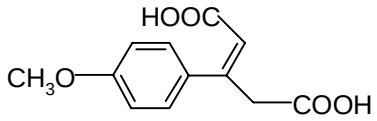
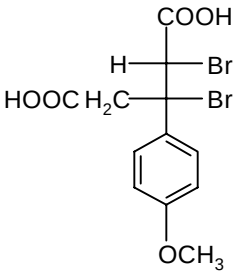
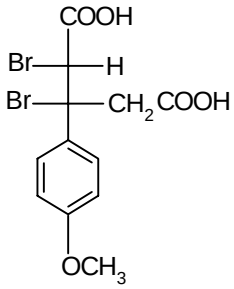


(Z) 3-(4-methoxyphenyl)-2-pentenedioic acid

d. Two products are possible when compound **A** reacts with bromine.



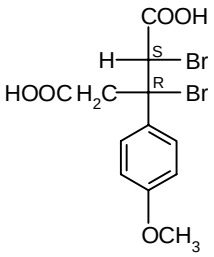
[1]

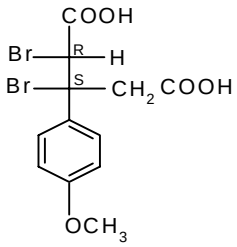


[2]

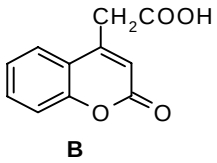
Structures 1 and 2 are enantiomers.

e.



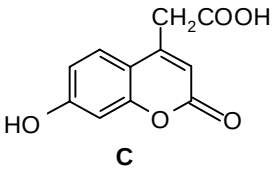


f.



B

Product obtained by reaction with phenol



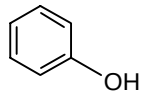
C

Product obtained by reaction with resorcinol

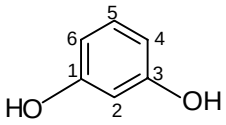
g. In the formation of compound **A** from anisole, the attack takes place at the *p*-position of the **OCH_3** group. However, when compound **B** is formed from phenol, the attack takes place at the *o*-position of the **OH** group. Steric

hindrance of **OCH_3** group favours the attack at the *para* position. Steric hindrance of the **OH** group is comparatively less. Thus, the attack is possible at the *ortho* or *para* positions. However, addition at *ortho* position is favoured as it leads to cyclization of the intermediate acid to stable **B**.

h. Phenol has only one **OH** group on the phenyl ring whereas resorcinol has two **OH** groups on the phenyl ring at the m-positions. Hence, position 4 is considerably more activated (i.e, electron rich) in the case of resorcinol.



Phenol

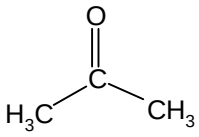


Resorcinol

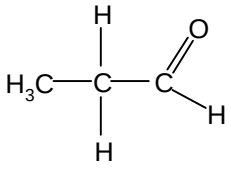
Therefore, under identical reaction conditions, the yield of compound **C** is much higher than that of **B.**

17. Organic spectroscopy and structure determination

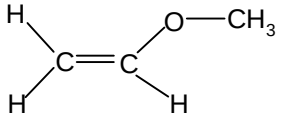
a. The given Molecular formula is **C_3H_60.** Therefore, the possible structures are:



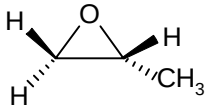
I



II

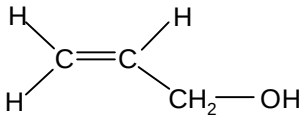


III



IV

V

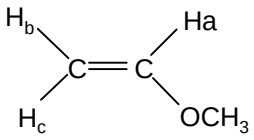


VI

The NMR spectrum of compound **A** shows a single peak which indicates that all the protons in **A** are equivalent. This holds true only for structure I. The IUPAC name of this compound is 2-propanone.

The NMR spectrum of compound **B** shows four sets of peaks, which indicate the presence of four non-equivalent protons**.** This holds true for structures III and IV. However, for structure IV, no singlet peak (see peak at $\delta = 3$) will be observed. So, compound **B** must have structure III. The IUPAC name is 1-methoxyethene.

b.



