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# **Topic 1 Carboxylic Acids**

#### **Objective Questions I** (Only one correct option)

 Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride? (2019 Main, 10 Jan I)



**2.** In the reaction,

$$CH_{3}COOH \xrightarrow{\text{LiAlH}_{4}} A \xrightarrow{\text{PCl}_{5}} B \xrightarrow{\text{Alc. KOH}} C$$
  
The product *C* is (2014 Main)

- (a) acetaldehyde (b) acetylene
- (c) ethylene (d) acetyl chloride
- 3. The compound that does not liberate CO<sub>2</sub>, on treatment with aqueous sodium bicarbonate solution, is (2013 Adv.)
  (a) benzoic acid
  - (b) benzenesulphonic acid
  - (c) salicylic acid
  - (d) carbolic acid (Phenol)
- 4. An organic compound *A* upon reacting with NH<sub>3</sub> gives *B*. On heating, *B* gives *C*. *C* in the presence of KOH reacts with Br<sub>2</sub> to give CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>. *A* is (2013 Main)
  (a) CH<sub>3</sub>COOH
  (b) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH
  (c) CH<sub>2</sub> CH<sub>2</sub>COOH
  - (c)  $CH_3$ —CH— COOH
    - CH<sub>3</sub>
  - (d) CH<sub>3</sub>CH<sub>2</sub>COOH

 The compound that undergoes decarboxylation most readily under mild condition is (2012)



- 6. The carboxyl functional group (—COOH) is present in
  (a) picric acid (2012)
  - (b) barbituric acid
  - (c) ascorbic acid
  - (d) aspirin
  - (d) aspirin
- 7. In the following reaction sequence, the correct structures of *E*, *F* and *G* are

$$\begin{array}{ccc} O & O \\ & & \\ Ph & & \\ & & \\ & & \\ & & \\ \end{array} \xrightarrow{\text{Heat}} [E] \xrightarrow{\text{I}_2} [F] + [G] \end{array}$$

(\* implies <sup>13</sup>C labelled carbon)

(2008, 3M)

(a) 
$$E = \frac{O}{Ph} + CH_3 F = \frac{O}{Ph} + OONa G = CHI_3$$

(b) 
$$E = \Pr^*_{CH_3} F = \Pr^*_{ONa} G = CHI_3$$

(c) 
$$E = \frac{O}{Ph} + \frac{F}{CH_3} = \frac{O}{Ph} + \frac{O}{ONa} = CHI_3$$

(d) 
$$E = Ph$$
  $CH_3$   $F = Ph$   $OH_3$   $G = CH_3I$ 

- 8. When benzene sulphonic acid and *p*-nitrophenol are treated with NaHCO<sub>3</sub>, the gases released respectively, are (2006, 3M) (a) SO<sub>2</sub>, NO<sub>2</sub> (b) SO<sub>2</sub>, NO (c) SO<sub>2</sub>, CO<sub>2</sub> (d) CO<sub>2</sub>, CO<sub>2</sub>
- 9. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be (2003, S, 1M)

   (a) optically active mixture
   (b) pure enantiomer
   (c) *meso* compound
   (d) racemic mixture
- 10. Benzoyl chloride is prepared from benzoic acid by
  (a) Cl<sub>2</sub>, hv
  (b) SO<sub>2</sub>Cl<sub>2</sub>
  (2000, S, 1M)
  (c) SOCl<sub>2</sub>
  (d) Cl<sub>2</sub>, H<sub>2</sub>O
- 11. When propionic acid is treated with aqueous sodium bicarbonate, CO<sub>2</sub> is liberated. The C of CO<sub>2</sub> comes from
  (a) methyl group
  (1999, 2M)
  (b) carboxylic acid group
  - (c) methylene group
  - (d) bicarbonate group

#### **Matching Type Questions**

**13.** The desired product *X* can be prepared by reacting the major product of the reactions in List-I with one or more appropriate reagents in List-II.

(given, order of migratory aptitude : aryl > alkyl > hydrogen)



**Topic 2** Acid Derivatives

#### **Objective Questions I**

(Only one correct option)

**1.** The major product of the following reaction is





(a)  $P \rightarrow 1$ ;  $Q \rightarrow 2$ , 3;  $R \rightarrow 1$ , 4;  $S \rightarrow 2$ , 4 (b)  $P \rightarrow 1$ , 5;  $Q \rightarrow 3$ ,4;  $R \rightarrow 4$ , 5;  $S \rightarrow 3$ (c)  $P \rightarrow 1$ , 5;  $Q \rightarrow 3$ ,4;  $R \rightarrow 5$ ;  $S \rightarrow 2$ ,4 (d)  $P \rightarrow 1$ , 5;  $Q \rightarrow 2$ , 3;  $R \rightarrow 1$ ,5;  $S \rightarrow 2$ ,3

#### **Subjective Questions**

- **14.** How will you bring about the following conversion? "Ethanal to 2-hydroxy-3-butenoic acid." (1990, 2M)
  - **2.** The major product of the following reaction is



 The increasing order of the reactivity of the following with LiAlH<sub>4</sub> is (2019 Main, 12 Jan II)



- (b) (A) < (B) < (C) < (D)
- (c) (B) < (A) < (D) < (C)
- (d) (B) < (A) < (C) < (D)
- $(\mathbf{u}) (\mathbf{b}) (\mathbf{n}) (\mathbf{c}) (\mathbf{b})$
- **4.** The major product obtained in the following reaction is (2019 Main, 10 Jan II)



