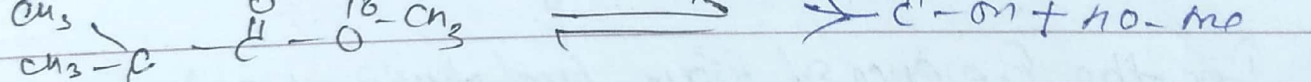
Mech^m :- Deperding upon Nature of R and R' it may occur by Anyone of following 3 Mech^m:-

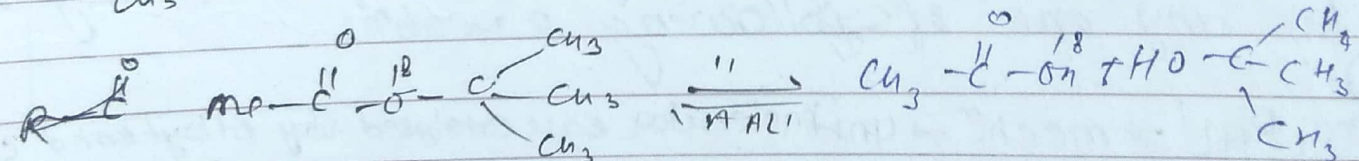
(1) - AAC^2 - Mech^m (Bimolecular Acid Catalysed by Acyl bond cleavage
(2) AAC^1 → Mech^m (Unimolecular " " " " "
(3) AAL^1 → Mech^m (" " " " Alkyl bond "

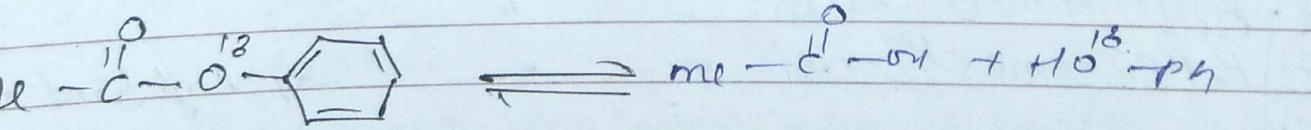


(1) → when R, R' ≠ 3R°
(2) " R = 3° Alkyne)
(3) " R' = 3° ")

Q. 

4 

(3) 

Q. 

Imp. Points :- 1) Hydrolysis of ester in the Presence of Acid gives Carboxylic acid and Alcohol

2) Hydrolysis of ester in the Presence of Acid is Reversible Process.

* In hydrolysis of ester in the presence of Acid Alkyl and Acyl both ~~would~~ may break.

It depends of Nature of R and R'. (Hydrolysis of esters mech^n occur)

* Hydrolysis of ester in the presence of Base:

$$R-\overset{O}{\overset{\|}{C}}-\ddot{O}-R' \xrightarrow{H_2O/NaOH} R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{Na} + HO-R'$$

salt of Acid.

* Hydrolysis of ester also occur in the presence of Base

* In the presence of Base we get salt of Carboxylic

* In the " " " Rx^n is Irreversible.

* Hydrolysis of ester in the presence of Base is called Saponification.

* In the presence of Base hydrolysis of ester may occur by any one of following 3 mech^m.

(1)

① BAL^1 → mech^m → unimolecular Base catalysed by Alkyl bond cleavage

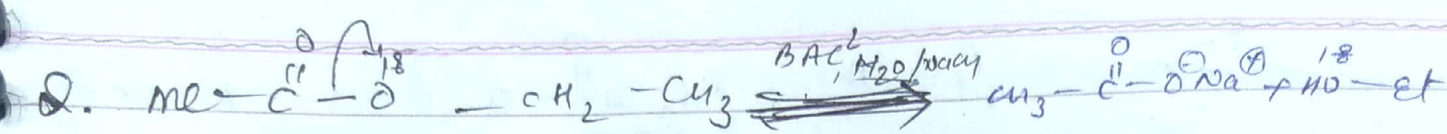
② BAl^2 → mech^m → Bi " " " " " " "

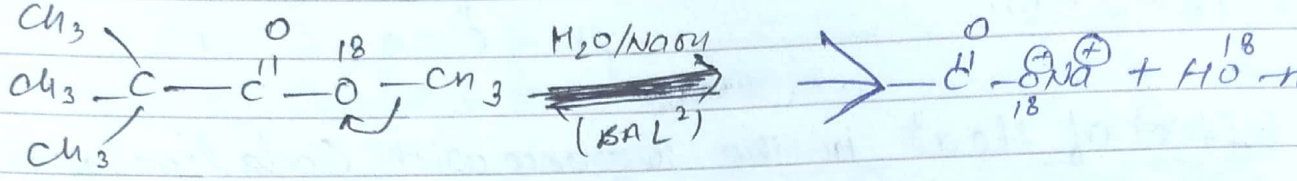
③ BAC^2 → mech^m → Bi " " " by Acyl bond " "

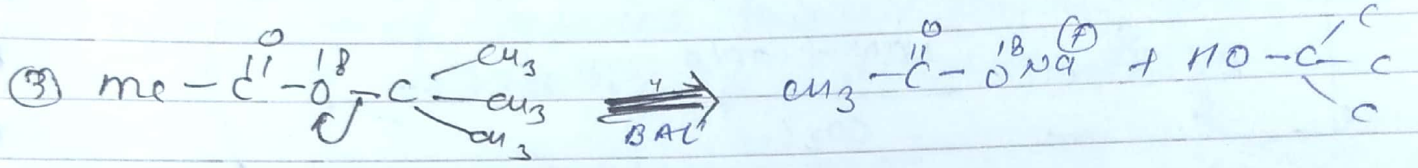
① when $R' = 3^\circ$ Alkyl

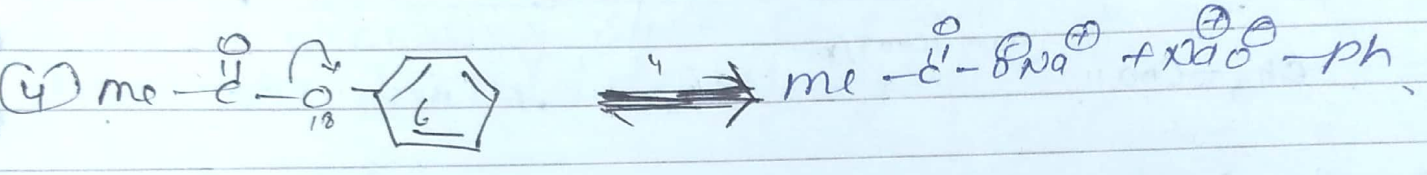
② " $R' = Me$

③ Rest occur.

Q. 

(2) 

(3) 

(4) 

* ~~General~~

* Rx^n's of Carboxylic acid :

* Effect of heat on Carboxylic acid & related Compound :

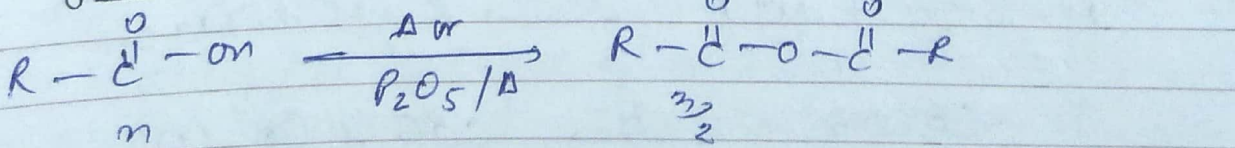
- M.C.A
- DCA
- Hydroxy acid
- Amino acid

M.C.A: $R-COOH$

DCA: $HOOC-(H_2C)_n-COOH$ $(n = 0, 1, 2, \ldots)$

- Direct Heat
- Heat with Sodalime.