Three doublets of doublets centred at 6.5 ppm, 3.9 ppm, 3.5 ppm are seen in the spectrum. The assignments in the spectrum are

H_a : 6.5 ppm
H_b : 3.5 ppm
H_c : 3.9 ppm

Due to the presence of electron donating **OCH_3**, the trans proton H_b has higher electron density and thus more shielded than H_c. Thus, H_b appears upfield as compared to H_c. There is also a singlet line at δ=3. This corresponds to the **H** in **OCH_3**.

c. Coupling constants

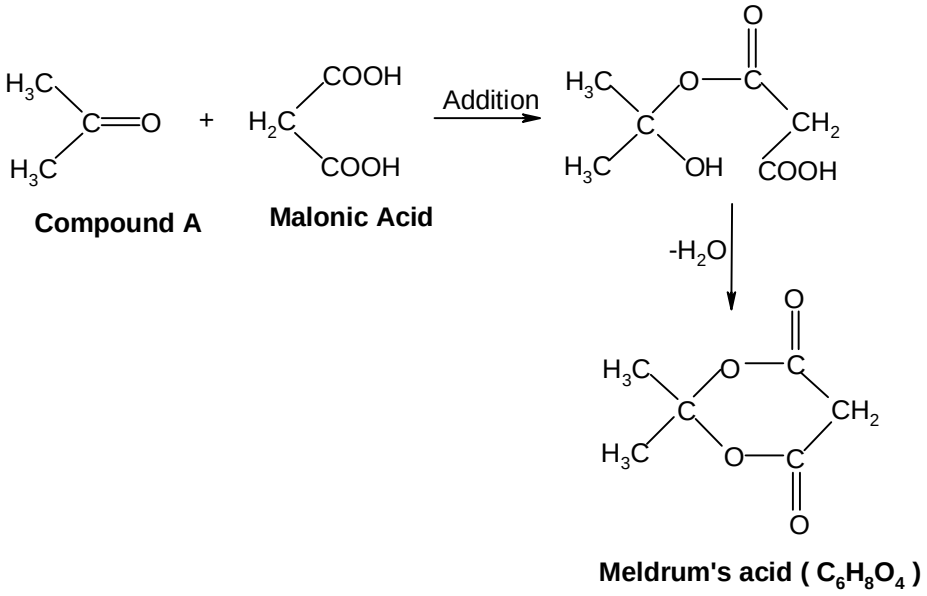
H_a	:	12, 16 Hz	J (H_a, H_b) = 12 Hz
			J (H_a, H_c) = 16 Hz
H_b	:	8, 12 Hz	J (H_a, H_b) = 12 Hz
			J (H_b, H_c) = 8 Hz
H_c	:	8, 16 Hz	J (H_b, H_c) = 8 Hz
			J (H_c, H_a) = 16 Hz

Note: J = (difference in two lines in ppm) x (Instrument frequency)
Geminal coupling < *cis*-vicinal coupling < *trans*-vicinal coupling

d.

Peak positions in Hz (for 400 MHz instrument)	Peak positions in Hz (for 600 MHz instrument)
2614	3921
2602	3903
2598	3897
2586	3879

e. Compound **A** will react with malonic acid in the following manner

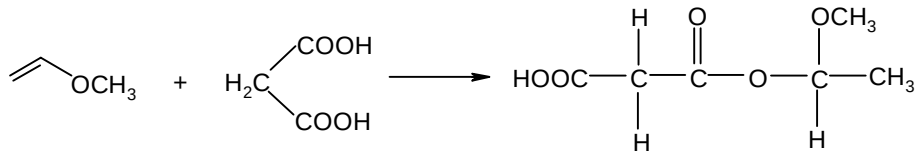


Compound A **Malonic Acid**

Meldrum's acid ($C_6H_8O_4$)

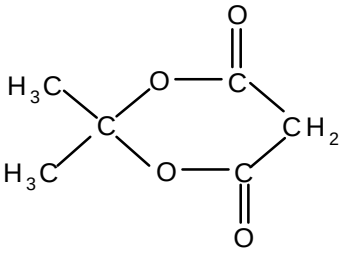
The structure of Meldrum's acid is consistent with the ^{1}H-NMR and IR data. The peak in the IR spectrum at 1700 –1800 cm^{-1} is because of the C=O stretching. The presence of peaks only between 0 – 7 δ in the ^{1}H-NMR spectrum indicates that the compound doesn't have any acidic group like COOH or OH.

