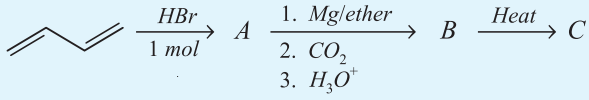
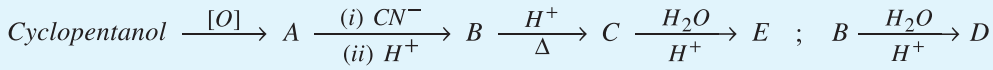
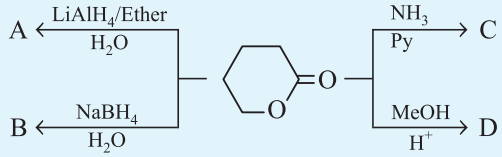
ILLUSTRATIONS — Section - 4

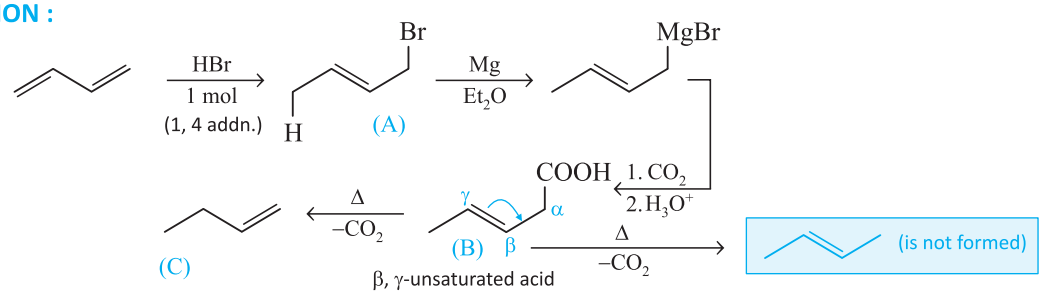
Illustration - 1 *Identify A, B, C, . . in the given reaction sequence.*

(a) 

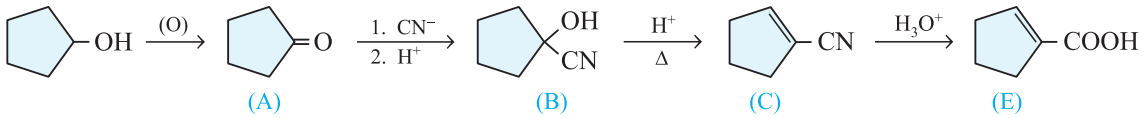
(b) 

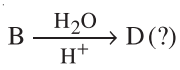
(c) 

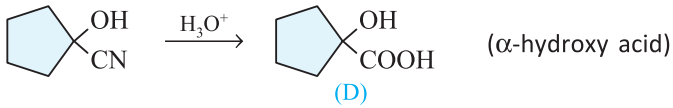
SOLUTION :

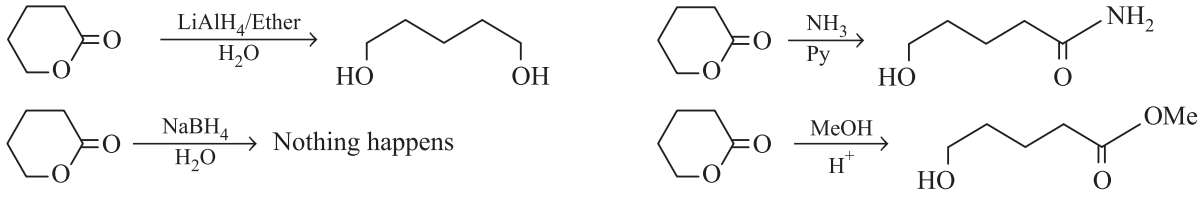
(a) 

(Observe the shift in the position of C = C bond)

(b) 





(c) 

$LiAlH_4$ reduces ester to alcohols. $NaBH_4$ reduces only aldehydes and ketones, but fails to reduce esters.
C is formed via acyl-O cleavage by ammonia. D is formed via trans-esterification of lactone by methyl alcohol.

Illustration - 2 *Identify A, B, C, . . in the given reaction sequence.*

(a) $D \xleftarrow[(ii)\ H^+]{(i)\ NaOH(aq.)} C \xleftarrow[excess\ h\nu]{P/Br_2} \boxed{CH_3COOH} \xrightarrow{SOCl_2} A \xrightarrow{R} CH_3CHO \xrightarrow[\Delta]{dil.\ NaOH} B$

(b)  $\xrightarrow[\Delta]{conc.\ H_2SO_4} A \xrightarrow[CCl_4]{NBS} B \xrightarrow{KCN} C \xrightarrow{H_3O^+} D \xrightarrow[2.\ \Delta]{1.\ [O]} E$

(c) $C_6H_5COOCH_3 + C_2H_5COOCH_3 \xrightarrow[2.\ H^+]{1.\ C_2H_5ONa} A \xrightarrow{H_3O^+} B + C\ ;\ B \xrightarrow{\Delta} D$

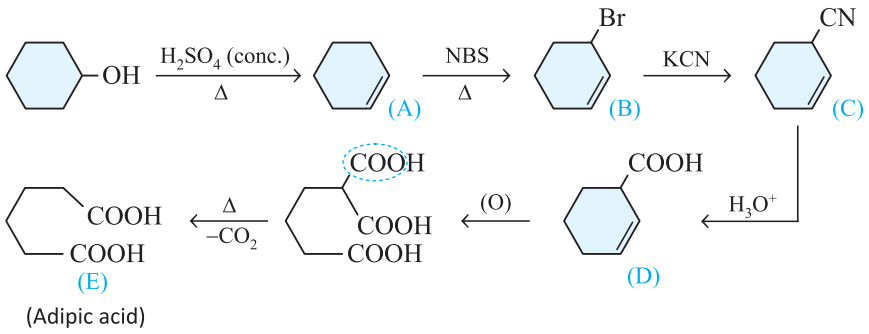
SOLUTION :

