Heating Effect:

On heating several possibilities can take place.

Compound
- $\xrightarrow{\Delta}$ $-H_2O$ (Dehydration)
- $\xrightarrow{\Delta}$ $-CO_2$ (Decarboxylation)
- $\xrightarrow{\Delta}$ $-CO$ (Decarbonylation)
- $\xrightarrow{\Delta}$ $-NH_3$ (Deamination)

Examples: : OMSGAPSA :

Oxalic Acid

$$\begin{matrix} CO_2H \\ | \\ CO_2H \end{matrix} \xrightarrow[\text{temp.}\Delta]{\text{low}} CO_2 + HCO_2H.$$

$$\begin{matrix} CO_2H \\ | \\ CO_2H \end{matrix} \xrightarrow[\text{temp}/\Delta]{\text{high}} CO_2 + CO + H_2O.$$

$$\begin{matrix} CO_2H \\ | \\ CO_2H \end{matrix} \xrightarrow[+\text{conc.}H_2SO_4]{MnO_2/\Delta} CO_2 + H_2O.$$

Malonic Acid.

$$\begin{matrix} CO_2H \\ / \\ H_2C \\ \backslash \\ CO_2H \end{matrix} \xrightarrow{\Delta} CH_3CO_2H + CO_2\uparrow.$$

Gemdicarboxylic acid always on heating is converted into monocarboxylic acid.

Succinic Acid.

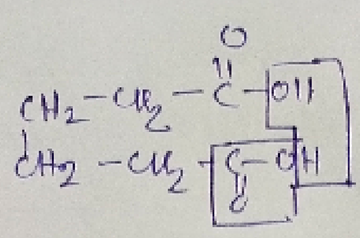
$$\begin{matrix} CH_2-CO_2H \\ | \\ CH_2-CO_2H \end{matrix} \xrightarrow{\Delta} \begin{matrix} CH_2-C \\ | \\ CH_2-C \end{matrix}\!\!\begin{matrix} O \\ \| \\ \diagup \\ \diagdown \\ O \end{matrix} + H_2O$$

Succinic anhydride
[5 membered cyclic ring].
stable.

Glutaric Acid.

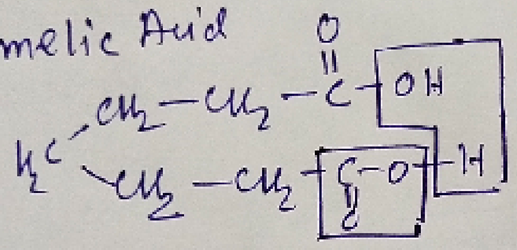
$$\begin{matrix} CH_2-CO_2H \\ / \\ H_2C \\ \backslash \\ CH_2-CO_2H \end{matrix} \xrightarrow{\Delta} \text{Glutaric Anhydride}$$

[6 membered stable cyclic product].

Adipic Acid  $+ CO_2 + H_2O$.

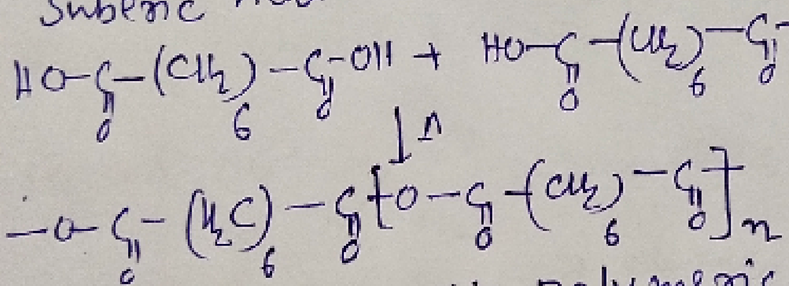
Cyclopentanone.

It looses CO_2 & H_2O to get 5 membered ring. So it is example of decarboxylation as well as dehydration.