If compound B reacts, the only possibility is that it will add across the double bond giving a product with molecular formula equal to **$C_6H_{10}O_5$**. This molecular formula does not match with the one stated in the problem.



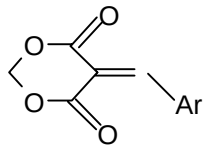
Compound B **Malonic Acid**

f. The increased acidity is due to active $–CH_2$ group of Meldrum's acid flanked by two – CO groups. The carbanion formed at $–CH_2$ will be stabilised by these –CO groups, which are coplanar.



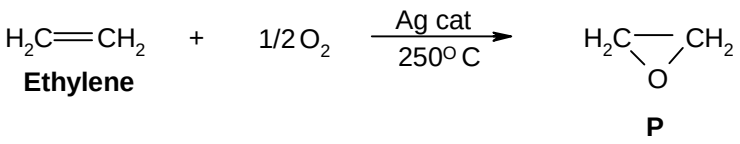
Meldrum's acid ($C_6H_8O_4$)

g. The condensation product of Meldrum's acid with an aromatic aldehyde has the structure

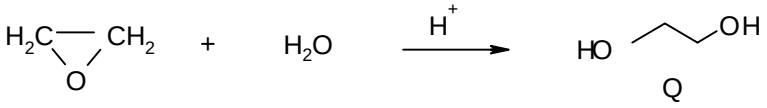


18. Polymer synthesis

a.

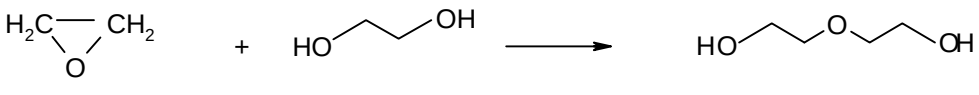


Ethylene **P**



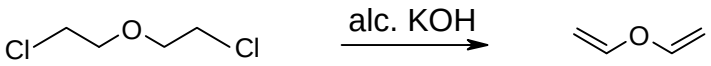
Q

b.