(a) $CH_3COOH \xrightarrow{SOCl_2} \underset{(A)}{CH_3-\overset{\overset{O}{\|}}{C}-Cl} \xrightarrow[BaSO_4]{H_2-Pd} CH_3CHO \xrightarrow[\Delta]{dil.\ NaOH} \underset{(B)}{CH_3CH=CHCHO}$

(Rosenmund Reaction) (Aldol condensation)

$CH_3COOH \xrightarrow[excess]{P/Br_2} Br_3C-COOH \xrightarrow[H^+]{NaOH} \underset{(D)}{\begin{matrix}COOH\\|\\COOH\end{matrix}}$ (hydrolysis of trihalides)

(HVZ reaction) (C)

(b) 

(Adipic acid)

Malonic acid on heating loses CO_2

(c) $C_6H_5COOCH_3 + CH_3\underset{\underset{H}{|}}{CH}-COOCH_3 \xrightarrow[2.\ H^+]{1.\ C_2H_5ONa} A$

This is an example of cross-Claisen condensation.

A is : $C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-COOCH_3 \xrightarrow{H_3O^+} \underset{(B)}{C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-COOH} + \underset{(C)}{CH_3OH}$

$\underset{(B)}{C_6H_5-\overset{\overset{O}{\|}}{\underset{\beta}{C}}-\underset{\underset{CH_3}{|}}{\overset{\alpha}{C}H}-COOH} \xrightarrow[-CO_2]{\Delta} \underset{(D)}{C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2CH_3}$

β-keto acid loses CO_2 on heating.

Illustration - 3 *Do the following conversion. (Try to minimize the steps involved)*

(i) 2-butanol to 2-methylbutanoic acid

(ii) 2-chlorobutanoic acid to 3-chlorobutanoic acid

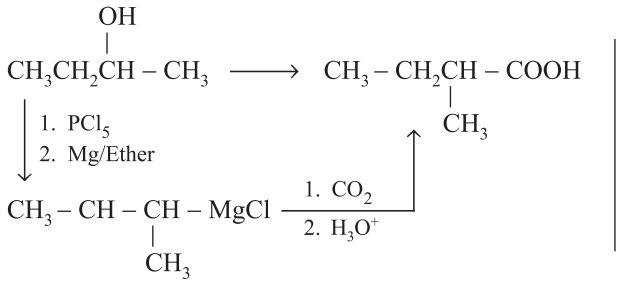
(iii) Benzene to adipic acid

(iv) 2-propanol to 2-hydroxy-2-methyl propanoic acid

(v) Toluene to 2-methyl-5-chlorobenzoic acid

SOLUTION :

(i)



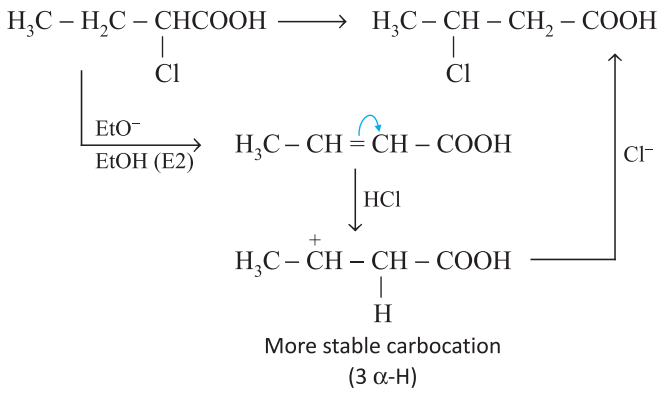
Alternate Method :

(i) PCl_5

(ii) alc. KCN

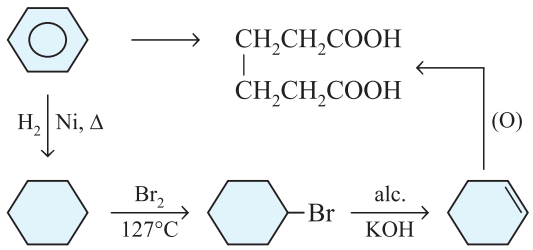
(iii) H_3O^+

(ii)

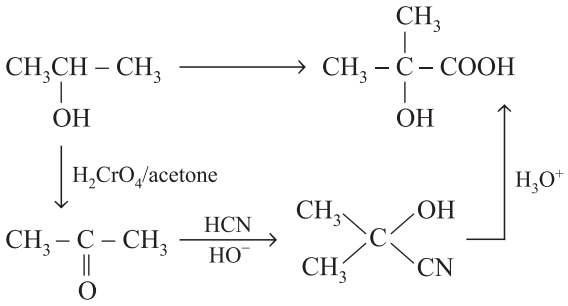


More stable carbocation
(3 α-H)

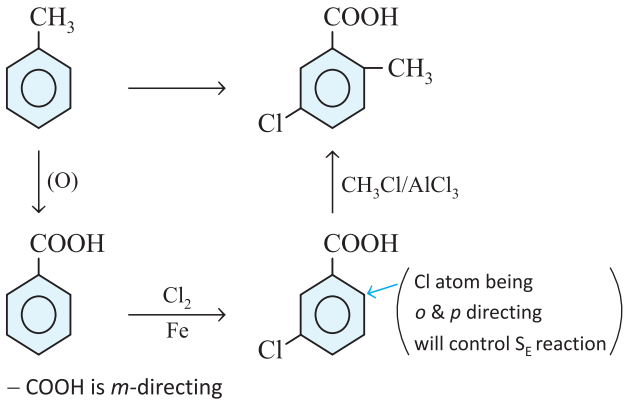
(iii)



(iv)



(v)



– COOH is *m*-directing

IN-CHAPTER EXERCISE

Choose the correct alternative. Only one choice is correct. Questions marked with '*' may have More than one correct options.