(1) Effect of Direct Heat on MCA (mono Carboxylic acid) :



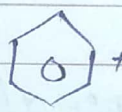
Q. $CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{P_2O_5/\Delta} \underbrace{CH_3-\overset{O}{\overset{\|}{C}}}_{Ac}-O-\underbrace{\overset{O}{\overset{\|}{C}}-CH_3}_{Ac}$ or $\underset{or}{Ac_2O}$

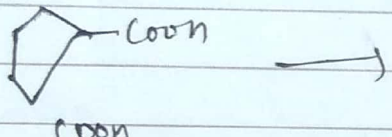
2) $Ph-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} Ph-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-Ph$

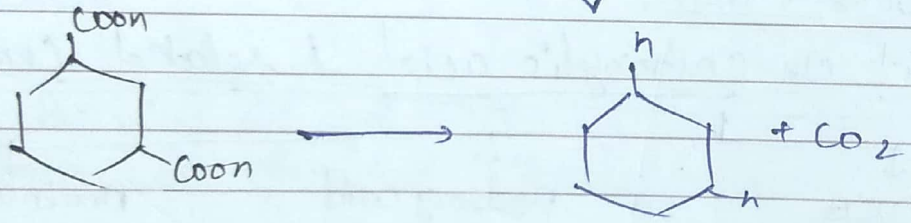
* Effect of Heat in the presence with Soda lime (NaOH + CaO):

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-CO_2(\uparrow)]{NaOH+CaO/\Delta} R-H + CO_2(\uparrow)$$

(1) $CH_3-COOH \xrightarrow{(NaOH+CaO)/\Delta} CH_4 + CO_2(\uparrow)$

(2) $Ph-COOH \longrightarrow Ph-H + CO_2(\uparrow)$ or  $+CO_2\uparrow$

(3) 

(4) 

(5) $H_2C=CH-COOH \longrightarrow H_2C=CH_2 + CO_2(\uparrow)$

Mech^m:

$$R-\overset{O}{\overset{\|}{C}}-OH + \overset{\oplus}{Na}\overset{\ominus}{OH} \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{Na} + H_2C$$

$$R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\overset{\oplus}{Na} + CaO \xrightarrow[slow]{RDS} \overset{\oplus}{Na}\overset{\ominus}{R} + CaCO_3$$

$$H-O-H + \overset{\oplus}{Na}\overset{\ominus}{R} \longrightarrow R-H + NaOH$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2(\uparrow)$$

Ex-2 ① ② ③
Alcohol & ether

Important points:- This Rxn is known as to be weak carboxylic acid Rx by this method carboxylic acid and its salt can be converted to hydrocarbon.

2) It occur by carbonanion formation.

3) Rx
↳ Reactivity of compound toward decarboxylic Rx is ∝ stability of carbanion form

Q. decide decreasing order of Reactivity of following molecules toward decarboxylation.

(a) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\ominus}{C}}OOH$ $\quad CH_3-CH_2-COOH$ $\quad CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{\downarrow}{C}}}H$ $\quad CH_3-\overset{\beta\text{ keto acid}}{\overset{\uparrow}{\overset{O}{\overset{\downarrow}{C}}}}-CH_2-COOH$

$CH_3-\overset{\ominus}{C}H_2$ $\quad CH_3-\underset{+I}{\underbrace{\overset{\ominus}{C}H-CH_3}}$ $\quad CH_3-\overset{O}{\overset{\downarrow}{C}}-\overset{\ominus}{C}H_2$

4 > 1 > 2 > 3

(b) $O_2N-\underset{\underset{NO_2}{|}}{\overset{\ominus}{C}}H$ $\quad CH_3-\overset{O}{\overset{\downarrow}{C}}-CH_2-COOH$ $\quad CH_3-CH_2-\overset{O}{\overset{\downarrow}{C}}-OH$

1 7 2 7 3

(c) $CH_2\begin{cases}COOH\\COOH\end{cases}$ $\quad > \quad CH_3-COOH$

Note:- Reactivity towards decarboxylation ∝ −m/−n/−I gp at ∝

2) if Strong (−M) withdrawing (−M) present on ∝ carbon then such carboxylic acid do decarboxylation Rx only on heating (without use of sodalime) for Ex:-
β keto acid, ∝ nitro acid, gem dicarboxylic acid, β-eminoacid, β γ unsaturated Ac

* Effect of Heat on β-keto acid / β-Imino acid / β, γ-unsaturated acid

→ $R-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\Delta,\ -CO_2} R-\overset{O}{\overset{\|}{C}}-CH_3$

β-keto acid

→ $R-\overset{NH}{\overset{\beta}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH \longrightarrow R-\overset{NH}{\overset{\|}{C}}-CH_3$

* $R-\overset{H_2C}{\overset{\beta}{C}}=CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta,\ -CO_2(\uparrow)} R-\overset{CH_2}{\overset{\|}{C}}-CH_3$

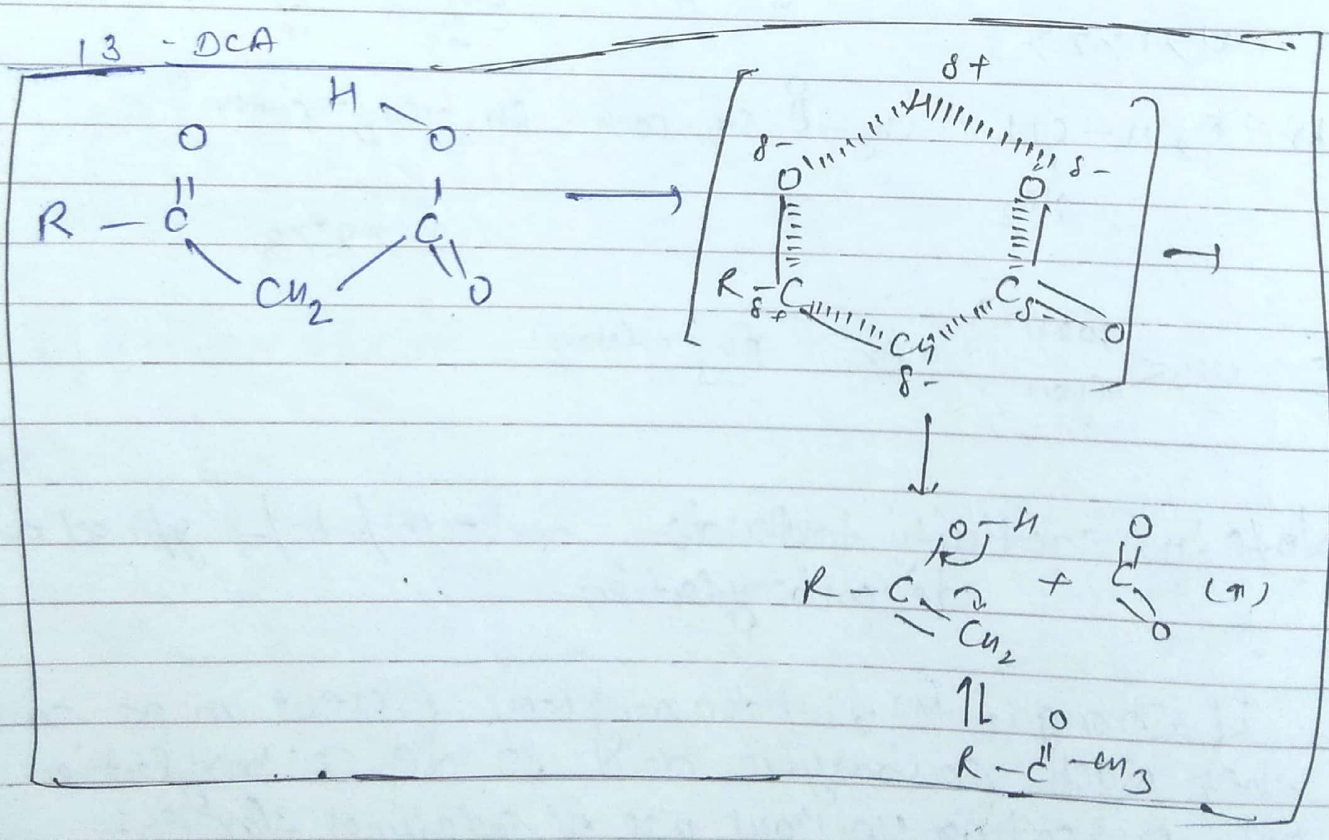
α β γ-unsaturated

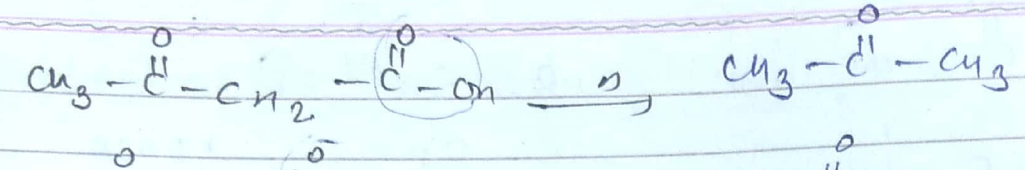
* $HO-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} HO-\overset{O}{\overset{\|}{C}}-CH_3$