 The decreasing order of ease of alkaline hydrolysis for the following esters is (2019 Main, 10 Jan I)



**6.** The compounds *A* and *B* in the following reaction are, respectively

$$\xrightarrow{\text{HCHO}+\text{HCI}} A \xrightarrow{\text{AgCN}} B$$
(2019 Main, 9 Jan I)

- (a) A = Benzyl alcohol, B = Benzyl isocyanide
- (b) A = Benzyl alcohol, B = Benzyl cyanide
- (c) A = Benzyl chloride, B = Benzyl isocyanide
- (d) A = Benzyl chloride, B = Benzyl cyanide
- 7. The major product of following reaction is

$$\begin{array}{ccc} R \longrightarrow C \equiv N & \xrightarrow{(i) \operatorname{AIH}(i \cdot \operatorname{Bu})_2} & & \\ & & & \\ & & & \\ & & & \\ (ii) \operatorname{H}_2O & & \\ (ii) \operatorname{H}_2O & & \\ & & \\ (2019 \text{ Main, 9 Jan I}) \\ & & \\ (a) R CHO & & \\ & & \\ (b) R CONH_2 & \\ & & \\ (c) R COOH & & \\ & & \\ (d) R CH_2NH_2 & \\ \end{array}$$

 Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from Column t I with an appropriate structure from Column II and select the correct answer using the code given below the lists. (2014 Adv.)

$$R \xrightarrow{O}_{(\text{Peroxyester})} R' \xrightarrow{R'} R' + R'O' \xrightarrow{Q}_{-\text{CO}_2} \uparrow R' + R'O' \xrightarrow{Q}_{-\text{CO}_2} R' + R'O' \xrightarrow{Q}_{-\text{CO}_2} R' + X' \xrightarrow{R'}_{-\text{Co}_2} R' + X'' \xrightarrow{R'}_{-\text{Co}_2} R' + X'' \xrightarrow{R'}_{-\text{Co}_2} R' + X'' \xrightarrow{R'}_{-\text{Co}_2} R' + R'O' \xrightarrow{R'}_{-\text{CO}_2} R' + R'O'$$



Codes				
	Р	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

9. A compound with molecular mass 180 is acylated with CH<sub>3</sub>COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is (2013 Main)
 (a) 2 (b) 5

(a) 
$$2$$
 (b)  $3$  (c)  $4$  (d)  $6$ 

10. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product? (2006, 5M)





- **11.** Benzamide on treatment with POCl3 gives<br/>(a) aniline<br/>(c) chlorobenzene(2004, S, 1M)<br/>(b) benzonitrile<br/>(d) benzyl amine
- **12.** Ethyl ester  $\frac{CH_3MgBr}{(excess)}P$ , the product 'P' will be (2003, S, 1M)



The product of acid hydrolysis of P and Q can be distinguished by (2003, S, 1M)



- **14.** Hydrogenation of benzoyl chloride in the presence of Pd on BaSO<sub>4</sub> gives (1992, 1M)

   (a) benzyl alcohol
   (b) benzaldehyde

   (c) benzoic acid
   (d) phenol
- 15. Acetamide is treated separately with the following reagents. Which one of these would give methyl amine? (1983, 1M)
  (a) PCl<sub>5</sub> (b) NaOH + Br<sub>2</sub>
  (c) Sodalime (d) Hot conc. H<sub>2</sub>SO<sub>4</sub>

#### **Objective Questions I**

(One or more than one correct options)

**16.** With reference to the scheme given, which of the given statement(s) about *T*, *U*, *V* and *W* is/are correct? (2012)



- (a) T is soluble in hot aqueous NaOH
- (b) U is optically active
- (c) Molecular formula of W is  $C_{10}H_{18}O_4$
- (d) V gives effervescence on treatment with aqueous NaHCO<sub>3</sub>

17. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme. (2012)



- (a)  $C_6H_5OH$  and  $C_6H_5COOH$
- (b) C<sub>6</sub>H<sub>5</sub>COOH and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH
- (c)  $C_6H_5CH_2OH$  and  $C_6H_5OH$
- (d)  $C_6H_5CH_2OH$  and  $C_6H_5CH_2COOH$
- 18. Reaction of RCONH<sub>2</sub> with a mixture of Br<sub>2</sub> and KOH gives R—NH<sub>2</sub> as the main product. The intermediates involved in this reaction are (1992, 1M)
  (a) RCONHBr
  - (b) *R*NHBr

$$c) R - N = C = 0$$

(d) RCONBr<sub>2</sub>

#### **Assertion and Reason**

Read the following questions and answer as per the direction given below :

- (a) Statement I is true; Statement II is true; Statement II is a correct explanation of Statement I.
- (b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
- (c) Statement I is true; Statement II is false.
- (d) Statement I is false; Statement II is true.
- **19.** Statement I *p*-hydroxybenzoic acid has a lower boiling point than *o*-hydroxybenzoic acid.