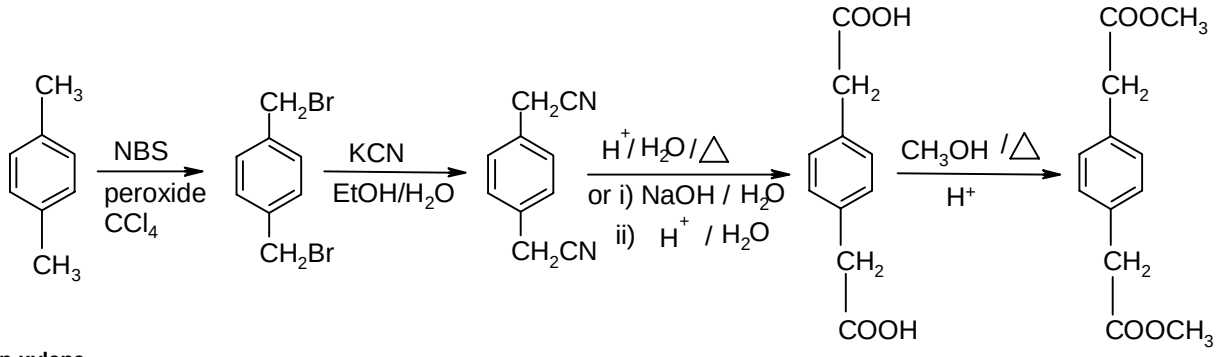
P **Q** **R**

R **S**



S **T**

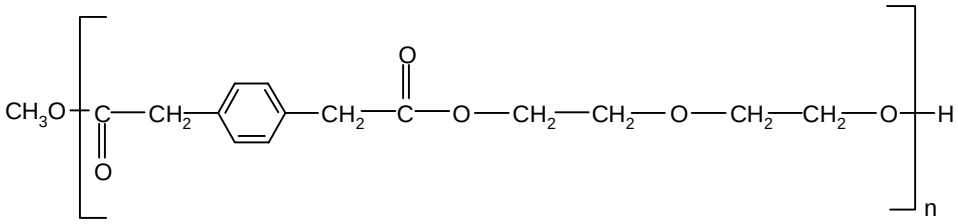
c.



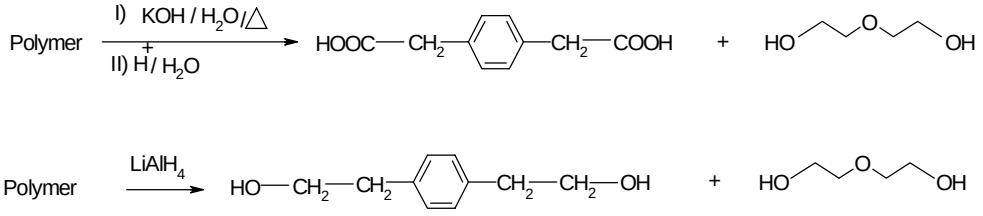
p-xylene **dimethyl benzene-1,4-*bis*(acetate)**

d. Three signals (three singlets for $-CH_3$, $-CH_2$ and aromatic protons)

e. Structure of polymer

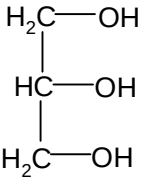


f.

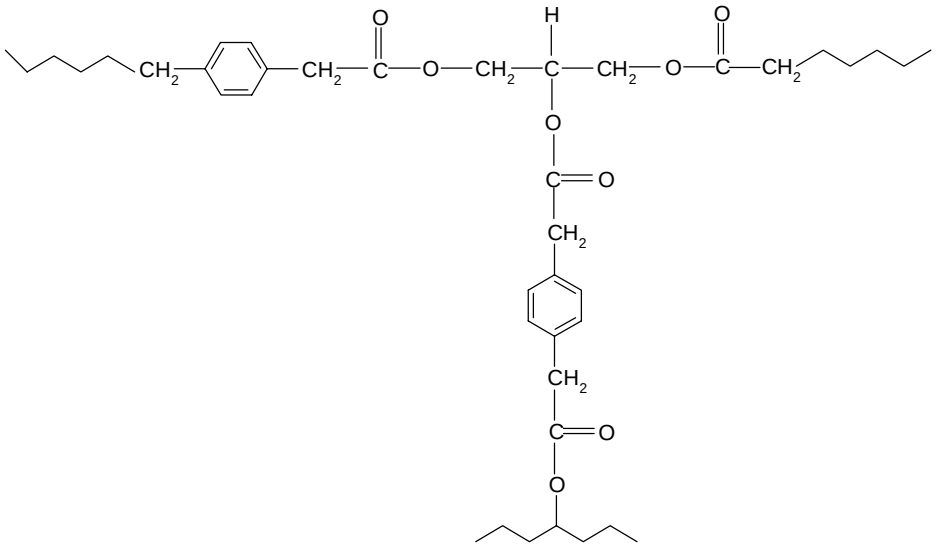


g. With Glycerol (being a triol), cross-links between the polymer chains involving

the secondary hydroxyl group will form giving a three-dimensional network polymer is possible.