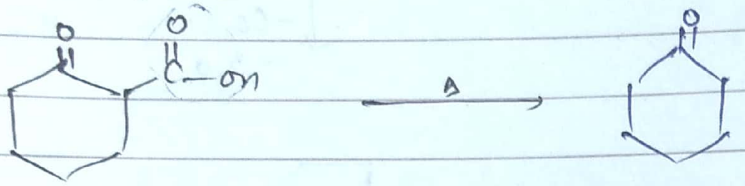
Keto-dCA

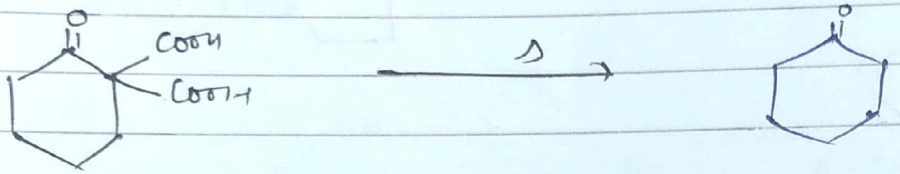
or

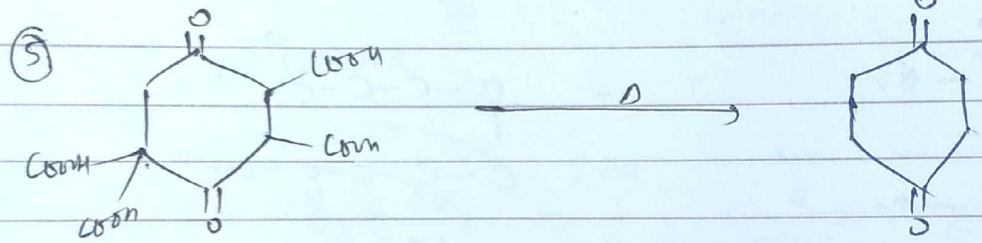
1,3 - DCA

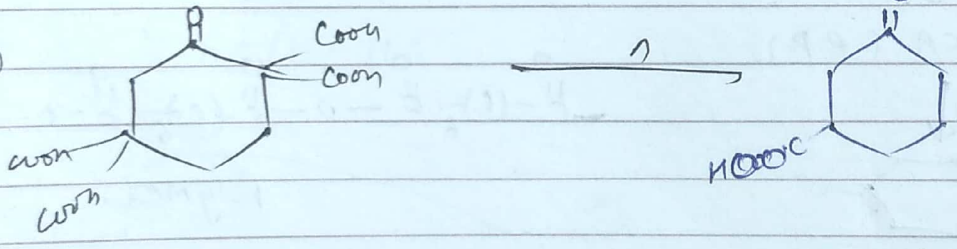


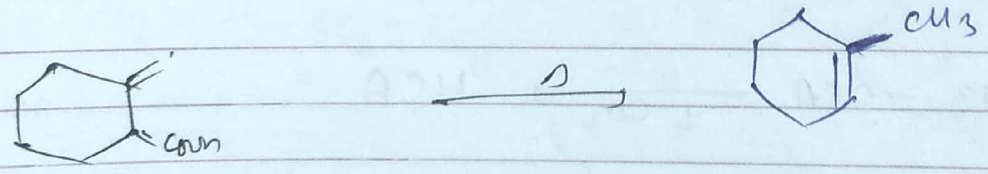
(2) 

(3) 

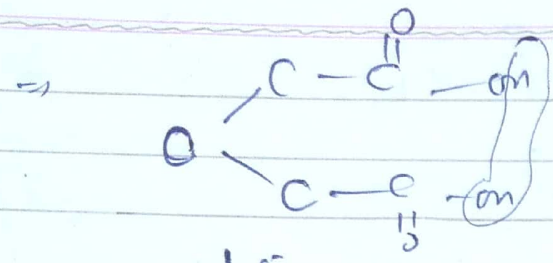
(4) 

(5) 

(6) 

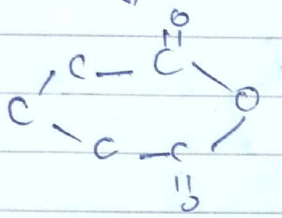
(7) 

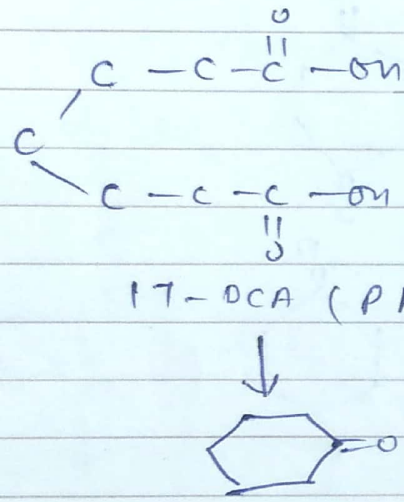
Effect of Heat on DCA:



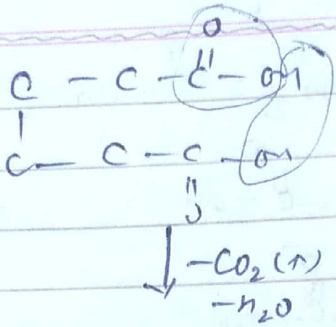
1,5 - DCA

GA





17 - DCA (PA)

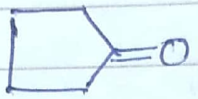


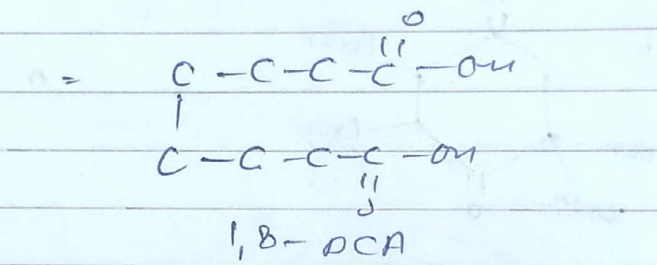
1,6 DCA

AA

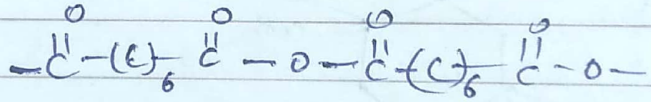
$-CO_2$ (n)

$-H_2O$





1,8 - DCA



Polymer.

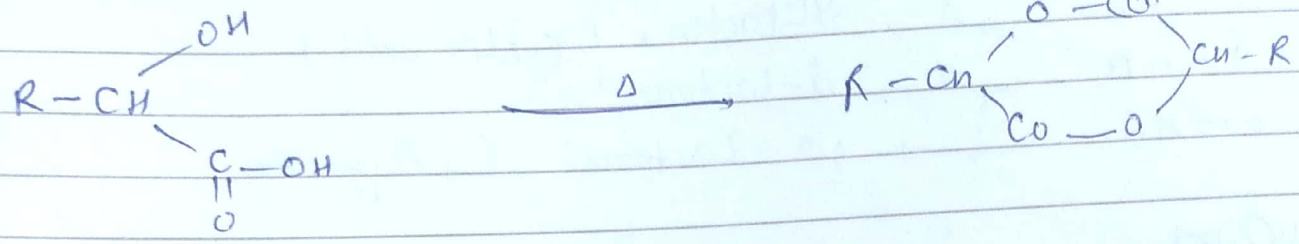
1,2 - / 13 - DCA $\xrightarrow[-CO_2]{-1}$ MCA