Statement II o-hydroxybenzoic acid has intramolecular<br/>hydrogen bonding.(2007, 3M)

**20.** Statement I Acetic acid does not undergo haloform reaction. Statement II Acetic acid has no alpha hydrogen. (1998, 2M)

#### **Passage Based Questions**

#### Passage 1

The reaction of compound *P* with  $CH_3MgBr$  (excess) in  $(C_2H_5)_2O$  followed by addition of  $H_2O$  gives *Q*. The compound *Q* on treatment with  $H_2SO_4$  at 0° C gives *R*. The reaction of *R* with  $CH_3COCl$  in the presence of anhydrous AlCl<sub>3</sub> in  $CH_2Cl_2$  followed by treatment with  $H_2O$  produces compound *S*. [Et in compound *P* is ethyl group]



#### **21.** The product *S* is

#### (2017 Adv.)



**22.** The reactions, *Q* to *R* and *R* to *S*, are

- (a) Aromatic sulfonation and Friedel-Crafts acylation
- (b) Friedel-Crafts alkylation and Friedel-Crafts acylation
- (c) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation
- (d) Dehydration and Friedel-Crafts acylation

#### Passage 2

P and Q are isomers of dicarboxylic acid C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>. Both decolourize Br<sub>2</sub>/H<sub>2</sub>O. On heating, P forms the cyclic anhydride. Upon treatment with dilute alkaline KMnO<sub>4</sub>. P as well as Q could





- 23. 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
- **24.** In the following reaction sequences V and W are respectively







 $RCONH_2$  is converted into  $RNH_2$  by means of Hofmann's bromamide degradation.



In this reaction, *R*CONHBr is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann's degradation reaction is an intramolecular reaction. ( $2006, 3 \times 4M = 12M$ )

- **25.** How can the conversion of (i) to (ii) be brought about?
  - (a) KBr(b) KBr + CH<sub>3</sub>ONa
  - (c) KBr + KOH
  - (d)  $Br_2 + KOH$
- **26.** Which is the rate determining step in Hofmann's bromamide degradation?
  - (a) Formation of (i)
  - (b) Formation of (ii)
  - (c) Formation of (iii)
  - (d) Formation of (iv)
- **27.** What are the constituent amines formed when the mixture of (1) and (2) undergoes Hofmann's bromamide degradation?





#### Fill in the Blank

**28.** Formic acid when heated with conc.  $H_2SO_4$  produces (1983, 1M)

#### **True/False**

**29.** The boiling point of propanoic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molecular weight.

(1991, 1M)

**30.** Hydrolysis of an ester in the presence of a dilute acid is known as saponification. (1983, 1M)

#### **Integer Type Question**

**31.** The total number of carboxylic acid groups in the product *P* (2013 Adv.) is



#### **Subjective Questions**

- **33.** Compound A of molecular formula  $C_0H_7O_2Cl$  exists in keto form and predominantly in enolic form B. On oxidation with  $KMnO_4$ , A gives m-chlorobenzoic acid. Identify A and B. (2003 Main, 2M)
- **34.**  $(\pm)$  2-phenylpropanoic acid on treatment with (+) 2-butanol gives (A) and (B). Deduce their structures and also establish stereochemical relation between them. (2003)
- **35.** Identify X and Y in the following synthetic scheme and write their structures. Explain the formation of labelled

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formaldehyde  $(H_2CO)$  as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C<sup>\*</sup> carbon in the entire scheme.

$$Ba \overset{\circ}{CO}_{3} + H_{2}SO_{4} \longrightarrow X \quad (\overset{\circ}{C} = C^{14} \text{ gas })$$

$$CH_{2} = CH \longrightarrow Br \xrightarrow{(i) Mg/ether}_{(ii) X} Y \xrightarrow{\text{LiAlH}_{4}} Z$$

$$(ii) H_{3}O^{+} \quad (2001 \text{ Main, 5M})$$

**36.** Write the structures of the products *A* and *B*.

$$CH_{3} \longrightarrow C \longrightarrow O C_{2}H_{5} \xrightarrow{H_{3}O^{+}} A + B$$
 (2000 Main, 3M)

**37.** Explain briefly the formation of the products giving the structures of the intermediates



**38.** Write the structures of the products :

$$CH_3CH_2NH_2 \xrightarrow{(CH_3CO)_2O, heat}$$
(1998)

- **39.** An ester A ( $C_4H_8O_2$ ), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol B as the sole organic product. Alcohol B, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of A and B. Show the reactions involved. (1998)
- **40.** Complete the following, giving the structures of the principal organic products

(i) 
$$(COOH)_2 + (CH_2OH)_2 + EtONa \longrightarrow A$$
  
(ii)  $(COOH)_2 + (CH_2OH)_2 \xrightarrow{\text{conc. } H_2SO_4} \longrightarrow B$   
(iii)  $H_2CCOCOC_6H_5 + NaOH \xrightarrow{H_3O^+} C$ 

iii) 
$$H_3CCOCOC_6H_5 + NaOH \xrightarrow{H_3O} C$$

- **41.** A hydrocarbon A of the formula  $C_8H_{10}$ , on ozonolysis gives compound  $B(C_4H_6O_2)$  only. The compound B can also be obtained from the alkyl bromide  $C(C_3H_5Br)$  upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify A, B and C and also give equations for the reactions. (1996, 3M)
- 42. Complete the following sequence of reactions with appropriate structures

$$CH_{3} \longrightarrow CH_{2} \longrightarrow COOH \xrightarrow{\text{Red-P}} A$$

$$A \xrightarrow{\text{(i) Alc. KOH (excess)}} B$$

$$(1995, 2M)$$

(1997, 2M)