Glycerol

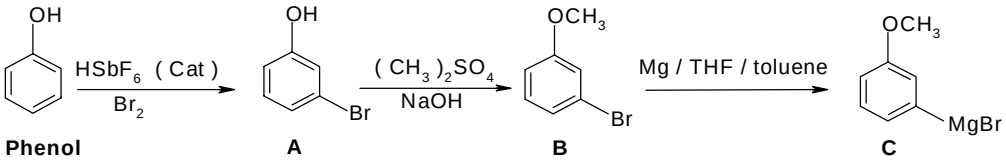


The polymer is unsuitable for drawing fibers because of its cross-linked, resin-like property.

19. Organic synthesis involving regioselection

a. The product obtained in the presence of catalyst $HSbF_6$ is *m*-bromophenol. From the mass spectra given in the problem, direct bromination of phenol gives o/p–bromo derivatives as OH group present in phenol is *o*/*p*- directing.

b.

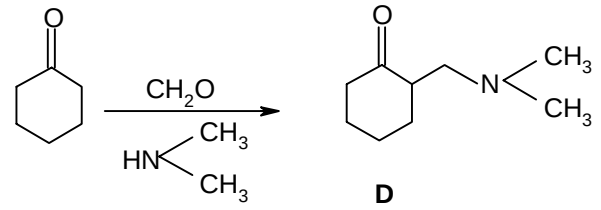


Phenol **A** **B** **C**

Compound **B** may undergo nucleophilic reaction at the carbon bearing bromine. Compound **C** contains a carbanion and hence functions as a

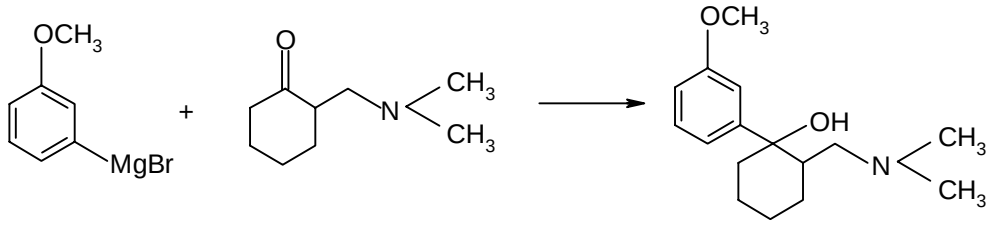
nucleophile and will attack an electrophile. Thus, reactivity of **B** is reversed on its conversion to **C** (umpolung).

c.



D

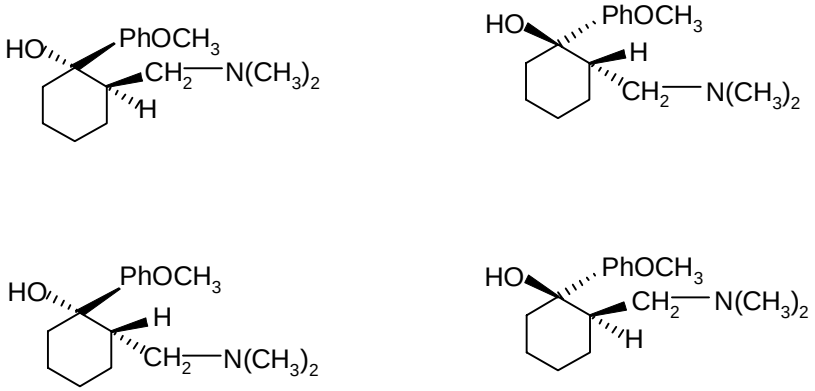
Cyclohexanone



C **D**

Tramadol

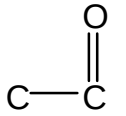
d.



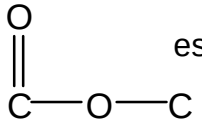
Tramadol has two asymmetric carbon atoms. It has two pairs of enantiomers .

20. Carbon acids

a. The molecular formula of the keto ester is **$C_5H_8O_3$**. Since **X** and **Y** are keto esters, they must have the following units-



keto group



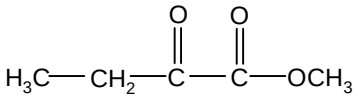
ester group

This accounts for C_4O_3 .The remaining part comprises of CH_8. Thus, only two types of ester groups are possible, methyl or ethyl.