1,4 - / 1,5 - DCA $\xrightarrow{-H_2O}$ Anhydrid cyclic

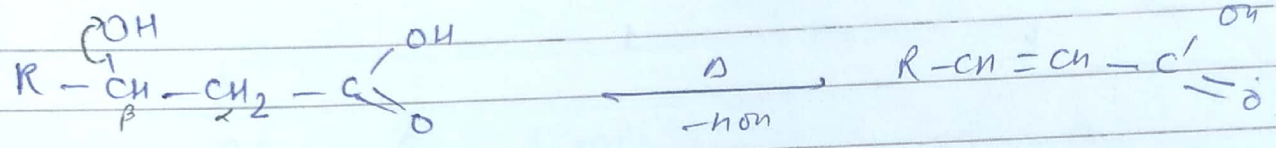
1,6 - / 1,7 - DCA $\xrightarrow{-CO_2, -H_2O}$ cyclic anhydride

18 - / 1n - DCA $\longrightarrow$ Polymer

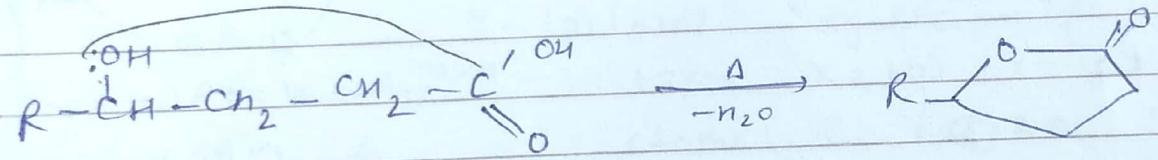
* Effect of Heat on Hydroxy acids :



∝ -HA / 2-HA

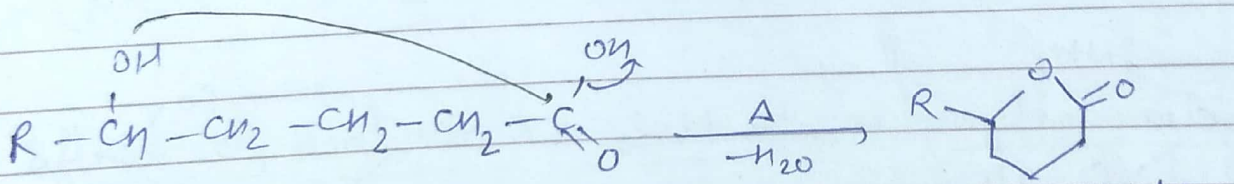


β -HA / 3-HA



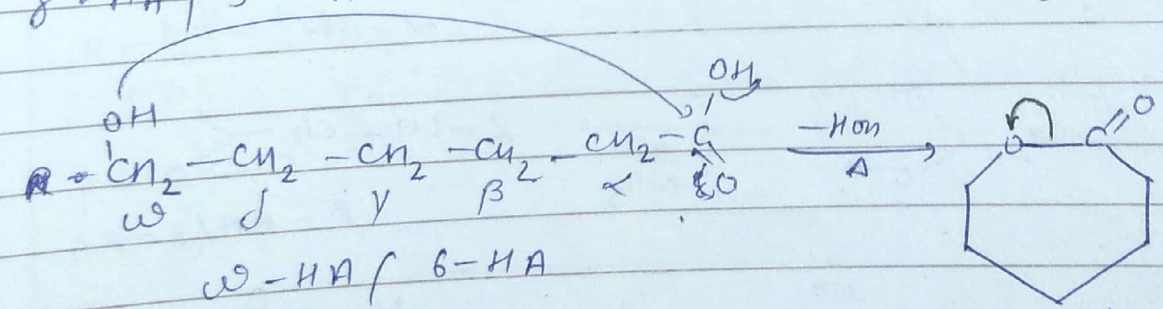
γ-Lactone

γ-HA / 4-HA



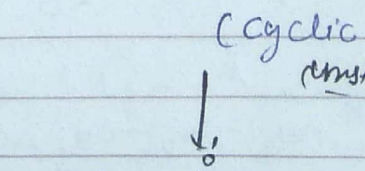
δ-Lactone

δ-HA / 5-HA



ω-HA / 6-HA

ω-Lactone
(Cyclic ester)
(unstable)



Polyster (Polymer)

→ α-HA $\xrightarrow{\Delta}$ Dimer

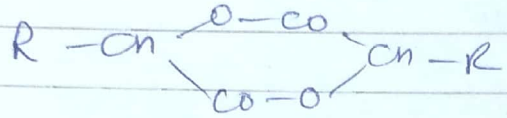
β-HA $\xrightarrow{\Delta}$ αβ-unsaturated Acid

γ-HA $\xrightarrow{\Delta}$ γ-Lactone (Cyclic estr.)

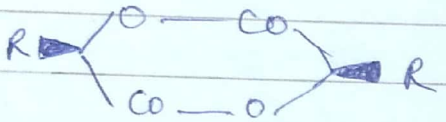
δ-HA $\xrightarrow{\Delta}$ δ-Lactone

ω-HA $\longrightarrow$ ω-Lactone $\xrightarrow{\Delta}$ Polymer

*



(P)

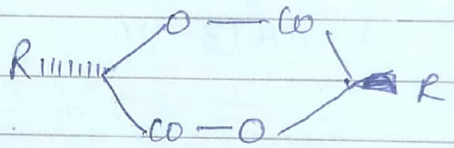


(2)

Pos = X Cos = X

OA (2)

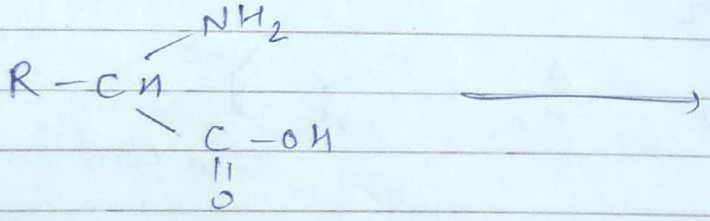
meso

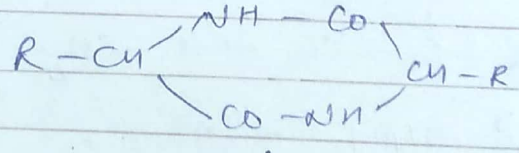


Pos = X Cos = ✓

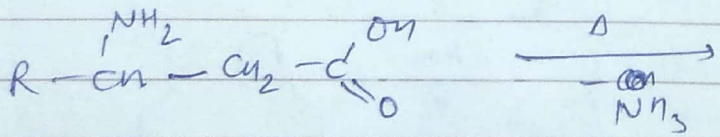
OIA (1)

* Effect of Heat on Amino acid :