Pimelic Acid  $+ CO_2 + H_2O$

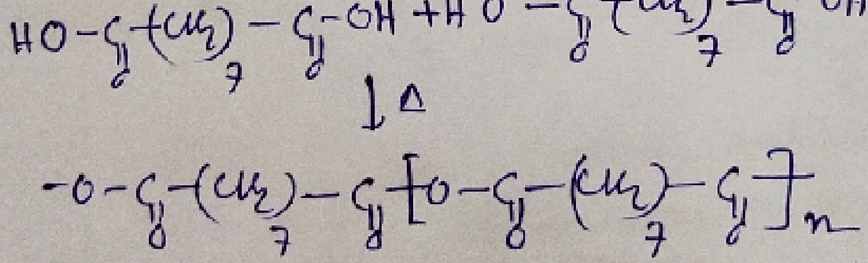
cyclohexanone.

Suberic Acid



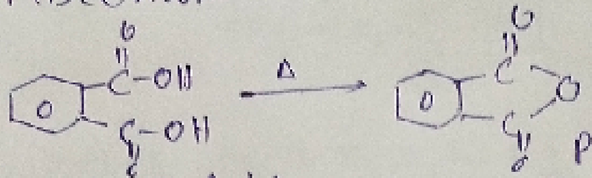
Linear acyclic polymeric anhydride

Azelaic Acid.

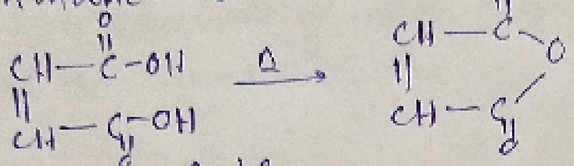


Linear acyclic polymeric anhydride.

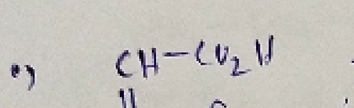
: Miscellaneous Questions:

a) 

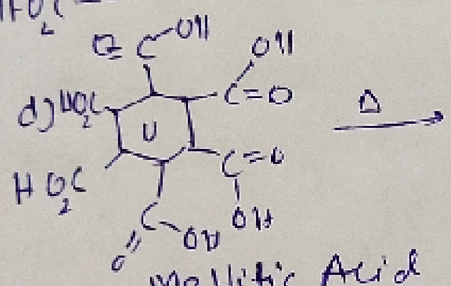
Phthalic Acid → Phthalic anhydride.

b) 

Maleic Acid → Maleic anhydride.

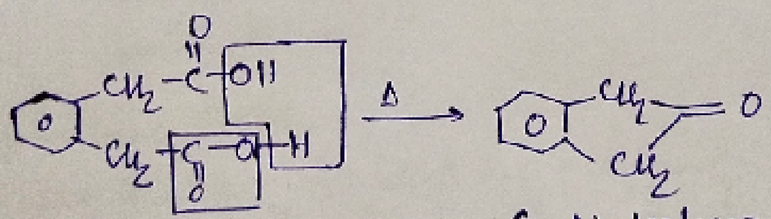
c) 

Fumaric Acid — anhydride can't be formed

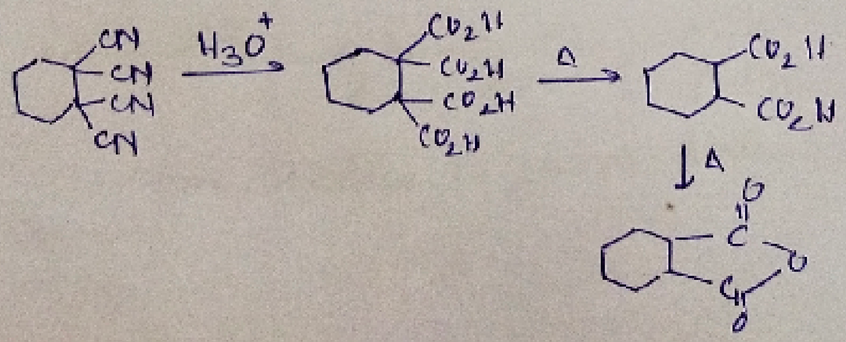
d) 

Mellitic Acid → $C_{12}O_9$ Carbon suboxide. Cyclic trianhydride

Mellitic Anhydride

e) 

Cyclic ketone.