1. CH_3Br can be prepared by :

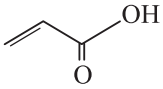
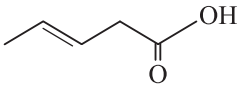
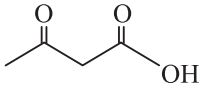
(A) $CH_3COOAg + Br_2 \xrightarrow{\Delta}$ **(B)** $CH_3COOH \xrightarrow{P/Br_2}$ Soda lime, $\Delta \rightarrow$

(C) Both of (A) and (B) **(D)** None of these

***2.** Acetyl chloride can react with :

(A) Water **(B)** Sodium acetate **(C)** 2-methylpropene **(D)** Phenol

3. Which of the following acids will undergo decarboxylation on heating ?

I.  II.  III. 

(A) I, II **(B)** II, III **(C)** I, III **(D)** I, II, III

4. An organic compound A on heating with ethanol gives compounds B and C, of which compound C is again a derivative of the compound B. The compound A is :

(A) CH_3COOH **(B)** $(CH_3CO)_2O$ **(C)** $CH_3COOC_2H_5$ **(D)** CH_3CH_2OH

5. $CH_3 - CH_2 - COOH \xrightarrow[\Delta]{HN_3 + \text{conc. } H_2SO_4} A$

$\xrightarrow[\Delta]{Br_2/P} B$

A and B are :

(A) $CH_3CH_2NH_2$; $CH_3CH(Br)COOH$ **(B)** $CH_3CH_2CONH_2$; CH_3CH_2COBr

(C) $CH_3CH_2NH_2$; CH_3CH_2COBr **(D)** $CH_3CH_2CH_2NH_2$; $CH_3CH_2CH_2Br$

6. $CH_3 - \overset{O}{\overset{\|}{C}} - Cl + Nu^- \longrightarrow CH_3 - \overset{O}{\overset{\|}{C}} - Nu + Cl^-$

Reactivity order of different nucleophiles (NH_2^-, CH_3COO^-, OH^-) is in order :

(A) $NH_2^- < CH_3COO^- < OH^-$ **(B)** $CH_3COO^- < OH^- < NH_2^-$

(C) $NH_2^- < OH^- < CH_3COO^-$ **(D)** $CH_3COO^- < NH_2^- < OH^-$

7. Consider : $CH_3 - \overset{O}{\overset{x\ \|}{C}} - O - CH_3$ and $CH_3 - \overset{O}{\overset{y\ \|}{C}} - O - \overset{O}{\overset{\|}{C}} - CH_3$. If bond length '$x$' in ester and '$y$' in anhydride are compared, then :

(A) $x = y$ **(B)** $x > y$ **(C)** $x < y$ **(D)** None is true

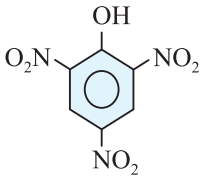
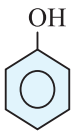
8. $CH_3CH_2ONa \xrightarrow[\text{Pressure}]{\text{(i) CO, } \Delta} \xrightarrow[\text{(ii) } H^+]{} A$ $\qquad CH_2 = CH_2 + CO + H_2O \xrightarrow[400^\circ C]{H_3PO_4} B.$

A and B are :

(A) CH_3CH_2COOH in both cases **(B)** CH_3CH_2CHO in both cases

(C) CH_3CH_2COOH, CH_3CHO **(D)** CH_3CHO, CH_3COOH

*9. Which of the following compounds will liberate CO_2 from $NaHCO_3$?

(A) $C_6H_5SO_3H$ (B) $C_6H_5CO_2H$ (C)  (D) 

10. Benzoic acid is esterified with methyl alcohol labelled with ^{18}O in the presence of dry HCl gas. After the reaction, labelled oxygen will appear in :

(A) $C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{18}{O}CH_3$ (B) $C_6H_5-\overset{\overset{^{18}O}{\|}}{C}-OCH_3$

(C) $\overset{18}{H_2O}$ (D) All of these

11. t-Butyl acetate is hydrolyzed in the presence of an acid catalyst in water labelled with ^{18}O. After the hydrolysis, the labelled oxygen will be present :

(A) acetic acid (B) t-butyl alcohol (C) the unchanged ester (D) water (entirely)

12. $(CH_3)_2C=CHCH_2CHO$ on vigorous oxidation by a permanganate solution gives :

(A) $(CH_3)_2CO$ and $OHCCH_2CHO$ (B) $(CH_3)_2\underset{OH}{C}-\underset{OH}{C}HCH_2CHO$

(C) $(CH_3)_2CO$ and $OHCCH_2COOH$ (D) $(CH_3)_2CO$ and $CH_2(COOH)_2$

13. The hydrolysis of an ester (A) gives an acid (B) and an alcohol (C). The acid (B) reduces Tollen's solution. Oxidation of the alcohol (C) gives the acid (B). The ester (A) is :