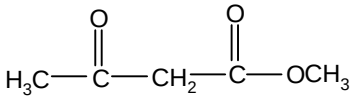
For a methyl ester: **CH_3** will be a part of the ester moiety. This leaves CH_5 to be attached.

For an ethyl ester: **CH_2CH_3** will be a part of the ester group. Therefore H_3 unit needs to be accounted for.

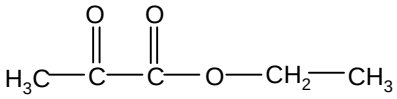
Therefore, possible structures of the keto esters are:



Structure I



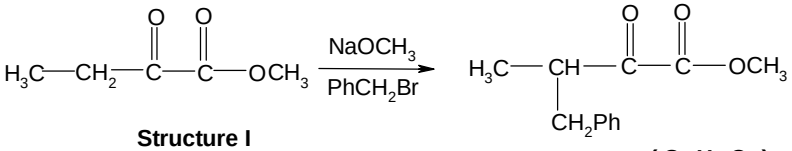
Structure II



Structure III

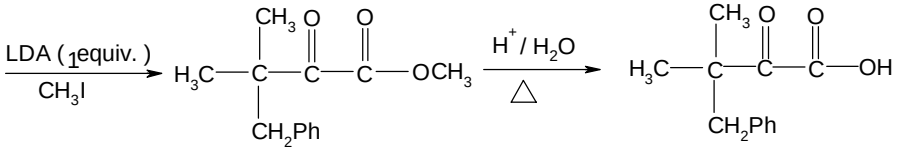
b. Reaction sequence for keto esters

*



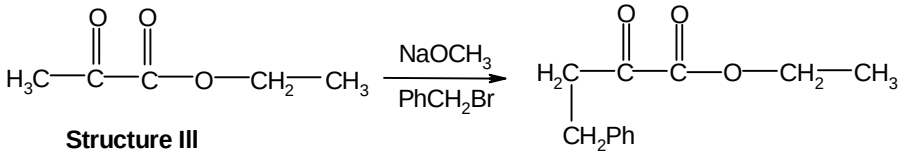
Structure I

Keto acid ($C_{12}H_{14}O_3$)

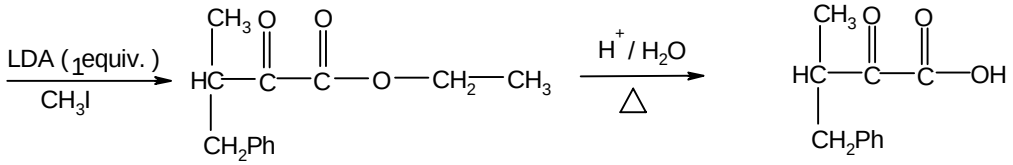


Keto acid ($C_{12}H_{14}O_3$)