**43.** Which of the following carboxylic acids undergoes decarboxylation easily ? Explain briefly.

(i) 
$$C_6H_5COCH_2COOH$$
  
(ii)  $C_6H_5COCOOH$   
(iii)  $C_6H_5CH(OH)COOH$   
(iv)  $C_6H_5CH(NH_2)$  COOH (1995, 2M)

44. Predict the major product in the following reaction :

$$C_6H_5$$
— $CH_2COCH_3 \xrightarrow{(i) CH_3MgBr (excess)}$  (1994, 1M)

**45.** In the following reactions, identify the compounds *A*, *B*, *C* and *D*.

(i)  $PCl_5 + SO_2 \longrightarrow A + B$ (ii)  $A + CH_3COOH \longrightarrow C + SO_2 + HCl$ (iii)  $2C + (CH_3)_2 Cd \longrightarrow 2D + CdCl_2$  (1994, 1M × 4 = 4M)

**46.** Complete the following sequence of the reactions with appropriate structures

(i) 
$$\longrightarrow$$
 SO<sub>3</sub>H  $\xrightarrow{\text{Fuming}}_{\text{H}_2\text{SO}_4} \cdots \cdots \xrightarrow{1.\text{NaOH}(\text{Fuse})}_{2.\text{H}^+} \cdots \cdots$   
(ii)  $\swarrow$  CONH<sub>2</sub>  $\xrightarrow{\text{P}_2\text{O}_5} \cdots \cdots \xrightarrow{\text{H}^+, \text{H}_2\text{O}}_{\Delta} \cdots \cdots$   
(1992, 1M)

**47.** In the following identify the compounds/reaction conditions represented by the alphabets *A*, *B*, and *C* :

$$C_{6}H_{5}COOH \xrightarrow{PCl_{5}} A \xrightarrow{NH_{3}} B \xrightarrow{P_{2}O_{5}} C_{6}H_{5}CN \xrightarrow{H_{2}/Ni} C$$
(1991, 2M)

- **48.** Arrange the following as stated: "Increasing order of acidic strength." ClCH<sub>2</sub>COOH, CH<sub>3</sub>CH<sub>2</sub>COOH, ClCH<sub>2</sub>CH<sub>2</sub>COOH, (CH<sub>3</sub>)<sub>2</sub>CHCOOH, CH<sub>3</sub>COOH (1991, 1M)
- 49. How will you bring about the following conversion?"Ethanoic acid to a mixture of methanoic acid and diphenyl ketone." (1990, 2M)
- **50.** Give reasons for : "Carbon-oxygen bond lengths in formic acid are 1.23 Å

and 1.36 Å and both the carbon-oxygen bonds in sodium formate have the same value, i.e. 1.27Å." (1988, 2M)

- 51. Write balanced equations for the following reaction : "Acetamide is reacted with bromine in the presence of potassium hydroxide." (1987, 1M)
- **52.** A liquid *X*, having a molecular formula  $C_6H_{12}O_2$  is hydrolysed with water in the presence of an acid to give a carboxylic acid *Y* and an alcohol *Z*. Oxidation of *Z* with chromic acid gives *Y*. What are the structures of *X*, *Y* and *Z*? (1986, 3M)
- **53.** An ester A (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>) on treatment with excess of methyl magnesium chloride followed by acidification, gives an alcohol *B* as the sole organic product. Alcohol *B*, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce structures of *A* and *B*. Show the reactions involved. (1998)
- 54. Complete the following with appropriate structures :

$$(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOH + ?$$
 (1986.1M)

55. Arrange the following in order of their increasing ease of hydrolysis: (1986, 1M)

CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>, CH<sub>3</sub>COCl, (CH<sub>3</sub>CO)<sub>2</sub>O, CH<sub>3</sub>CONH<sub>2</sub>

- **56.** Give reasons in one or two sentences for the following : "Formic acid is a stronger acid than acetic acid." (1985, 1M)
- **57.** Write down the reactions involved in the preparation of the following using the reagents indicated against in parenthesis. "Propionic anhydride from propionaldehyde"

**58.** Give reasons for the following in one or two sentences.

[AgNO<sub>3</sub>, NH<sub>4</sub>OH,

"Acetic acid can be halogenated in the presence of P and  $Cl_2$ , but formic acid cannot be halogenated in the same way." Why? (1983, 1M)

- **59.** State with balanced equation, what happens when, "Acetic anhydride reacts with phenol in presence of a base." (1982, 1M)
- 60. Write the structural formula of main organic product formed when ethyl acetate is treated with double the molar quantity of methyl magnesium bromide and the reaction mixture is poured into water. (1981, 1/2 M)
- Write the chemical equation to show what happens when, "Ethyl acetate is treated with sodium ethoxide in ethanol and the reaction mixture is acidified". (1981, 2 M)

# Answers

Topic 1			
<b>1.</b> (b)	<b>2.</b> (c)	<b>3.</b> (d)	<b>4.</b> (d)
<b>5.</b> (b)	<b>6.</b> (d)	<b>7.</b> (c)	<b>8.</b> (d)
<b>9.</b> (d)	<b>10.</b> (c)	<b>11.</b> (d)	<b>12.</b> (a)
<b>13.</b> (d)			
Topic 2			
<b>1.</b> (d)	<b>2.</b> (d)	<b>3.</b> (a)	<b>4.</b> (b)