(A) methyl formate (B) ethyl formate (C) methyl acetate (D) ethyl acetate

14. In the reaction $CH_3COOH + X \xrightarrow{H_2SO_4} Y + CO_2 + N_2$ (X) and (Y) are, respectively :

(A) NH_3 and CH_3CONH_2 (B) NH_3 and CH_3NH_2

(C) HN_3 and CH_3CONH_2 (D) HN_3 and CH_3NH_2

15. The conversion of acetophenone into benzoic acid can be achieved by reaction with :

(A) sodium hydoxide followed by acidification

(B) iodine and sodium hydroxide, followed by acidification

(C) hydroxylamine followed by reaction with H_2SO_4

(D) m-chloroperoxobenzoic acid

16. Consider the following sequence of reactions.

$$BaCO_3 + H_2SO_4 \longrightarrow X(gas)\,; \qquad CH_2=CHBr \xrightarrow[2.\ X\\ 3.\ H_3O^+]{1.\ Mg,\ THF,\ heat} Y$$

The product (Y) is :

(A) $CH_2=CHCHO$ (B) $CH_2=CHCOOH$ (C) $CH_2CH=CHCOBr$ (D) $HCOOCH=CH_2$

17. Consider the following sequence of reactions.

$$CH_3CH=CHCHO \xrightarrow[2.\ HCl,\ ZnCl_2]{1.\ NaBH_4} A \xrightarrow[2.\ H_3O^+]{1.\ KCN} B$$

The end product (B) is :

(A) $CH_3CH_2CH_2CH_2COOH$ (B) $CH_3CH(Cl)CH_2CH_2COOH$

(C) $CH_3CH=CHCH_2COOH$ (D) $CH_3CH=CHCH_2CH_2NH_2$

18. Consider the following sequence of reactions.

$$\underset{(C_4H_8O_3)}{A} \xrightarrow{CrO_3} B \xrightarrow{warm} CH_3\overset{\overset{O}{\|}}{C}CH_3 + CO_2$$

The compound (A) is :

(A) $HOCH_2CH_2CH_2COOH$ **(B)** $CH_3CH(OH)CH_2COOH$

(C) $CH_3CH_2CH(OH)COOH$ **(D)** $(CH_3)_2C(OH)COOH$

19. The leaving group ability of the following groups in a nucleophilic acyl substitution by a given nucleophile decreases in the order :

(A) $-NH_2 > -Cl > -OCOR > -OR$ **(B)** $-Cl > -OCOR > -OR > -NH_2$

(C) $-OCOR > -OR > -Cl > -NH_2$ **(D)** $-OR > Cl > -NH_2 > -OCOR$

20. Consider the following sequence of reactions.

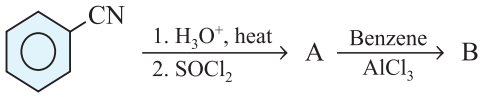
$$C_6H_5CH_2OH \xrightarrow[2.\ KCN]{1.\ PBr_3} A \xrightarrow[NaOH,\ H_2O]{H_2O_2} B \xrightarrow[P_4O_{10}]{\Delta} C$$

The end product (C) is :

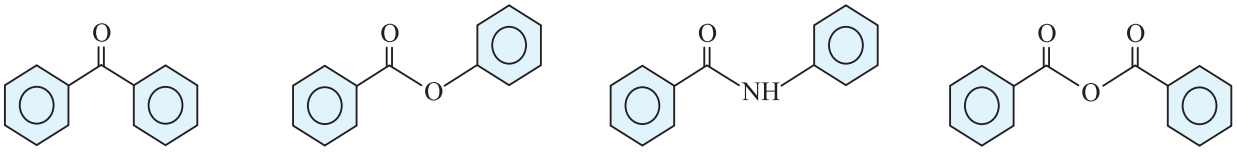
(A) $C_6H_5CH_2COOH$ **(B)** $C_6H_5CH_2CN$

(C) $C_6H_5CH_2CONH_2$ **(D)** $C_6H_5CH_2CHO$

21. Consider the following reaction sequence.

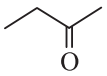
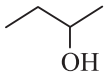
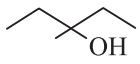
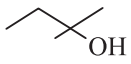


The structure of the product (B) is :

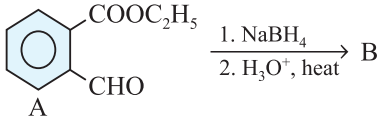


(A) **(B)** **(C)** **(D)**

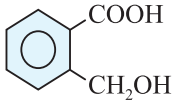
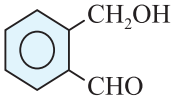
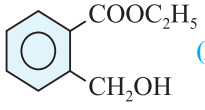
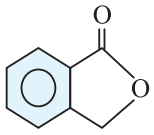
22. Ethyl propionate is allowed to react with an excess of methylmagnesium iodide in dry ether and subsequently treated with dilute H_2SO_4 in the cold. Which of the following products is expected ?

(A)  **(B)**  **(C)**  **(D)** 

23. The following reactions were carried out with compound (A) to give a compound (B).



The structure of the product (B) is :

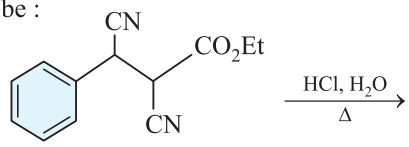
(A)  **(B)**  **(C)**  **(D)** 

24. An ester (A) undergoes self-condensation in the presence of C_2H_5ONa to give a β-keto ester (B) and ethanol. (B) on being heated with aqueous H_2SO_4 gives 3-pentanone. The ester (A) is :

(A) $CH_3COOC_2H_5$ **(B)** $CH_3CH_2COOC_2H_5$

(C) $(CH_3)_2CHCOOC_2H_5$ **(D)** $CH_3CH_2CH_2COOCH_3$

25. The major product of the reaction given will be :



(A) Monocarboxylic acid

(B) Tricarboxylic acid

(C) Vicinal dicarboxylic acid

(D) Gem - dicarboxylic acid

26. Consider the following sequence of reactions.

$$PCl_5 + SO_2 \longrightarrow A + B$$

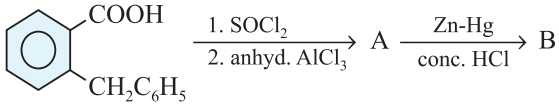
$$CH_3COOH + A \longrightarrow C + SO_2 + HCl$$

$$2C + (CH_3)_2Cd \longrightarrow 2D + CdCl_2$$

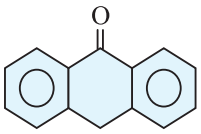
The end product (D) is :

(A) CH_3COCl **(B)** CH_3COOCH_3 **(C)** CH_3COCH_3 **(D)** $(CH_3)_2CHCOCl$

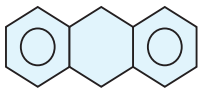
27. Consider the following sequence of reactions.