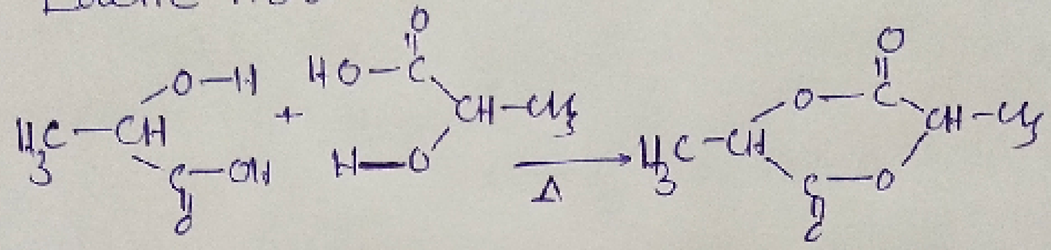
f) 

Hydroxy acid.

$CH_3-\underset{OH}{CH}-CO_2H \xrightarrow{\Delta}$ Molecular weight is increased. [90 → 144]

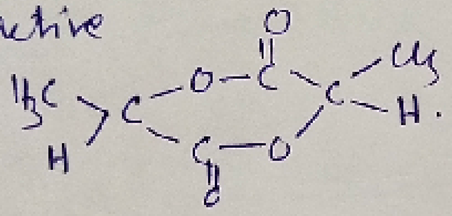
α-hydroxy acid

Lactic Acid



Product shows G.I.

Cis isomer is optically active



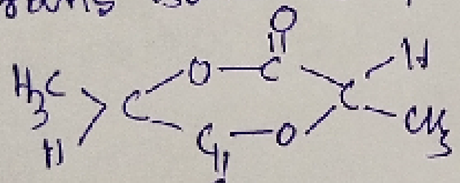
cyclic diester

Lactide.

(no POS ; no COS)

ENT exists. (2 pairs).

Trans isomer is optically inactive.



(COS exist)

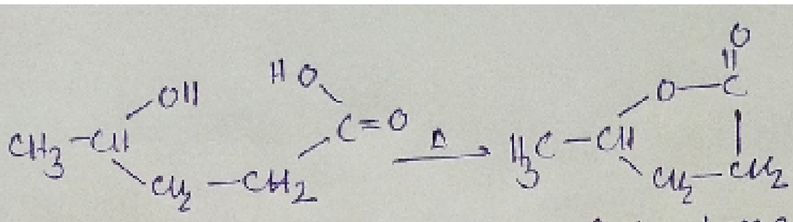
Total 3 products are obtained when Lactic Acid or $R\underset{OH}{CH}-CO_2H$ undergoes heating.

$CH_3-\underset{OH}{CH}-CH_2-\underset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} CH_3-CH=CH-\underset{O}{\overset{\|}{C}}-OH$

β-hydroxy acid. α-β unsaturated acid.

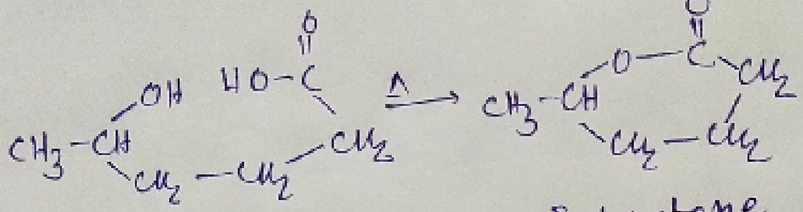
During heating chirality is lost.

products show G.I but reactants show O.I.



γ-hydroxy acid

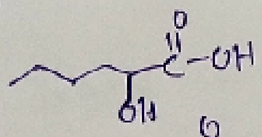
γ-Lactone. [5 membered ring].
(cyclic ester)

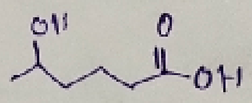


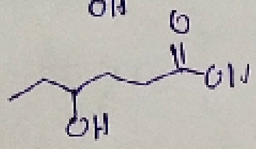
δ-hydroxy acid

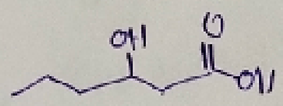
δ-Lactone
(cyclic ester).
(6 membered ring)

Q. Which of the following will give cyclic product when heated?

a) 

b) 

c) 

d) 

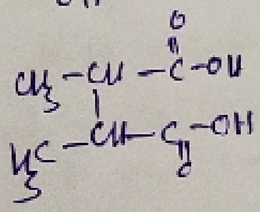
[a, b, c].