5.	(b)	<b>6.</b> (c)	<b>7.</b> (a)	<b>8.</b> (a)
9.	(b)	<b>10.</b> (c)	<b>11.</b> (b)	<b>12.</b> (a)
13.	(c)	14. (b)	15. (b)	<b>16.</b> (a,c,d)
17.	(b,d)	<b>18.</b> (a,c)	<b>19.</b> (d)	<b>20.</b> (c)
21.	(a)	<b>22.</b> (c)	<b>23.</b> (b)	<b>24.</b> (a)
25.	(d)	<b>26.</b> (d)	<b>27.</b> (b)	
28.	$H_2O$ and $CO$	gas	<b>29.</b> False	<b>30.</b> False
31.	(2)			

# **Hints & Solutions**

# **Topic 1 Carboxylic Acids**

1. Heating of  $(CH_2)_4 < COOH COOH$  (adipic acid) with a dehydrating agent,

decarboxylates (—CO $_2$ ) to give a ketone (cyclopentanone), not an anhydride.

$$\begin{array}{c} \hline COOH & \underline{A} \\ \hline COOH & \underline{-CO_2} \\ -H_2O \end{array} \end{array} \xrightarrow{} 0$$

#### Codes

 $P \rightarrow 1$ ,  $Q \rightarrow 3$ ,  $R \rightarrow 4$ ,  $S \rightarrow 2$ Thus, (a) is the correct choice.

- **2.** This problem is based on successive reduction, chlorination and elimination reaction. To solve such problem, use the function of the given reagents.
  - (i) LiAlH<sub>4</sub> causes reduction
  - (ii) PCl<sub>5</sub> causes chlorination
  - (iii) Alc. KOH causes elimination reaction

$$\begin{array}{c} \text{CH}_{3}\text{COOH} \xrightarrow{\text{LIAIH}_{4}} & \text{CH}_{3}\text{CH}_{2}\text{OH} \\ \xrightarrow{(A)} & \xrightarrow{(A)} & \text{CH}_{3}\text{CH}_{2}\text{CI} \xrightarrow{\text{Alc.KOH}} & \text{CH}_{2} = \text{CH}_{2} \\ \xrightarrow{(B)} & \xrightarrow{(B)} & \text{CH}_{2}\text{CI} \xrightarrow{(C)} & \text{Ethylene} \end{array}$$

**3.** PLAN NaHCO<sub>3</sub>  $\implies$  Na<sup>+</sup> + HCO<sub>3</sub><sup>-</sup>

 $HCO_3^-$  is decomposed by acid releasing  $CO_2$ 

$$HCO_3^- + H^+ \longrightarrow H_2O + CO$$

0

If acid is stronger than  $HCO_3^-$  then  $CO_2$  is released. Phenol is less acidic and thus does not liberate  $CO_2^-$  with NaHCO<sub>3</sub>.

4. 
$$CH_{3}CH_{2} \xrightarrow{O}_{(A)} C \longrightarrow OH \xrightarrow{NH_{3}} OH_{3}CH_{2}COONH_{4} \xrightarrow{\Delta} CH_{3} \xrightarrow{O}_{(C)} CH_{2} \xrightarrow{O}_{(C)} OH_{2} \xrightarrow{H_{2}} OH_{2} \xrightarrow{O}_{(C)} OH_{2} \xrightarrow{H_{2}} OH_{2} OH_{2} \xrightarrow{H_{2}} OH_{2} \xrightarrow{H_{2}} OH_{2} OH_{2} \xrightarrow{H_{2}} OH_{2} OH_{2} \xrightarrow{H_{2}} OH_{2} OH_{2} OH_{2} \xrightarrow{H_{2}} OH_{2} OH_{2}$$

 It is a β-keto acid which undergo decarboxylation in very mild condtion, i.e. on simple heating. This occur through a six member cyclic transition state as



NOTE

- Ordinary carboxylic acid require soda-lime catalyst for decarboxylation.
- Final step of decarboxylation in the above shown mechanism involve tautomerism, therefore, for decarboxylation of  $\beta$ -keto acid by above mechanism, the acid must contain an  $\alpha$ -H].
- 6. Structures of the various compounds are



Reaction occur at planar  $sp^2$  carbon giving racemic mixture of product.

- **10.**  $C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5-COCl$
- **11.**  $CH_3$ — $CH_2$ — $COOH + NaHCO_3$   $\longrightarrow$   $CH_3CH_2COONa$ +  $H_3O + CO_2$

12. Ethanol is the weakest acid among these, hence it is most basic.



The correct match is 1 i.e., I<sub>2</sub>, NaOH and 5 i.e., NaOBr The reactions proceed as



The correct match is 2 i.e.  $[Ag(NH_3)_2]OH$  and 3 i.e., Fehling's solution.

The reactions proceed as



The correct match is 1, 5 again.

The reaction proceed as





#### **Topic 2** Acid Derivatives

**1.** Given reaction involves acidic hydrolysis of esters followed by the intramolecular cyclisation. The chemical equation is as follows:



**2.** The major product of the given reaction is (d). This reaction proceed *via* Friedel-Craft acylation. Here, — Cl group present on chlorobenzene is *ortho* and *para*-directing. It can be easily understood by resonating structures of chlorobenzene.