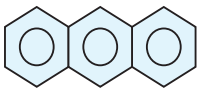
The end product (B) is :



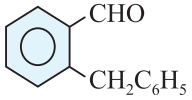
(A)



(B)

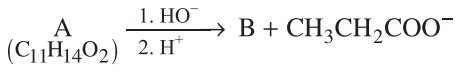


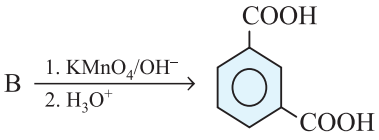
(C)



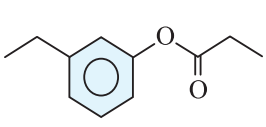
(D)

28. Consider the following sequence of reactions.

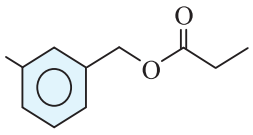




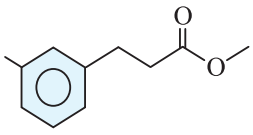
The products (A) is :



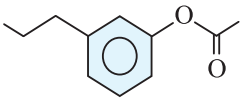
(A)



(B)



(C)

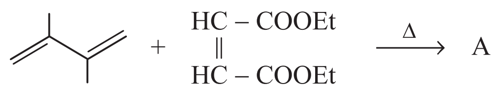


(D)

Illustration - 4 *Identify A, B, C, . . in the given reaction sequence.*

$$B \xrightarrow[\text{2. Heat in CaO}]{\text{1. NaOH}} C \xrightarrow[\text{2. }OH^-/\text{Heat}]{\text{1. }O_3/Zn\text{–}H_2O} D$$

SOLUTION :



This is an illustration of Diel-Alder reaction.

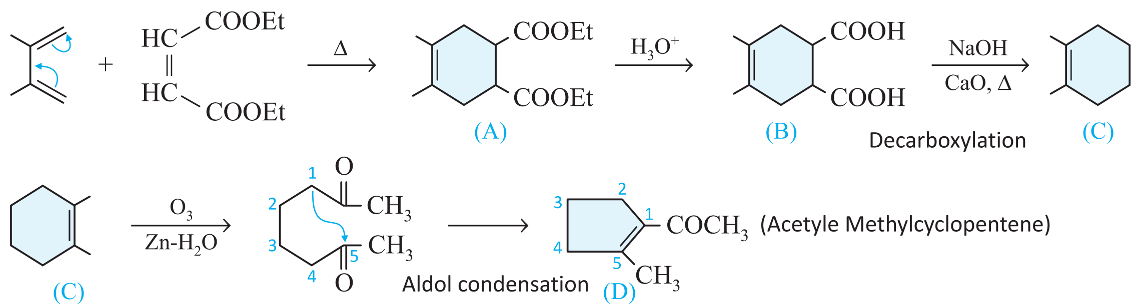


Illustration - 5 *An organic compound (A) with C_2H_5OH gives compounds (B) and (C). On hydrolysis, (C) under acidic conditions gives (B) and (D). Oxidation of (D) with $KMnO_4$ also gives (B). (B) on heating with $Ca(OH)_2$ gives E (C_3H_6O). E does not give Tollen's test or reduce Fehling solution but forms 2, 4 DNP derivative. Identify A, B, C, D and E.*

SOLUTION :

$$A + C_2H_5OH \longrightarrow (B) + (C)$$

$$(C) \xrightarrow{H_3O^+} (B) + (D) \xrightarrow[KMnO_4]{(O)} B$$

$$B \xrightarrow[\Delta]{Ca(OH)_2} E\ (C_3H_6O)$$

- Tollen's reagent → No reaction
- Fehling Solution → No reaction
- 2, 4 DNP hydrazine → Reacts

⇒ E is Ketone

E is $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ (C_3H_6O)

Calcium salt of B gives E on heating, hence B is CH_3COOH. Accordingly D will be CH_3CH_2OH. Clearly (C) is an ester.

$$C \text{ is } CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow{H_3O^+} CH_3-\overset{\overset{O}{\|}}{C}-OH + C_2H_5OH$$

$$A \xrightarrow{C_2H_5OH} \underset{(B)}{CH_3COOH} + \underset{(C)}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5}$$

Hence A is anhydride.