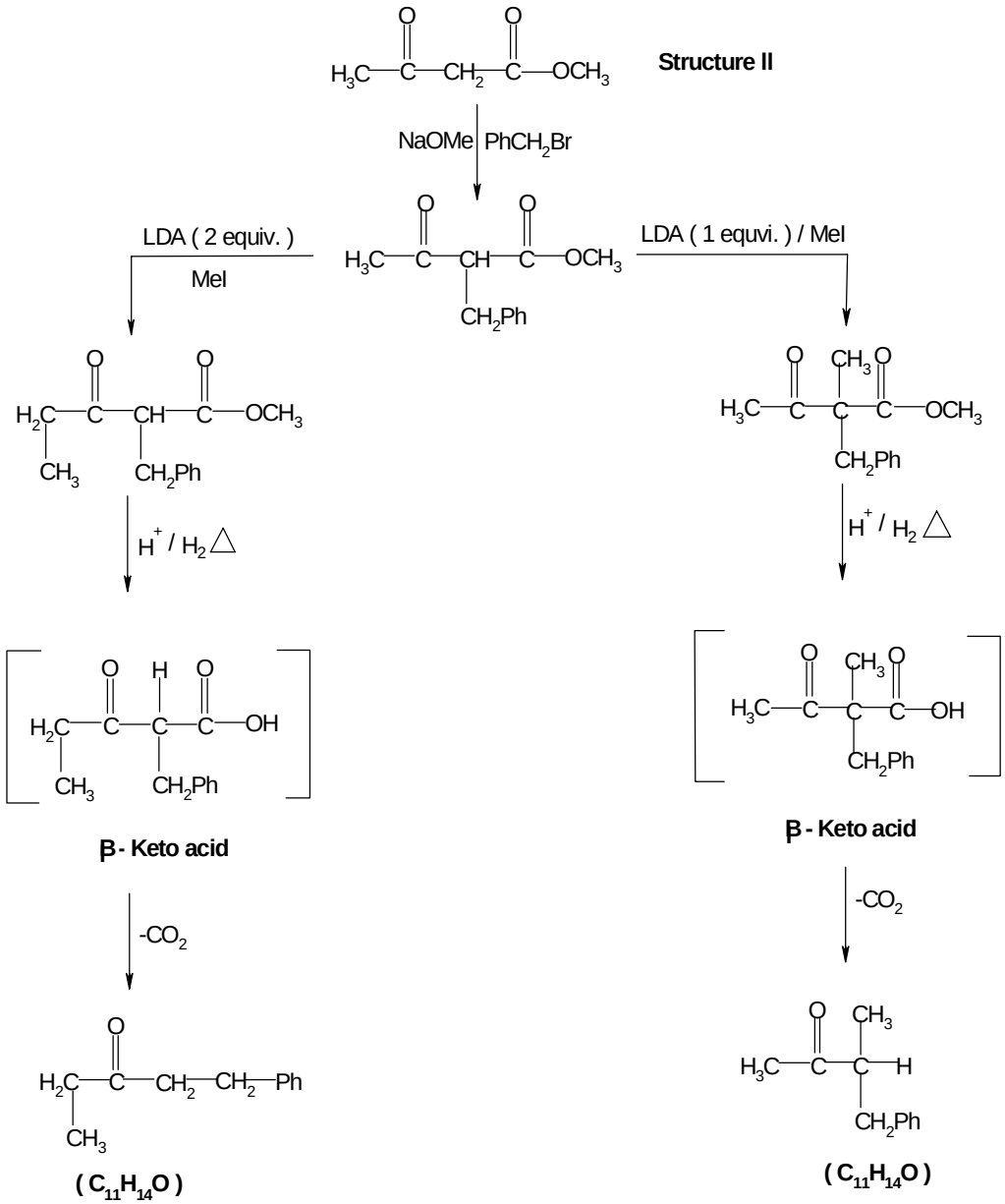
*



Structure III

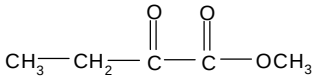


Keto acid ($C_{11}H_{12}O_3$)



- Structure I gives a keto acid with molecular formula **$C_{12}H_{14}O_3$** which matches with the formula of the keto acid obtained from **Y.** ∴ Structure I is **Y**.
- Structure II gives a neutral compound with molecular formula **$C_{11}H_{14}O$** that matches with the molecular formula of the neutral acid stated for **X**. ∴ Structure II is **X**.
- Structure III gives a keto acid with molecular formula **$C_{11}H_{12}O_3$** that also does not match with any given molecular formula.

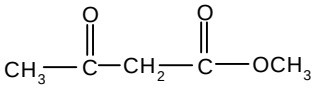
Hence the two keto esters are :



Compound **Y**

(Structure I)