The given reaction proceed as follows :



- **3.** All the given compounds are acid derivatives, thus contain carbonyl group in them. LiAlH<sub>4</sub> reduces these compounds through nucleophilic substitution *via* addition elimination  $(S_{N_4} E)$  reaction. The rate of reaction depends upon the following factors :
  - (i) Size of alkyl group.
  - (ii) Steric hinderance around the >C ==O group.
  - (iii) (+) ve charge on the C-atom of >C==O group.

The alkyl groups are more or less same in the given compounds. Thus, the reactivity order of given compounds depends upon 2nd and 3rd factor written above. The cumulative effect of these two factors results to leaving group ability (LGA) of the substituents in the following order :

$$\begin{array}{c} Cl^{-} \\ Good \ leaving \\ group \end{array} > O^{-} \underbrace{ C}_{C} CH_{3} > O^{-} CH_{3} > NH_{2} \\ Poor \ leaving \\ group \\ group \end{array}$$

This leaving group ability (weak conjugate base) corresponds directly to the reactivity order. Hence, the correct reactivity order is:



Note The -I effect of — Cl and + *m* effects of

$$\overset{O}{\parallel} \\ \overset{H}{\longrightarrow} \overset{O}{\longrightarrow} \overset{O}{\longrightarrow} \overset{C}{\longrightarrow} \overset{C}{\longrightarrow} \overset{C}{\longrightarrow} \overset{C}{\longrightarrow} \overset{O}{\longrightarrow} \overset$$

group leaving ability.

**4.** In presence of strong base, acidic H can easily be removed that result in formation of anion. The resulting anion undergoes intramolecular nucleophilic addition which on hydrolysis followed by heating gives the required product.



5. Alkaline hydrolysis of an ester (carboxylic acid derivative) follows acyl  $S_N 2$  mechanism.

Rate of  $S_N^2$  mechanism depends on the polarity of >C=0 group of -COOR group. Electron withdrawing group (-R > -I) increases the rate of  $S_N^2$  reaction whereas electron donating group (+R > +I) decreases the rate of  $S_N^2$  reaction. Here, the nature of functional groups attached *para* to the benzene ring are:

$$-\!\!\!\underset{(-R)}{\operatorname{NO}_2} \! > \!\!-\!\!\underset{(-I)}{\operatorname{Cl}} \! > \!\!-\!\!\underset{(+R)}{\operatorname{OCH}_3}$$

So, the order of hydrolysis will be,

$$\underset{(-R)}{\coprod} > \underset{(-I)}{\coprod} > I > \underset{(+R)}{\coprod}$$

**6.** The mechanism of the given reaction is as follows:



Thus, both benzyl cyanide and benzyl isocyanide are the products of reaction but benzyl isocyanide being the major product gives the correct option as (c).

7. Key Idea DIBAL-H is diisobutyl aluminium hydride,  $[(CH_3)_2CHCH_2]_2AlH$ . It is a selective reducing agent. It reduces carboxylic acids, carboxylic acid derivatives and nitriles into aldehydes. It is an electrophilic reducing agent.

The mechanism of the reaction is as follows:



8. PLAN his problem can be solved by usin the stability of radical obtained after fra mentation of peroxyester.

Allylic radical are more stable than alkyl radical, so when there is a possibility of formation of allyl radical, it will undergo fragmentation through formation of allyl radical. i.e. fragmentation produces stable radical. On the basis of stability of radical, fragmentation can be done as

Column 1	I	Column II	Explanation
Р.	1.	C <sub>6</sub> H <sub>5</sub> H <sub>2</sub> C O CH <sub>3</sub>	$C_6H_5$ — $CH_2$ + $CO_2$ + $CH_3O$ •
Q.	3.	$C_6H_5H_2C$ $O$ $CH_3$ $CH_3$ $CH_2C_6H_5$	$C_6H_5 - CH_2 + CO_2 + Ph - CH_2 - CH_3 \longrightarrow Ph - CH_2 + CH_3 - CO - CH_3$
R.	4.	$C_6H_5$ $O$ $O$ $CH_3$	$C_{6}H_{5}-CO_{2}+CH_{3}-C-CH_{3}\xrightarrow{-CO_{2}}Ph^{\bullet}+CH_{3}-CO-Ph+CH_{3}^{\bullet}+CO_{2}$
S.	2.		$ \begin{array}{c} C_{6}H_{5} \longrightarrow C_{6}H_{5}^{\bullet} + CO_{2} \end{array} $

9. 
$$R$$
—NH<sub>2</sub>+CH<sub>3</sub>—C—Cl  $\xrightarrow[(-HCl)]{}$   $R$ —NH—C—CH<sub>3</sub>

Since, each  $-COCH_3$  group displace one H atom in the O || reaction of one mole of  $CH_3$  -C -Cl with one  $-NH_2$  group,

the molecular mass increases with 42 unit.

Since the mass increases by (390 - 180) = 210, hence the number of  $--NH_2$  group is  $\frac{210}{42} = 5$ .