Q. In which compound chiral centre is not affected on heating.

a) $CH_3-\underset{OH}{CH}-CO_2H$

b) $CH_3-\underset{OH}{CH}-CH_2-CO_2H$

c) $CH_3-\underset{CH_2CO_2H}{CH}-CO_2H$

d) 

[a, c, d].

$CH_2(CO_2H)_2 \xrightarrow[\Delta]{P_4O_{10}} O=C=C=C=O$

Carbon suboxide [C_3O_2]

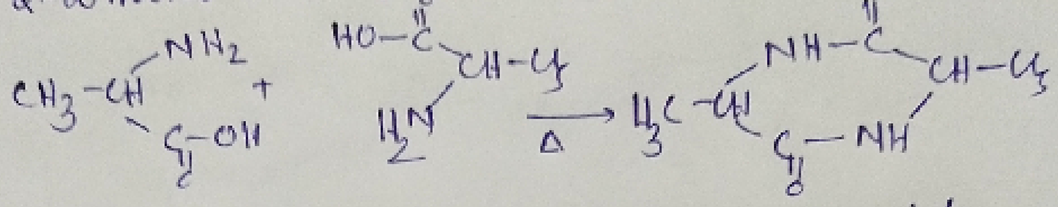
$\downarrow \Delta$

CH_3CO_2H (Acetic Acid)

: Amino Acid:

i) $CH_3-\underset{NH_2}{CH}-CO_2H \xrightarrow{\Delta}$ Molecular weight is increased.

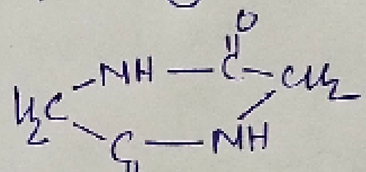
α-amino acid. [Alanine].



cyclic diamide.

3 products possible.
2 products are optically active (cis isomer)
1 product is optically in active (Trans).

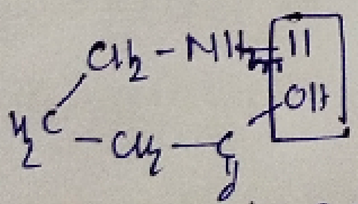
glycine $\xrightarrow{\Delta}$



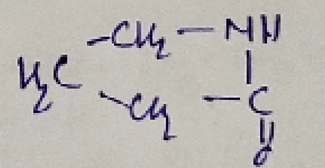
CH_2-CO_2H
NH_2

(only 1 product possible)

$CH_2-CH_2-\underset{O}{\overset{\|}{C}}-OH \xrightarrow[-NH_3]{\Delta} CH_2=CH-\underset{O}{\overset{\|}{C}}-OH$
NH_2 β-amino acid (deamination)



γ-amino acid

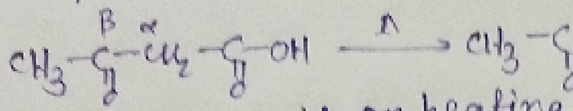


γ-Lactum

δ-amino acid $\xrightarrow{\Delta}$ δ-Lactum.

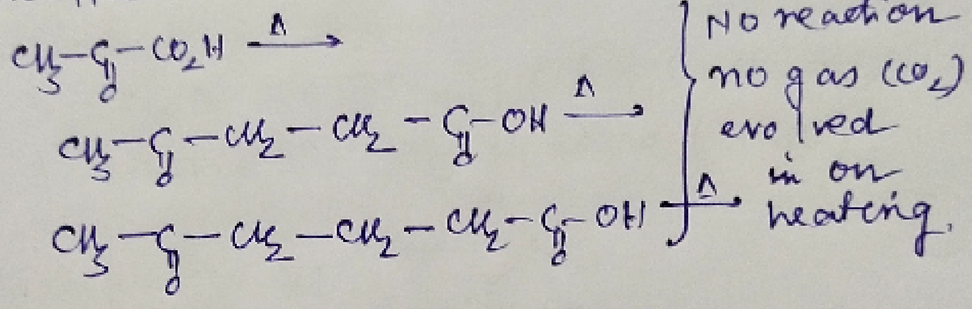
[because 5/6 membered ring is highly stable].