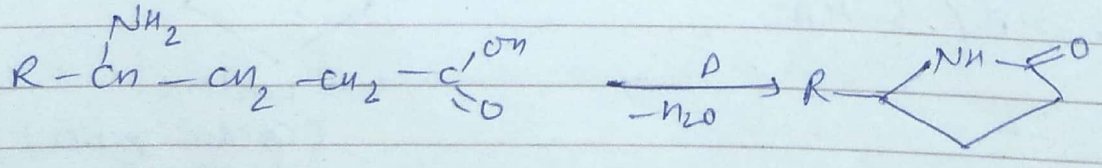




α-AA / 2-AA

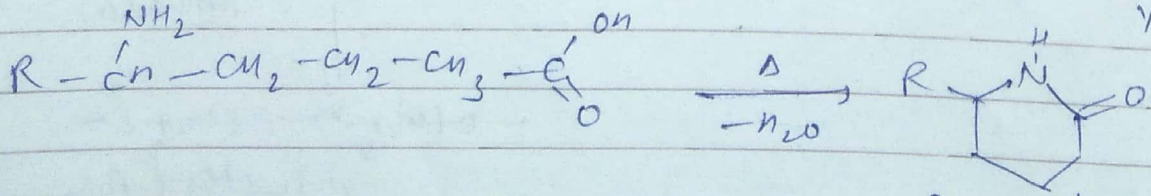


β-AA / 3-AA



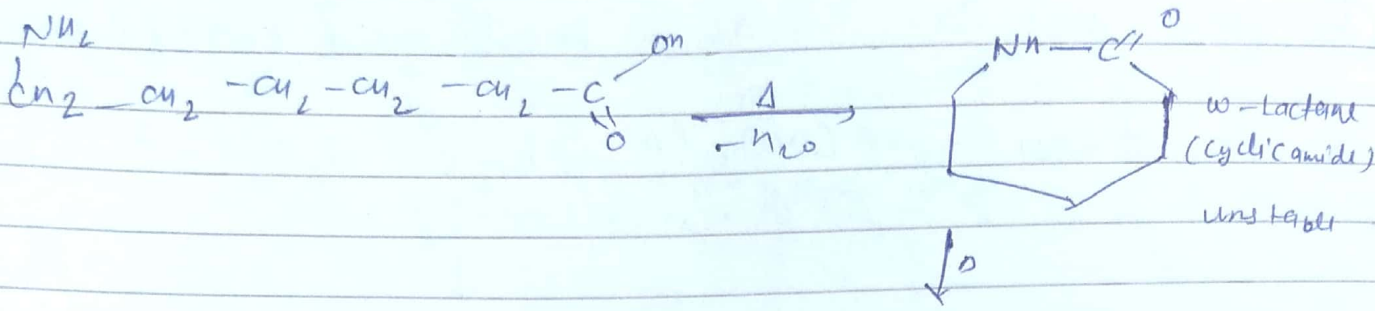
γ-Lactame

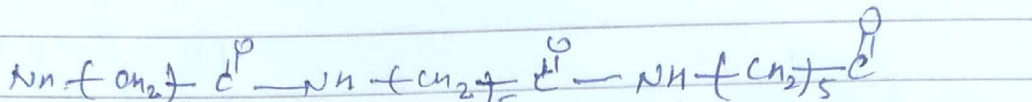
γ-AA / 4-AA



δ-Lactame

δ-AA / 5-AA

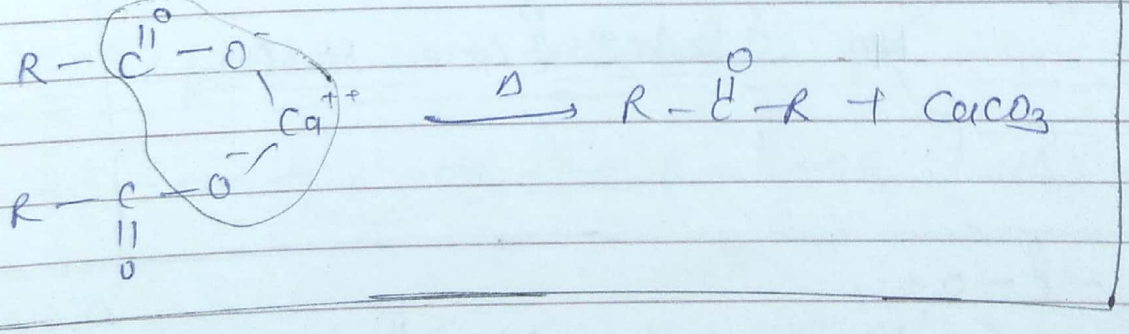




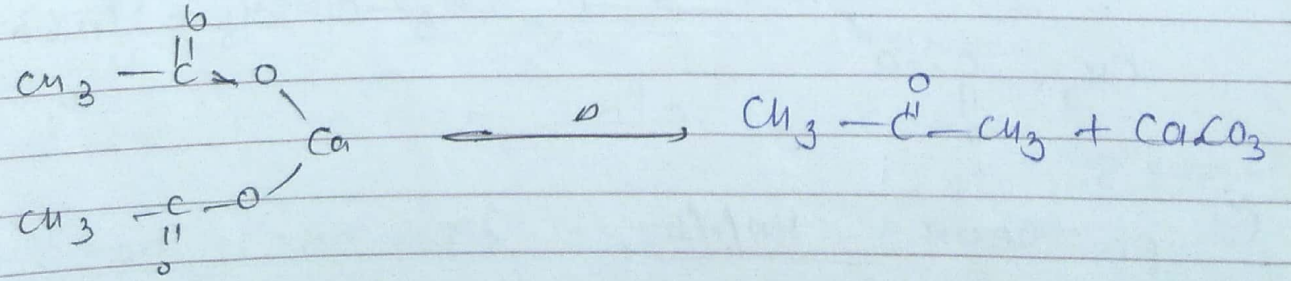
α – AA	$\xrightarrow{\Delta}$	Dimer
β – AA	$\xrightarrow{\Delta}$	$\alpha\beta$ – unsaturated Acid
γ – AA	$\longrightarrow$	γ – lactame (cyclic amide)
δ – AA	$\xrightarrow{\Delta}$	δ – lactame
ω – AA	$\xrightarrow{\Delta}$	ω – lactame $\xrightarrow{\Delta}$ Polymer Nylon 6

in Previous page. (R) — O → NH. OH → NH_2

* Effect of Heat on Ca-Salt of Carboxylic acids:



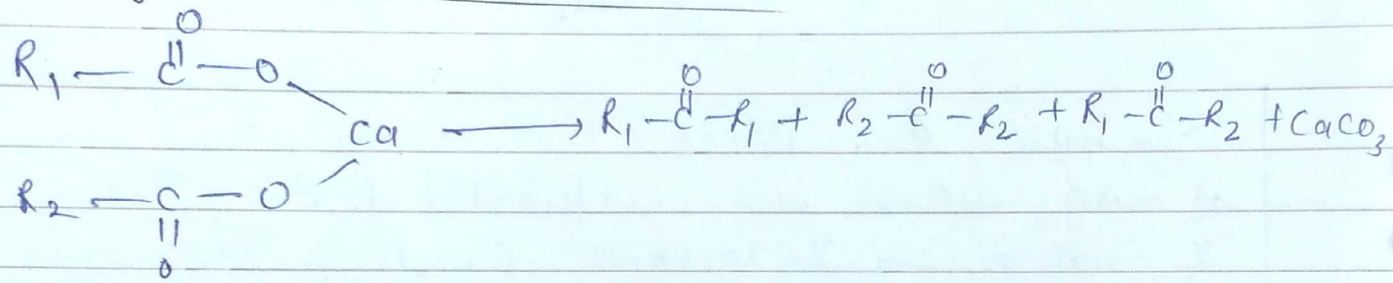
Que:

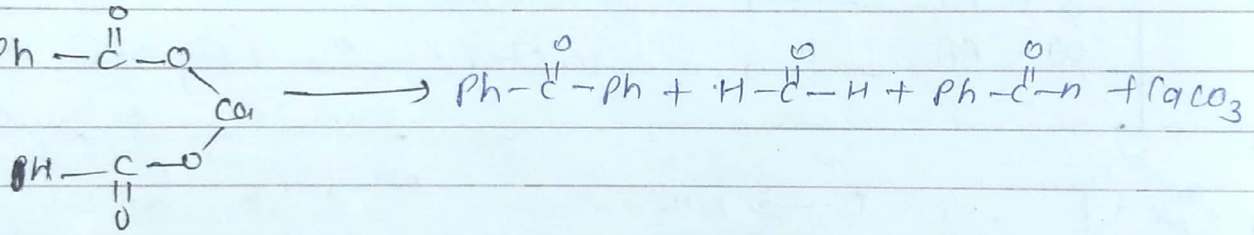


(2) $(H-COO)_2Ca \xrightarrow{\Delta} H-\overset{O}{\overset{\|}{C}}-H + CaCO_3$

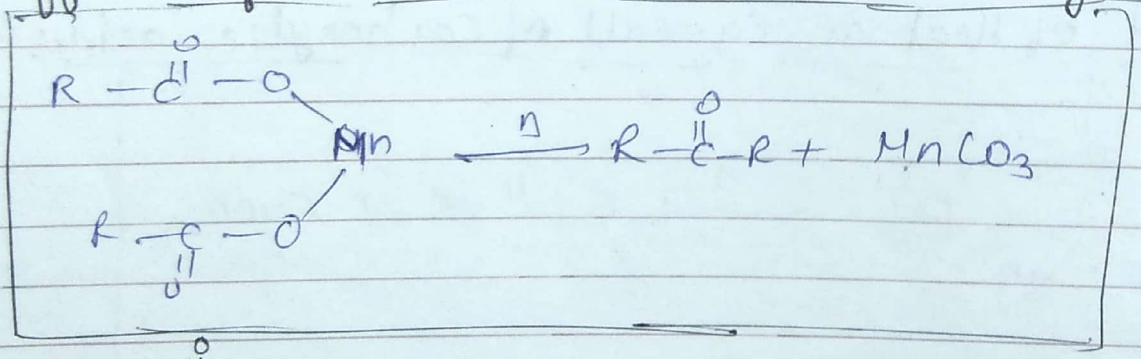
(3) $Ph-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-H_2O]{Ca(OH)_2/\Delta} (Ph-\overset{O}{\overset{\|}{C}}-O)_2Ca \xrightarrow{\Delta} Ph-\overset{O}{\overset{\|}{C}}-Ph$