11. 
$$C_6H_5 \longrightarrow C \longrightarrow NH_2 \xrightarrow{POCl_3} C_6H_5 \longrightarrow CN$$
  
12.  $CH_3 \longrightarrow C \longrightarrow C_2H_5 \xrightarrow{CH_3MgBr}_{excess} CH_3 \longrightarrow CH_3$ 

$$\xrightarrow{H_2O} CH_3 \xrightarrow{CH_3} OH_{CH_3}$$

**13.** 
$$P \xrightarrow{H^+}_{H_2O} CH_3 \xrightarrow{OH}_{C} CH_2 \xrightarrow{O}_{H_3} CH_3 \xrightarrow{H_3}_{Vellow}$$

$$Q \xrightarrow{H^{+}} CH_{3} \longrightarrow CH = CH \longrightarrow OH \Longrightarrow CH_{3}CH_{2}OH$$

$$\xrightarrow{\text{Fehling solution}} Cu_{2}O\downarrow$$
Red
$$(CHO)$$



**15.**  $CH_3 \longrightarrow CH_3 NH_2 + Br_2 + NaOH \longrightarrow CH_3 NH_2$  "Hofmann's bromamide reaction".

**16.** (a) T undergoes an ester hydrolysis in hot aqueous alkali as

$$\begin{array}{c} O \\ H_{3}C & \xrightarrow{\text{NaOH}(aq)} \\ H_{3}C & \xrightarrow{\text{NaOH}(aq)} \\ T & \xrightarrow{\text{NaOH}(aq)} \\ HO & \xrightarrow{\text{CH}_{3}[]} \\ HO &$$

- (b) LiAlH<sub>4</sub> reduces ester to alcohol as
   "U" No chiral carbon optically inactive.
- (c) U on treatment with excess of acetic anhydride forms a diester as
- (d) U on treatment with CrO<sub>3</sub>|H<sup>+</sup> undergo oxidation to diacid which gives effervescence with NaHCO<sub>3</sub>.

$$U + CrO_3 \xrightarrow{H^+} H_3C \xrightarrow{V} OH \xrightarrow{NaHCO_3} CO_2 \uparrow$$

- **17.** For separation by differential extraction one of the component must form salt with the given base so that the salt will be extracted in aqueous layer leaving other component in organic layer.
  - (a) Both phenol and benzoic acid forms salt with NaOH, hence this mixture can't be separated.
  - (b) Benzoic acid forms salt with NaOH while benzyl alcohol does not, hence the mixture can be separated using NaOH. Also benzoic acid forms salt with NaHCO<sub>3</sub> but benzyl alcohol does not, hence NaHCO<sub>3</sub> can be used for separation.
  - (c) Neither benzyl alcohol nor phenol forms salt with NaHCO<sub>3</sub>, mixture cannot be separated using NaHCO<sub>3</sub>.
  - (d) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>COOH forms salt with NaOH, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH does not, hence mixture can be separated using NaOH. C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>COOH forms salt with NaHCO<sub>3</sub>. C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH does not, hence mixture can be separated using NaHCO<sub>3</sub>.

**18.** 
$$R - C - NH_2 + OH^- + Br_2 \longrightarrow R - C - \frac{\|}{(A)} NHBr$$
  
 $Q = 0 - \frac{\|}{(A)} NHBr$   
 $R - C - NHBr + OH^- \longrightarrow R - C - \frac{\|}{(B)} - Br$   
 $\longrightarrow R - N = C = O + Br^-$ 

**19.** *p*-hydroxy benzoic acid has higher boiling point than *o*-hydroxy benzoic acid because former prefers intermolecular H-bonding while the latter prefer intramolecular H-bonding.



0

**20.** Compounds with  $CH_3$ —C— or  $CH_3$ —CH(OH)-group gives haloform reaction but this reaction is given only by aldehydes, ketones and alcohols, so acetic acid does not give haloform reaction. However acetic acid has three  $\alpha$ -H, therefore, statement I is true but statement II is false.



**22.** (a)

- **22.** (c)
- **23.** PLAN lkenes decolourise  $Br_2$  water

-isomer  $\xrightarrow{\text{dil}\cdot\text{KMnO}_4}$  isomers by addition -isomer  $\xrightarrow{\text{dil}\cdot\text{KMnO}_4} d(+)$  and l(-) isomers by

Formation of anhydride from dicarboxylic acid indicates -isomer.

P and Q are isomers of dicarboxylic acids.

$$P, Q \xrightarrow{\text{Br}_2 \text{ water}} \text{decolourised}$$

P and Q have (C=C) bond

 $P \xrightarrow{\Delta}$  anhydride

Thus, *P* is *cis*-isomer.





T and U (in 1 : 1 molar ratio) form optically inactive (racemic mixture) due to external compensation.

**24.** PLAN Ni /  $H_2$  reduces (C = C) bond.

Benzene undergoes Friedel-Crafts reaction Zn-Hg/HCl reduces carbonyl group (Clemmensen reduction)



an intermediate (ii)

26. Rearrangement of (iii) to (iv) is the rate determining step :



**27.** The rate determining step of Hofmann's bromamide reaction is unimolecular rearrangement of bromamide anion (iii) and no cross-products are formed when mixture of amides are taken.



- **28.** HCOOH +  $H_2SO_4 \xrightarrow{\Delta} H_2O + CO \uparrow$  conc.
- **29.** Propanoic acid has higher boiling point than *n*-butanol because of more exhaustive H-bonding in former case.
- **30.** Saponification is hydrolysis of ester in presence of dilute base rather in presence of dilute acid.
- **31. PLAN** eactant is cyclic anhydride and chan es to dicarboxylic acid on hydrolysis.

