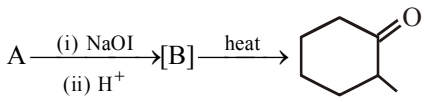
28 Chapter

CARBOXYLIC ACID & ITS DERIVATIVE

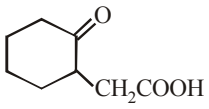
A SINGLE CORRECT CHOICE TYPE

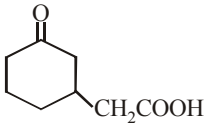
Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

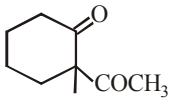
1. From the given set of reactions,

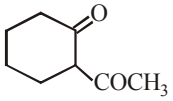


starting compound A corresponds to

(a) 

(b) 

(c) 

(d) 

2. Methanoic acid is heated with conc. H_2SO_4, to form

(a) CO (b) CO_2
(c) CH_4 (d) $(COOH)_2$

3. When ethane –1, 2-dioic acid is heated with conc. H_2SO_4, it gives

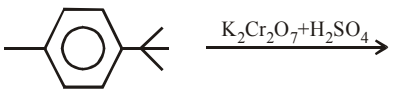
(a) CO + HCOOH (b) CO_2 + HCOOH
(c) $CO+CO_2+HCOOH$ (d) $CO+CO_2+H_2O$

4. When sodium formate is heated with soda lime, we get

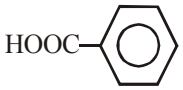
(a) CH_4 (b) H_2
(c) sod. oxalate (d) no action

5. Sodium formate is heated at 360ºC to give

(a) CO (b) CO_2
(c) sodium oxalate (d) no action

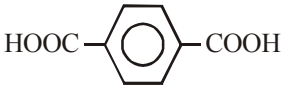
6. 

Z. Here Z is

(a) 

(b) $(CH_3)_3CCOOH$

(c) Both (a) and (b)

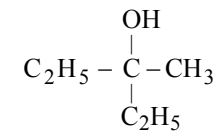
(d) 

7. Which of the following gives effervescences of CO_2 with $NaHCO_3$ solution ?

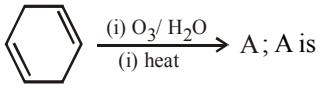
(a) HCOOH (b) 2, 4, 6-Trinitrophenol
(c) Both (d) None

8. 

(a) 

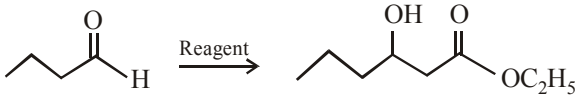
(b) 

(c) CH_3COOH (d) CH_3COCH_3

9. 

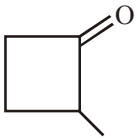
(a) $CH_2(COOH)_2$ (b) CH_3COOH
(c) HCOOH (d) HCHO

10. Which of the following reagent can be used for carrying out the reaction outlined below?

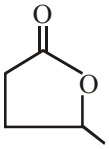


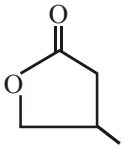
(a) $BrMgCH_2COOC_2H_5$ (b) $BrZnCH_2COOC_2H_5$
(c) $LiCH_2COOC_2H_5$ (d) Any of the three

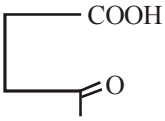
MARK YOUR RESPONSE					
	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ

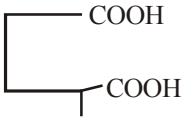
11.  $\xrightarrow{C_6H_5COOOH}$ Product.

Here the product is

(a) 

(b) 

(c) 

(d) 

12. Acetyl chloride does not react with

(a) Water

(b) Sodium acetate

(c) 2-methylpropene

(d) It reacts with all the three

13. Which of the following statement is not true ?

(a) At room temperature, formyl chloride is present in the form of CO and HCl

(b) Acetamide behaves as a weak base as well as a weak acid.