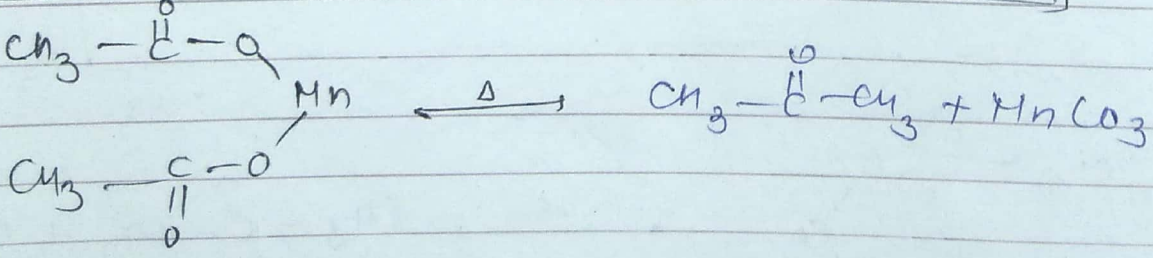
Unsymmetrical Ca-Salt of Acid



Que: 

* Effect of Heat on Mn-Salt of Carboxylic acids:

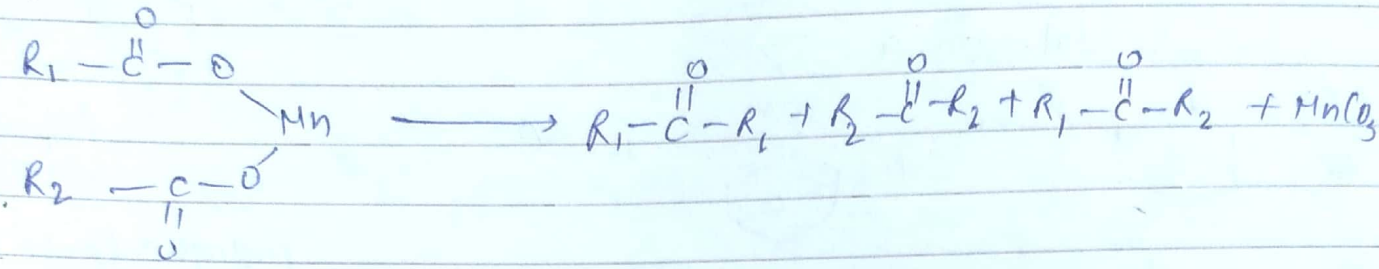


(1) 

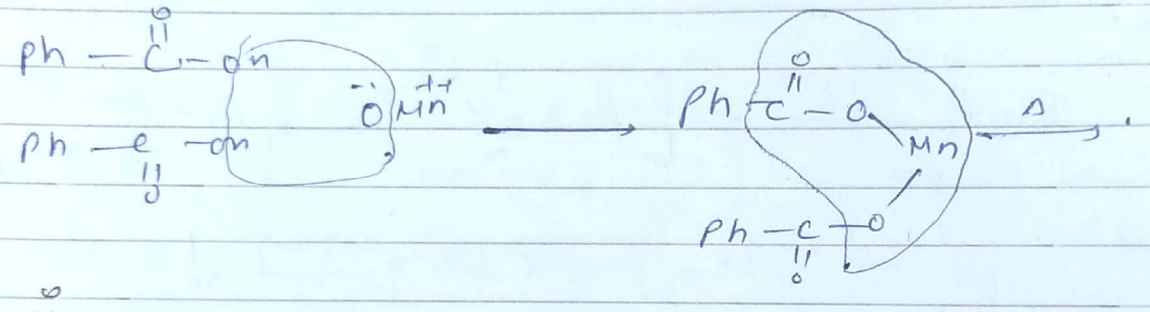
(2) $Ph-COOH \xrightarrow{MnO/\Delta}$?

Next Row

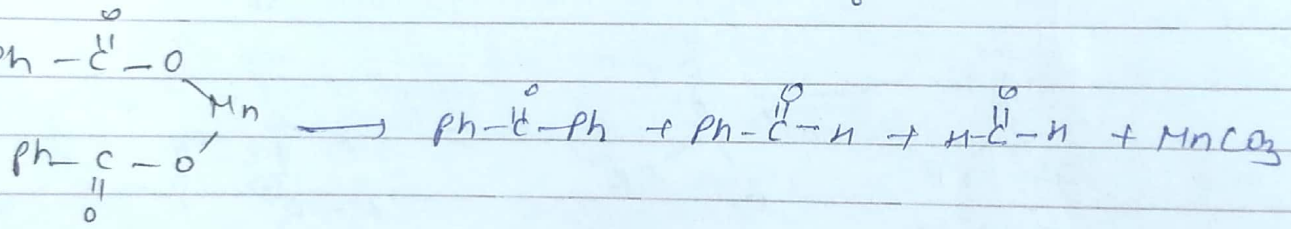
Unsymmetrical Mg-salt of Acid



c. $Ph-COOH \xrightarrow{MnO/\Delta}$



d.



* Esterification

Fisher - Esterification or

or

Rxn of Acid with Alcohol:

$$R-\overset{O}{\overset{\|}{C}}-OH + R'-OH \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

Q. $Ph-\overset{O}{\overset{\|}{C}}-OH + HO-Et \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OEt$

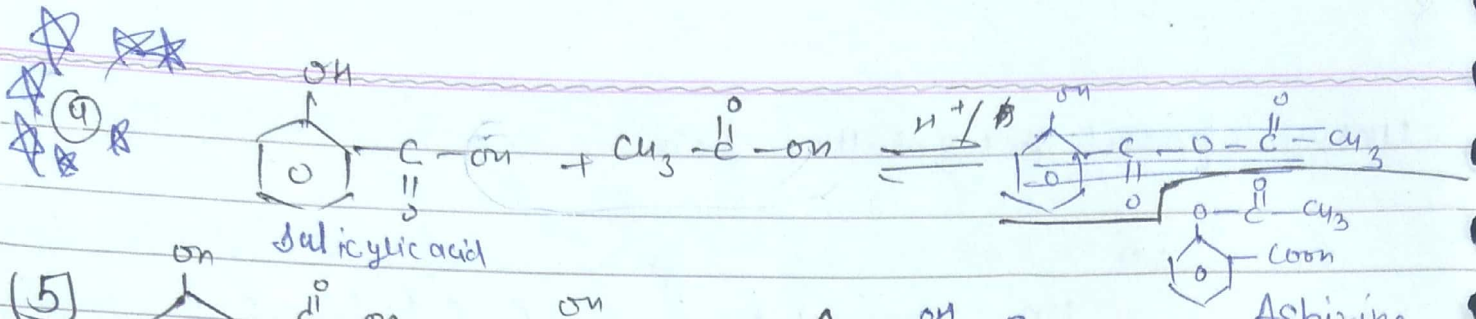
Benzoic acid — ethyl benzoate

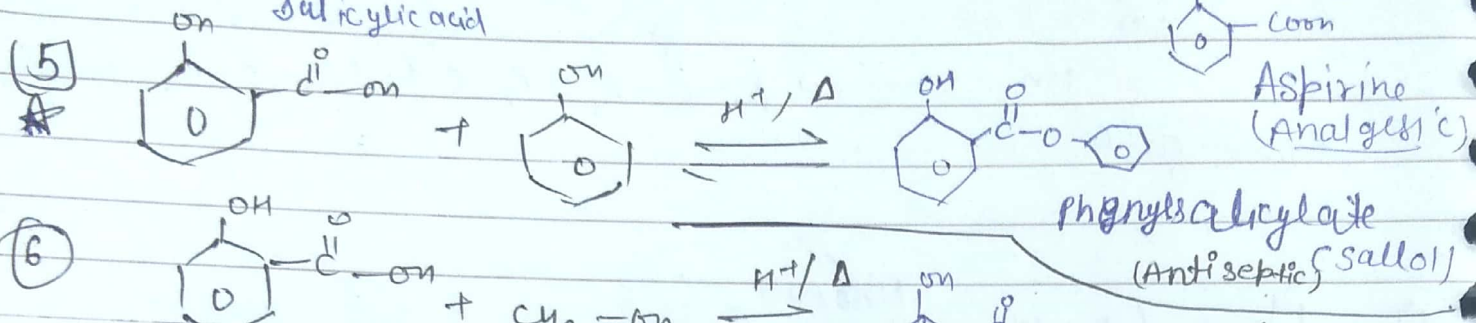
(2) $CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-Et \overset{H^+}{\rightleftharpoons} CH_3-\overset{O}{\overset{\|}{C}}-OEt$