A is :

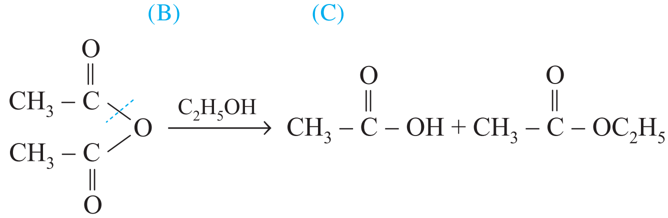
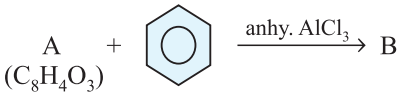


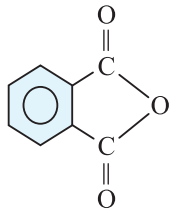
Illustration - 6 *An organic compound (A) $C_8H_4O_3$ (in dry benzene) in the presence of anhydrous $AlCl_3$ gives a compound (B). The compound (B) on treatment with PCl_5, following by reaction with H_2-Pd/$BaSO_4$ gives compound (C). The compound (C) on reaction with NH_2NH_2 gives a cyclic compound (D), $C_{14}H_{10}N_2$. Identify A, B, C, D. Also explain formation of D from C.*

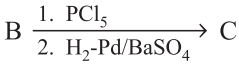
SOLUTION :

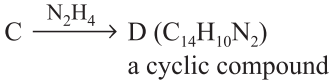


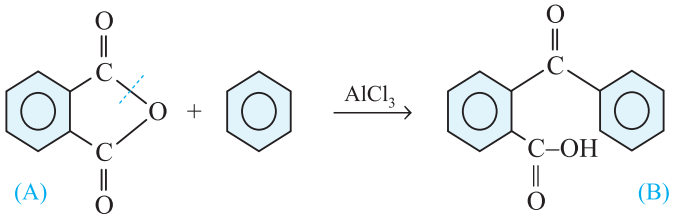
The above reaction is certainly Friedal Craft acylation. The compound (A) can be anhydride (as it contains three oxygen atoms). Also observe that the formula of A suggest a benzene ring.

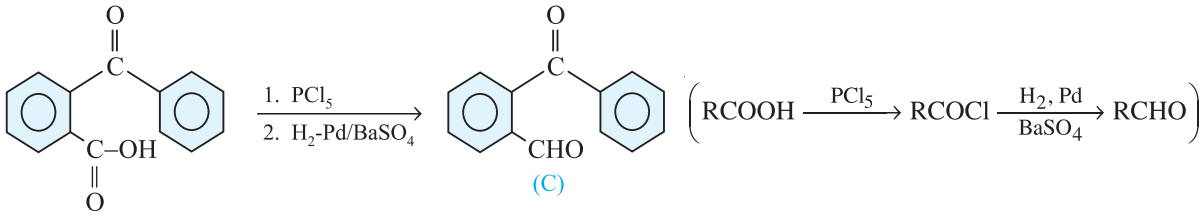
A will certainly be :











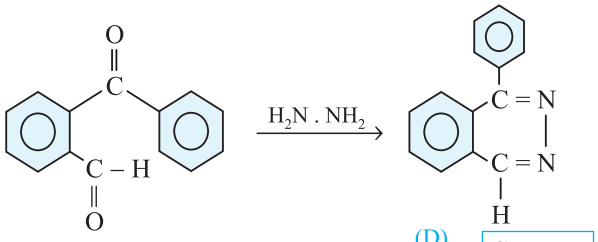
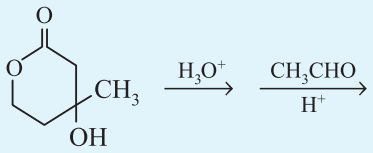


Illustration - 7 *Identify the product(s) formed in each of the following reactions and explain their formation.*



SOLUTION :

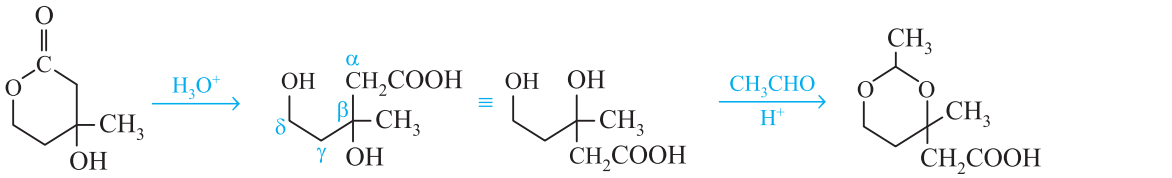
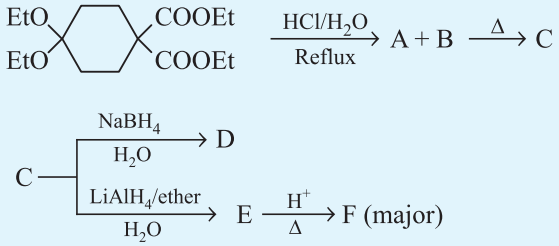


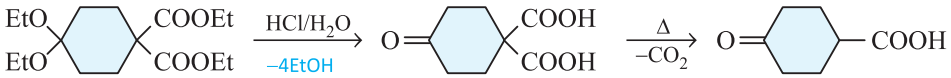
Illustration - 8 *Identify the compounds A, B, C, D, E and F, is the following reaction sequence.*

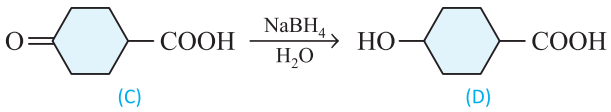


SOLUTION :

Observe that gem diether (acetal) will be hydrolysed to give carbonyl group.

Malonic acid derivative will undergo decarboxylation to give mono-carboxylic acid on heating.