: β keto acid & similar type of compounds:

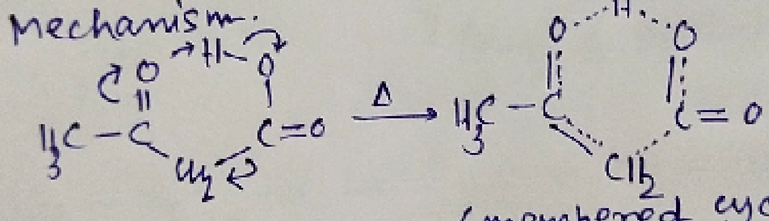


β-keto acid on heating decarboxylation takes place & carbonyl compound is formed as product.

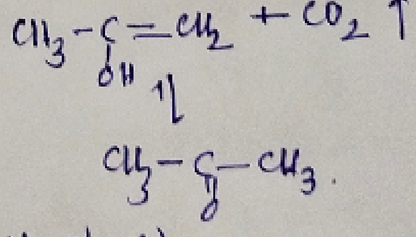
α keto acid, γ-keto acid, δ-keto acid no effect on heating.

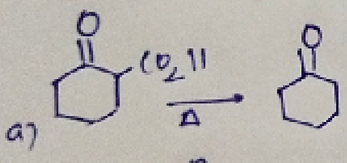


Mechanism:



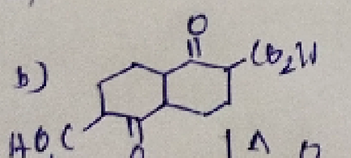
6 membered cyclic T.S. (stable). 6MCTS

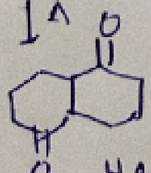




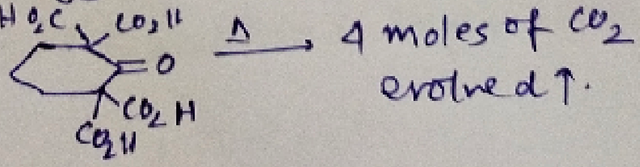
a)

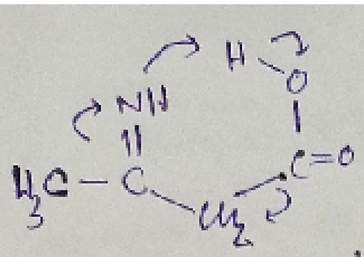
b)





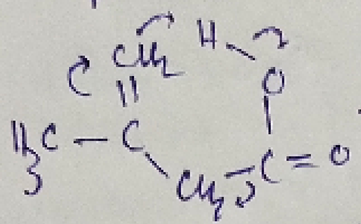
(cyclic diketone)





$\xrightarrow{\Delta}$ $CH_3-C(=NH_2)-CH_2$ (Imine) $+ CO_2\uparrow$

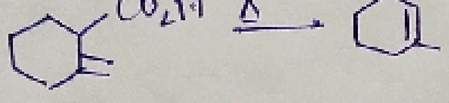
β-imino acid.