ethyl acetate

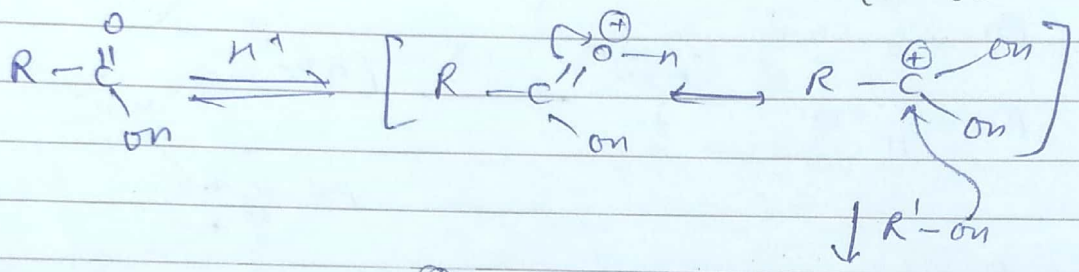
(3) $Ph-\overset{O}{\overset{\|}{C}}-OH + HO-Ph \rightleftharpoons Ph-\overset{O}{\overset{\|}{C}}-OPh$

Phynl Benzoic

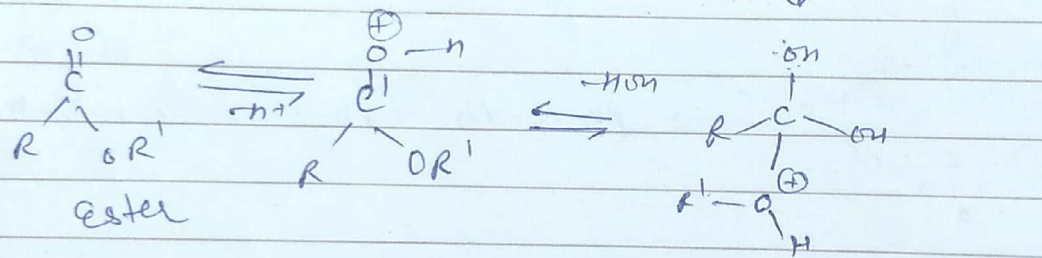




Mechm:



• SNAE



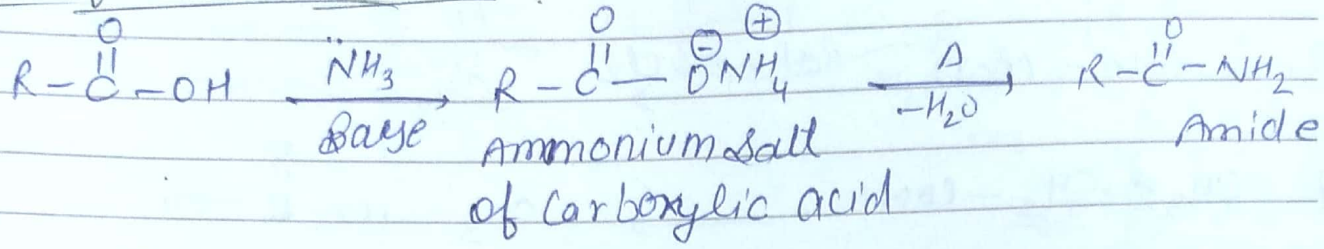
Q. Decide reactivity order of following Acid / Alcohol toward Esterification

(a) H-COOH > Me-COOH > Et-COOH > >COOH > →COOH

(b) Me-OH > Et-OH > >OH > →OH.

Esterification ∝ $\frac{1}{\text{steric hinderence}}$

* Rxn of acid with Ammonia :



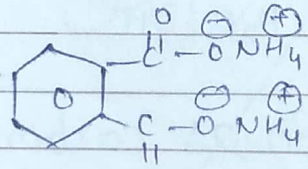
Q. $CH_3-C(=O)-OH \xrightarrow{NH_3} CH_3-C(=O)-O^{\ominus}NH_4^{\oplus}$ (Ammonium acetate)

$CH_3-C(=O)-NH_2$ (Acetamide) ← $\xrightarrow{NH_3/\Delta}$

(2) $Ph-C(=O)-OH \xrightarrow{NH_3} Ph-C(=O)-O^{\ominus}NH_4^{\oplus} \xrightarrow{NH_3/\Delta} Ph-C(=O)-NH_2$

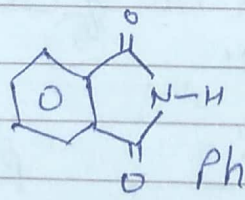
Benzoic acid

(3) Phthalic acid $\xrightarrow{NH_3}$ (A) $\xrightarrow{\Delta}$ (B)

(A): 

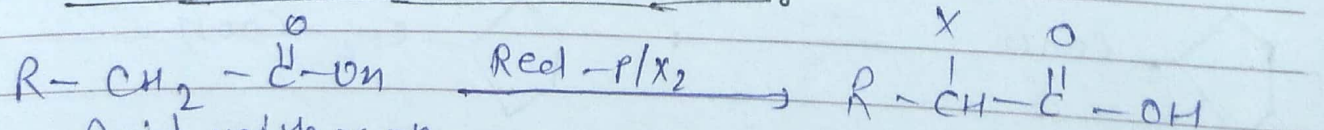
(B): Phthalamide

Phthalamide $\xrightarrow[SN_AC]{\text{A strong Heat}}$ Phthalimide (with $-NH_3$)



HVZ Rxn (Hel-Volhard-Zelinsky Rxn) :

(4) Rxn of Acid with Red-P/X_2 :



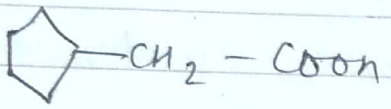
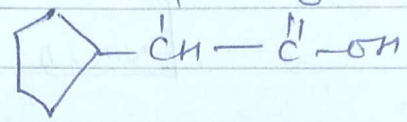
Here Red-P taken as in small amount.

• This Rx^n is also known as α-Halogination Rx^n.

Q. $CH_3-COOH \xrightarrow{Red-P + Cl_2} ClCH_2-C(=O)-OH$

2) $CH_3-CH_2-COOH \longrightarrow CH_3-CHCl-C(=O)-OH$

3) $Ph-CH_2-COOH \longrightarrow Ph-CHCl-COOH$

4)  $\longrightarrow$ 

***

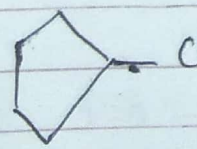
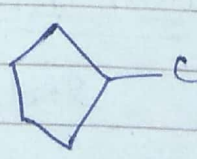
5) Arndt Eistert synthesis :-

$$R-COOH \xrightarrow[\text{(ii) } CH_2N_2 \text{ (Diazomethane)}]{\text{(i) } SOCl_2} \xrightarrow[\text{(iv) } H_2O/H^+]{\text{(iii) } Ag_2O/\Delta} R-CH_2-COOH$$

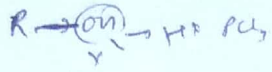
* This Rx^n is known as carbon-upgradation Rx^n In this Rx^n Lower no. of Carboxylic acid changed to higher member