α-keto ester

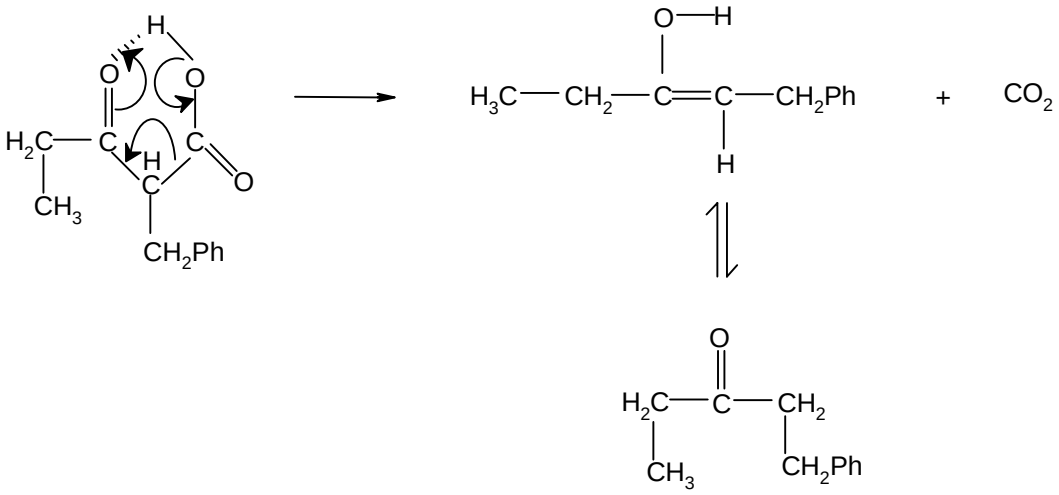


Compound **X**

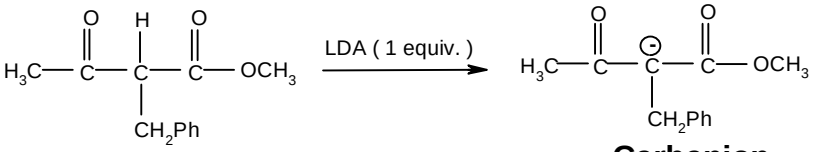
(Structure II)

β-keto ester

c. The β-keto ester gives on hydrolysis a β-keto acid. This acid readily undergoes decarboxylation involving a 6-membered transition state, giving a neutral product (Ketone).

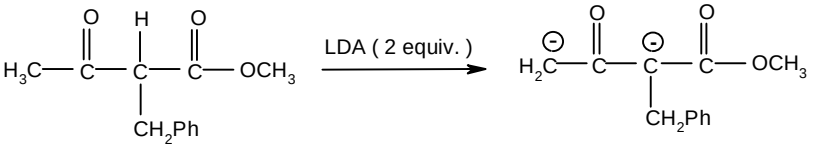


d. **i.** When 1 equivalent of LDA is used compound **X** produces a carbanion (monoanion) as shown below.



Compound X **Carbanion (monoanion)**

ii. Use of 2 equivalents of LDA leads to the formation of a dianion .



Compound X **Dianion**

21. Amino acids and enzymes

a. The protonated amino group has an electron withdrawing effect. This enhances the release of proton from the neighboring –COOH, by stabilizing the conjugate base $–COO^-$. This effect is greater when the $–COO^-$ is physically closer to $–NH_3^+$. As $–NH_3^+$ group is present on the α-carbon, the effect is greater on α-COOH than on the γ-COOH. So the pKa value of α-COOH is lower than that of γ-COOH.

b. The ratio of ionized to unionized γ-COOH group is obtained by using Henderson-Hasselbalch equation,

$$pH = pK_a + \log\frac{[COO^-]}{[COOH]}$$

The pH = 6.3 and pKa of γ-COOH group is 4.3. Substituting these values in the above equation we get,

$$6.3 = 4.3 + \log\frac{[COO^-]}{[COOH]}$$

$$\therefore [COOH] = \frac{100}{101} = 0.99\% \text{ at pH } 6.3$$

c. Glutamic acid has two pKa values lower than 7.0 and one pKa value higher than 7.0. Thus, the isoelectric point (pI) for glutamic acid will lie between the two acidic pKa values.

pI = (2.2 + 4.3)/ 2 = 3.25

At pH = 3.25, net charge on glutamic acid will be zero since this pH coincides with pI of glutamic acid. Hence, glutamic acid will be stationary at pH 3.25.