$\xrightarrow{\Delta}$ $H_3C-C(CH_3)=CH_2$ (Alkene) $+ CO_2\uparrow$

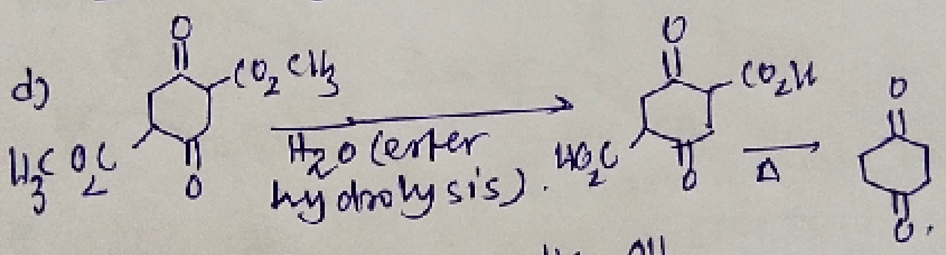
β-γ-unsaturated acid

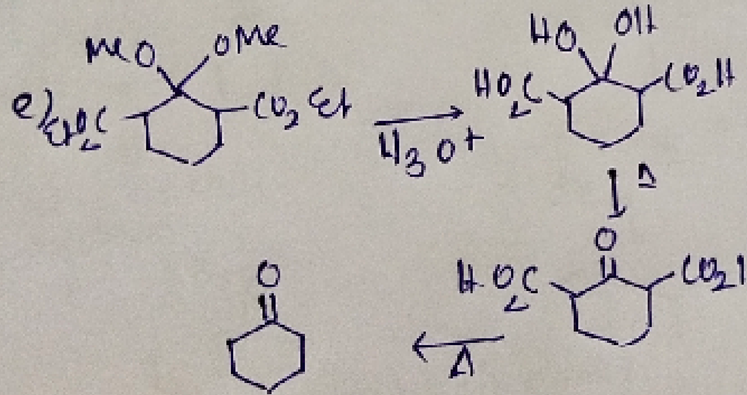
Q.

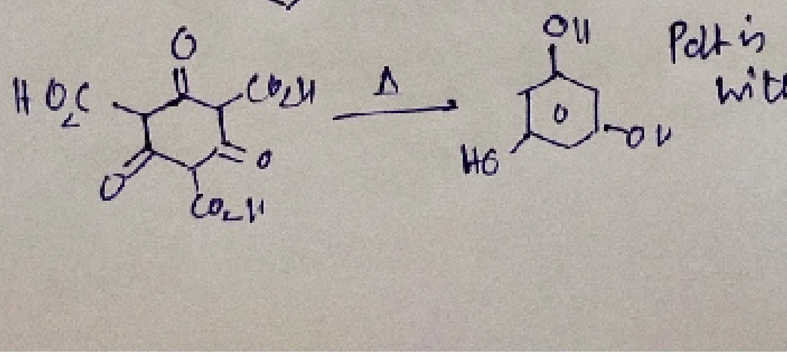
a) 

b) $CH_3-CH=CH-CH_2-CO_2H \xrightarrow{\Delta} CH_3-CH_2-CH=CH_2$

c) $O_2N-CH_2-C(=O)-OH \xrightarrow{\Delta} H_3C-NO_2$.

d) 

e) 



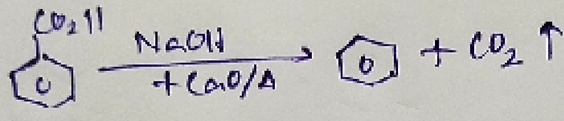
: Monocarboxylic Acid:

Monocarboxylic acid on heating with sodalime ($NaOH + CaO$) undergoes decarboxylation & alkane is formed as product. This is known as decarboxylation.

$$CH_3CO_2H \xrightarrow[\Delta]{NaOH+CaO} CH_4 + CO_2\uparrow$$

$$CH_3CH_2CO_2H \xrightarrow[\Delta]{NaOH+CaO} CH_3CH_3 + CO_2\uparrow$$

This is example of stepdown reaction.



$$EtCO_2H + CH_3MgX \longrightarrow A_1\,(gas)$$

$$+ NaOH + CaO \xrightarrow{\Delta} A_2\,(gas) + A_3\,(gas)$$

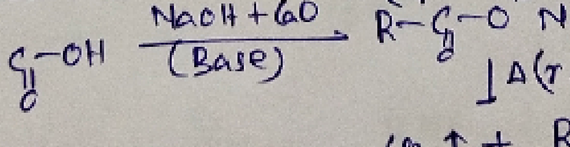
$$+ NaOH \xrightarrow[lysis]{Electro} A_3\,(hydrocarbon)$$

$$+ EtOH \xrightarrow[H_2SO_4/\Delta]{conc.} A_4\,(fruity\ smell)$$

Ans: $A_1 \Rightarrow CH_4$; A_2; $A_3 \Rightarrow EtH / CO_2$

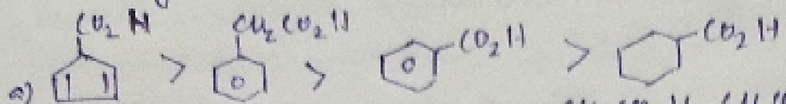
$A_3 \Rightarrow Et-Et$ $\quad A_4 \Rightarrow EtCO_2Et$.