(1) $Ph-COOH \xrightarrow{::} Ph-CH_2-COOH$

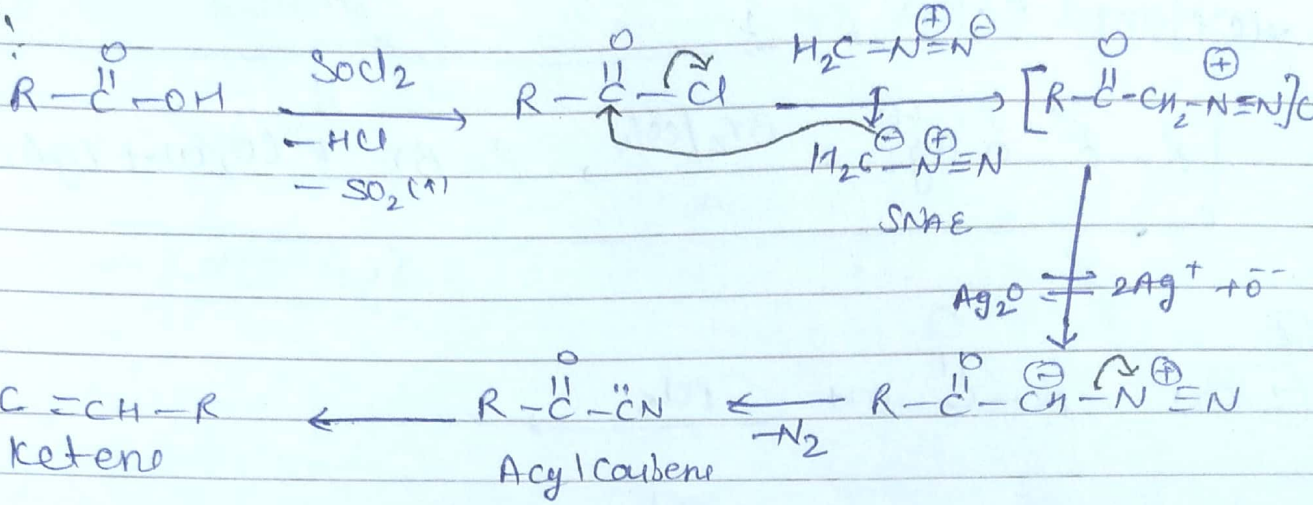
(2) $CH_3-COOH \xrightarrow{::} CH_3-CH_2-COOH$

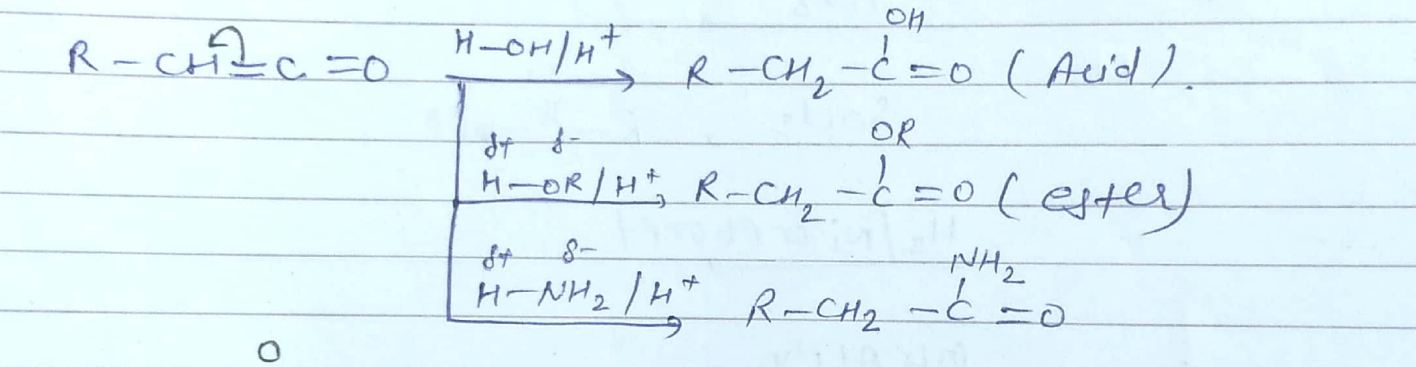
(3)  $\xrightarrow{::}$ 

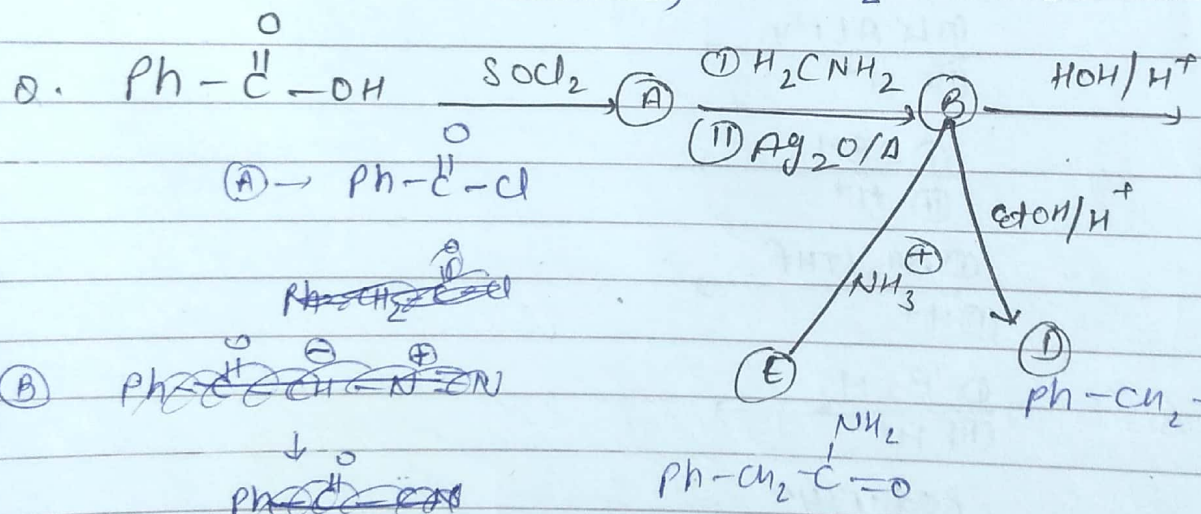
(4) $CH_3-CH_2-COOH \xrightarrow{::} CH_3-CH_2-CH_2-COOH$.



Mech^{m}:







Q. $Ph-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{SOCl_2} (A) \xrightarrow[(II)\ Ag_2O/\Delta]{(I)\ H_2CNH_2} (B) \xrightarrow{HOH/H^+} (C)$

(A) → $Ph-\overset{O}{\overset{\|}{C}}-Cl$

(B) → $Ph-CH=C=O$

(C) $Ph-CH_2-\overset{OH}{\overset{|}{C}}=O$

$\xrightarrow{EtOH/H^+}$ (D) $Ph-CH_2-\overset{OEt}{\overset{|}{C}}=O$

$\xrightarrow{NH_3}$ (E) $Ph-CH_2-\overset{NH_2}{\overset{|}{C}}=O$

SBG STUDY

*⑥ Hunsdiecker Rxn :

$$R-\overset{\overset{O}{\|}}{C}-O^{\ominus}\,Ag^{\oplus} \xrightarrow[\Delta]{Br_2/CCl_4} R-Br + CO_2(\uparrow) + AgBr$$

(*)

(7) 8. $R-\overset{\overset{O}{\|}}{C}-OH$ $\xrightarrow{PCl_5}$

$\xrightarrow{PCl_3}$

$\xrightarrow{SOCl_2}$ $R-\overset{\overset{O}{\|}}{C}-Cl$

$\xrightarrow{H_2/Ni \text{ or } Pt \text{ or } Pd}$

$\xrightarrow[\text{(ii) } H^+]{\text{(i) } LiAlH_4}$

$\xrightarrow[\text{(ii) } H^+]{\text{(i) } SBH}$

$\xrightarrow[\text{(ii) } H^+]{\text{(i) } BH_3/THF}$

$\xrightarrow[\text{(ii) } H^+]{\text{(i) } B_2H_6}$

14

$\xrightarrow{Red.\ P/HI}$

$\xrightarrow[\Delta]{(NaOH + CaO)}$

$\xrightarrow{Na-metal}$

$\xrightarrow{NaH}$

$\xrightarrow{NaOH}$