Also there is decarboxylation on heating if there is keto group w.r.t — COOH group. Ozonolysis cleaves (C=C) bond and  $H_2O_2$  oxidises — CHO to — COOH group.



(D)

**33.** Compound *A* of molecular formula  $C_9H_7O_2Cl$  exist in keto and predominantly in enolic form *B*. Hence, *A* must be a carbonyl compound which contain  $\alpha$ -H. Enolic forms of *B* predominates because of presence of intramolecular H-bonding.

![](_page_13_Figure_9.jpeg)

**34.** The two stereoisomers of 2-phenyl propanoic acid in the racemic mixture are :

![](_page_13_Figure_11.jpeg)

![](_page_14_Figure_1.jpeg)

**41.** *B* is 
$$C_3H_5COOH$$
 and *A* is  $C_3H_5-C \equiv C-C_3H_5$ 

4

Also *A* on ozonolysis gives *B* indicates that there is no olefinic bond in  $C_3H_5$ -unit of *A* and it is cyclopropyl group.

$$\Rightarrow A = \bigcirc -C = C - \bigcirc C$$

$$B = \bigcirc -COOH$$
and  $C = \bigcirc -Br$ 

**42.** 
$$CH_3CH_2COOH \xrightarrow{\text{red-P}} CH_3 \xrightarrow{\text{CH}} CH \xrightarrow{\text{COOH}} A \xrightarrow{\text{Br}} (HVZ \text{ reaction})$$

$$\xrightarrow{\text{(i) alc.KOH}} \text{CH}_2 = \xrightarrow{\text{CH}} \text{COOH}$$

#### **43.** A $\beta$ -keto acid undergo very fast decarboxylation

![](_page_14_Figure_8.jpeg)

![](_page_14_Figure_9.jpeg)

48. Electron withdrawing inductive effect increases acid strength while electron donating inductive effect decreases acid strength.
 + *I*-effect

$$H_{3}C$$
 — CH — COOH < CH<sub>3</sub>CH<sub>2</sub>COOH < CH<sub>3</sub>COOH  
CH<sub>3</sub> + *I*-effect + *I*-effect  
+ *I*-effect CH<sub>2</sub>—CH<sub>2</sub>COOH < CH<sub>2</sub>—COOH  
CI  $-I$ -effect (greater distance) Q

**50.** Both formic acid and sodium formate exhibit the phenomenon of resonance as :

$$H = C = O^{-} H \leftrightarrow H = C = O^{-} H$$
$$H = C = O^{-} H$$
$$H = C = O^{-} H$$
$$H = C = O^{-} H$$

In formic acid, the extent of delocalisation is less compared to sodium formate because of charge separation in the former case. Due to this reason, the bond length between carbon and  $sp^3$  oxygen in formic acid is slightly greater than the same between carbon and  $sp^2$  oxygen. In formate ion, there is no separation of charge and both the resonance structures are equivalent giving equal bond length of both carbon oxygen bonds.

- **51.**  $CH_3CONH_2 + Br_2 \xrightarrow{NaOH} CH_3NH_2 + Na_2CO_3$ Hoffman bromamide reaction
- **52.** *X* is an ester and both its acid and alcohol fragments have same number of carbons. Hence, X is :

**54.** 
$$(CH_3CO)_2O \xrightarrow{C_2H_5OH} CH_3COOH + CH_3 - C - OC_2H_5$$

**55.** Among acid derivatives, the reactivity towards nucleophilic acyl substitution is in the order of :

Amide < Ester < Anhydride < Acid chloride

Hydrolysis is an example of nucleophilic acyl substitution, hence the reactivity towards hydrolysis is :

 $\rm CH_3CONH_2 < \rm CH_3COOC_2H_5 < (\rm CH_3CO)_2O < \rm CH_3COCl$ 

**56.** 
$$\begin{array}{c} O \\ \parallel \\ -H_3 - C - OH \\ +I \text{ -effect} \\ \text{decreases acid-strength} \end{array}$$
  $\begin{array}{c} O \\ \parallel \\ H - C - OH \\ \text{does not affect acidity.} \end{array}$ 

57. 
$$CH_3CH_2CHO + AgNO_3 \xrightarrow{NH_4OH} CH_3CH_2COOH$$
  
 $\xrightarrow{P_2O_5} (CH_3CH_2CO)_2O$ 

**58.**  $CH_3$ —COOH +  $Cl_2 \xrightarrow{\text{Red-P}} CH_2$ —COOH (HVZ reaction) |Cl

For this reaction to occur, presence of a  $\alpha$ -H is essential requirement. Formic acid does not has any  $\alpha$ -H, fails in HVZ reaction.

![](_page_15_Figure_16.jpeg)

**61.** 
$$CH_3COOC_2H_5 \xrightarrow{C_2H_5O^-} \overline{C}H_2COOC_2H_5$$

$$\begin{array}{c} \overset{O}{\longrightarrow} & \overset{O}{\longrightarrow} \\ \overset{H_{3}}{\longrightarrow} & & \overset{H_{3}}{\longrightarrow} \\ \overset{H_{3}}{\longrightarrow} \\ \overset{H_{3}}{\longrightarrow} \\ \overset{H_{3}}{\longrightarrow} & \overset{H_{3}}{\longrightarrow} \\ \overset{H_{3}}{\longrightarrow}$$