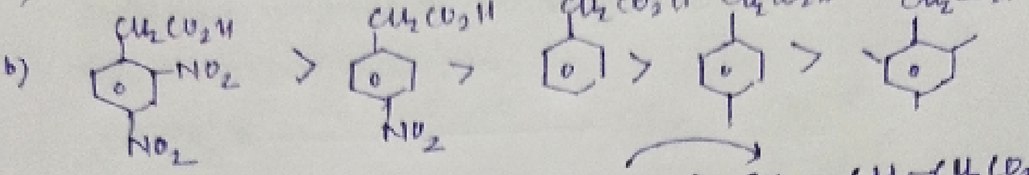
Mechanism:



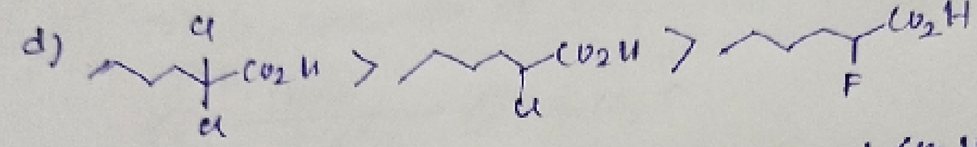
Carbanion is formed as intermediate in r.d.s. So more stable carbanion, faster is the reaction.

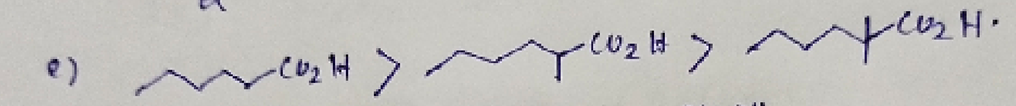
Q. Order of reactivity towards heating with NaOH+CaO.

a) 

b) 

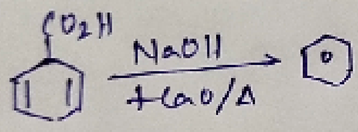
c) $C\equiv C-CO_2H > CH_2=CH-CO_2H > CH_2=CH-CH_2CO_2H$

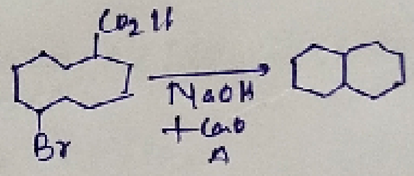
d) 

e) 

f) $CH_3-CH_2-Br \xrightarrow[D.E]{Mg} A \xrightarrow[H+]{CO_2} B \xrightarrow[+CaO]{NaOH} C.$

$A \Rightarrow CH_3CH_2-MgBr$; $B \Rightarrow CH_3CH_2CO_2H$ $C \Rightarrow CH_3CH_3$.

g) 

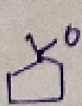
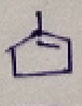
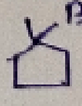
h) 

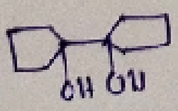
i) Ethyl Malonic Acid $\xrightarrow{\Delta} X_1 \xrightarrow[Lime/\Delta]{Soda} X_2$

$X_1 \Rightarrow EtCH_2CO_2H$. $X_2 \Rightarrow EtCH_3$.

j) Adipic Acid $\xrightarrow{\Delta} X_1 \xrightarrow[H_2O]{CH_3MgX} X_2 \begin{cases} \xrightarrow{H_2SO_4/\Delta} X_3 \\ \xrightarrow[HBr]{} X_4. \end{cases}$

$X_1 \xrightarrow[H+]{Mg(Hg),H^+} X_5 \xrightarrow{\Delta} X_6.$

$X_1 \Rightarrow$  $X_2 \Rightarrow$  $X_3 \Rightarrow$  $X_4 \Rightarrow$ 

$X_5 \Rightarrow$  $X_6 \Rightarrow$