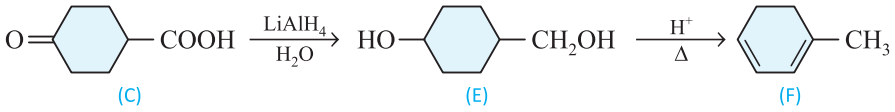
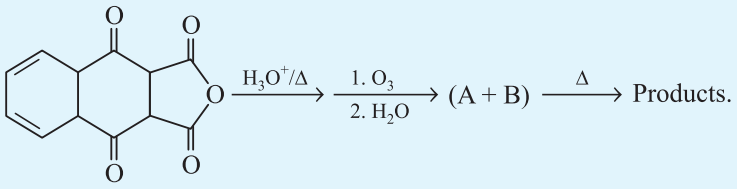


Illustration - 9 *Identify all the possible products in the following reaction sequence.*



SOLUTION :

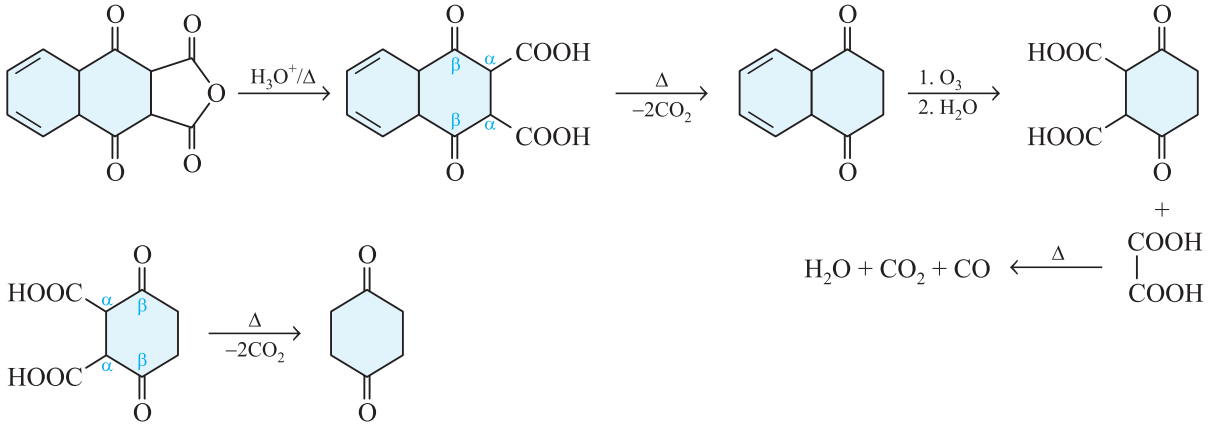
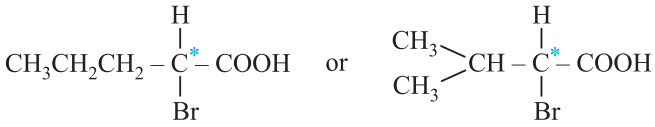


Illustration - 10 *An organic compound (A), $C_5H_{10}O_2$ reacts with Br_2 is presence of phosphorus to give (B). The compound (B) contains an assymetric carbon atom and yields (C) on debromination. The compound (C) does not show geometric isomerism and on decarboxylation with sodalime gives an alkene (D) which on reductive ozonolysis gives compounds (E) and (F). The compounds (E) and (F) on heating in alkali gives a compound (G). Identify the compounds (A) to (G).*

SOLUTION :

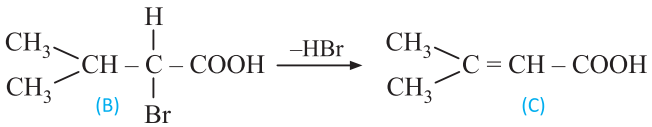
$$A(C_5H_{10}O_2) \xrightarrow[P]{Br_2} \underset{\text{having a symetric carbon atom}}{(B)} \xrightarrow{-HBr} \underset{\text{no geometric isomerism}}{(C)} \xrightarrow{-CO_2} \underset{(D)}{\text{Alkene}} \xrightarrow[Zn]{O_3} E + F \,.\, (E + F \xrightarrow[\Delta]{OH^-} G)$$

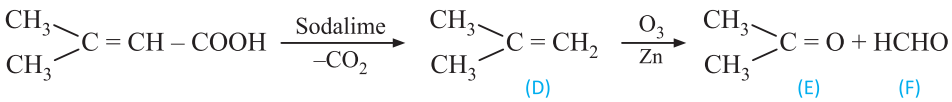
(A) has to be an acid (with α-H) undergoing HVZ reaction to give (B), an optically active compound. So B can have two possible structures :



Since debromination gives an alkene showing no geometric isomers, it means (B) will be the branched one.

The structure of (A) will be clearly : $(CH_3)_2CHCH_2COOH$





Visualise cross-aldol condensation between acetone and formaldehyde.

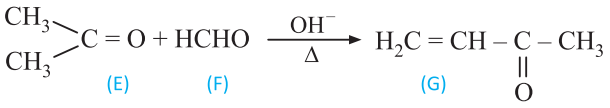
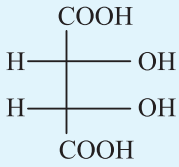
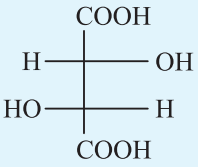


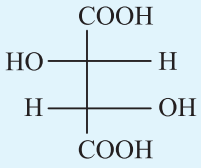
Illustration - 11 *P and Q are isomeric dicarboxylic acid $C_4H_4O_4$. Both decolorize Br_2/H_2O. On heating, P forms a cyclic anhydride. Upon treatment with dilute alkaline $KMnO_4$. P as well as Q could produce one or more than one from compounds S, T and U given:*



[S]



[T]



[U]

Choose the correct option for I and II :

I. *Compounds formed from P and Q are, respectively* :

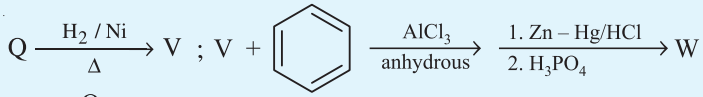
(A) *Optically active S and optically active pair (T, U)*

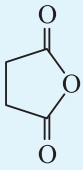
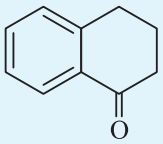
(B) *Optically inactive S and optically inactive pair (T, U)*

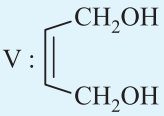
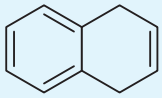
(C) *Optically active pair (T, U) and optically active S*

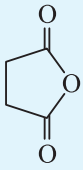
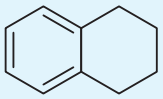
(D) *Optically inactive pair (T, U) and optically inactive S*

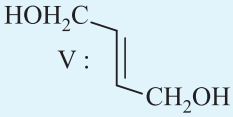
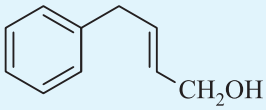
II. *In the following reaction sequences V and W are, respectively* :



(A) V :  and W : 

(B) V :  and W : 

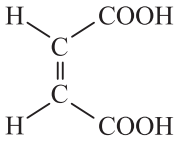
(C) V :  and W : 

(D)  and W : 

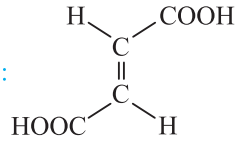
SOLUTION :

I.(B) P and Q are certainly unsaturated dicarboxylic acids ($C_4H_4O_4$) : Maleic and Fumaric acids

P must be maleic acid (*cis* form) as it forms anhydride on heating, hence Q is obviously fumaric acid (*trans* form).

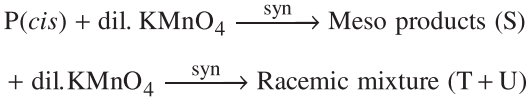
P : 

Maleic acid

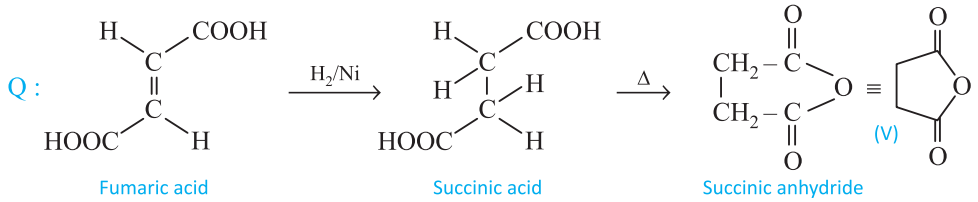
Q : 

Fumaric acid

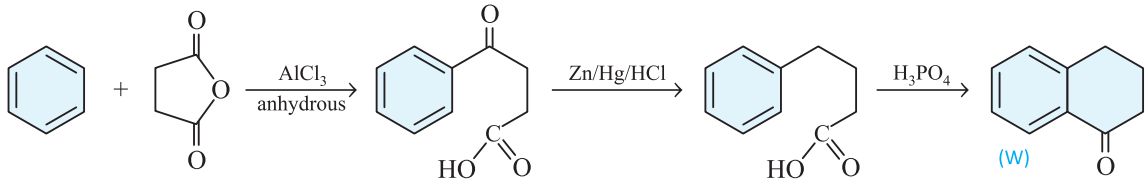
Visualise *syn hydroxylation* (addition) by dilute alkaline $KMnO_4$ in *cis* and *trans* alkenes.



II.(A)

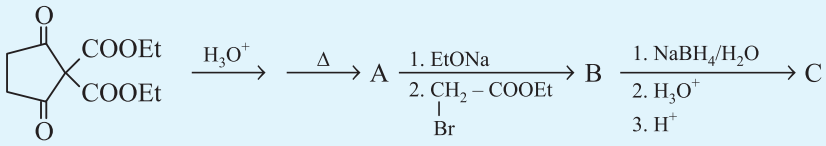


Fumaric acid | Succinic acid | Succinic anhydride

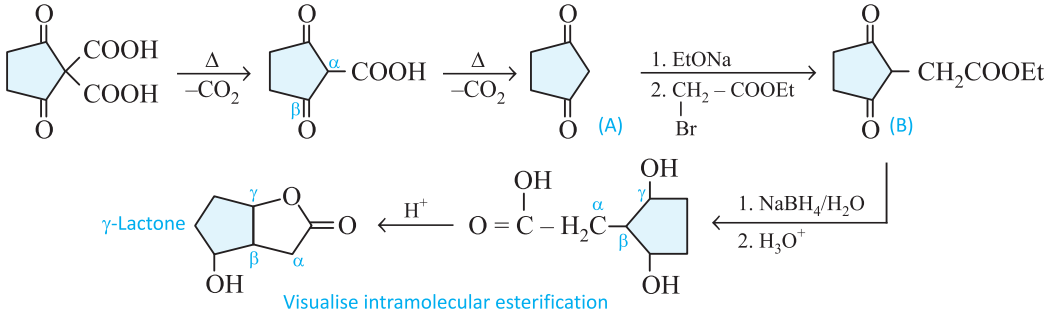


Visualise inter-molecular F.C. acylation | Visualise intra-molecular F.C. acylation

Illustration - 12 *Identify A, B, C in the following reaction sequence.*



SOLUTION :



Visualise intramolecular esterification

ANSWERS TO IN-CHAPTER EXERCISES

1. C	**2.** ABD	**3.** B	**4.** B	**5.** A	**6.** B	**7.** B	**8.** A	**9.** ABC	**10.** A
11. B	**12.** D	**13.** A	**14.** D	**15.** B	**16.** B	**17.** C	**18.** B	**19.** B	**20.** B
21. A	**22.** D	**23.** D	**24.** B	**25.** C	**26.** C	**27.** B	**28.** B		