(c) $CH_3CONH_2 \xrightarrow{LiAlH_4} CH_3CH_2NH_2$

(d) None of the three

14. Which of the following reaction is possible ?

(i) $CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$

(ii) $CH_3COOCH_3 + HBr \rightarrow CH_3COBr + CH_3OH$

(iii) $CH_3CONH_2 + HBr \rightarrow CH_3COBr + NH_3$

(iv) $CH_3COOCOCH_3 + H_2O \rightarrow 2CH_3COOH$

(a) (i) and (iv) (b) (i), (iii) and (iv)

(c) (i), (ii) and (iv) (d) All the four

15. Acid amides do not undergo the usual properties of carbonyl, C = O group because

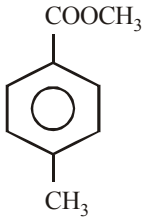
(a) it is a weak base

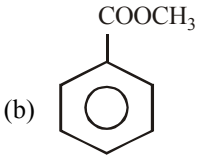
(b) it is a weak acid

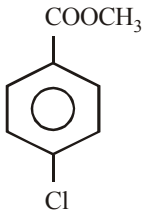
(c) it is amphoteric

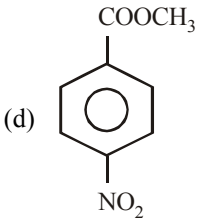
(d) its carbonyl carbon is not electron deficient

16. Which of the following will undergo alkaline hydrolysis most rapidly ?

(a) 

(b) 

(c) 

(d) 

17. H. V. Z reaction involves the use of P and Cl_2

$CH_3CH_2COOH \xrightarrow{P,\ Cl_2} CH_3CHClCOOH$

The function of phosphorus is

(a) as a catalyst.

(b) in the formation of PCl_3 which carries out halogenation at the α-carbon atom.

(c) in the formation of PCl_3 which converts –COOH into –COCl.

(d) none of the three.

18. Hydrolysis of esters in presence of an acid is a reversible reaction, what is true about ester hydrolysis in presence of a base?

(a) It is irreversible because salts of carboxylic acids are insoluble.

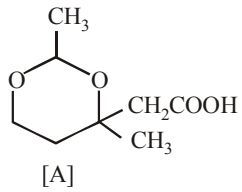
(b) It is irreversible because salts of carboxylic acids have high melting points.

(c) It is irreversible because carboxylate ion is resonance stabilized.

(d) It is reversible reaction.

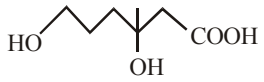
MARK YOUR RESPONSE					
	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ
	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ		

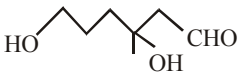
19. Compound A is formed by the interaction of

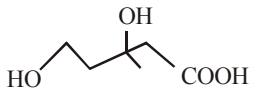


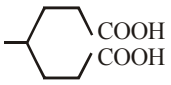
[A]

(a) CH_3COOH and 

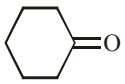
(b) CH_3CHO and 

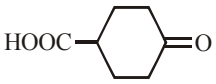
(c) CH_3COCH_2COOH and 

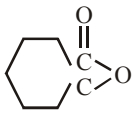
(d) CH_3CHO and 

20. What is the main product when  is heated ?

(a) 

(b) 

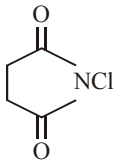
(c) 

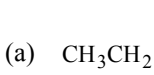
(d) 

21. The yield of ester in esterification can be increased by

$CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$

(a) removing water
(b) taking ethanol in excess
(c) taking acetic acid in excess
(d) all the above factors

22. $CH_3CH_2CH_2COOH +$  $\xrightarrow{HCl}$ Product is

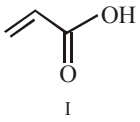
(a) 

(b) $ClCH_2CH_2CH_2COOH$

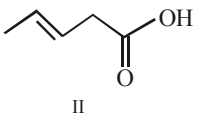
(c) 

(d) All the three

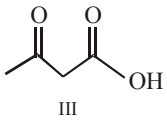
23. The correct order of decarboxylation of the three acids is



I



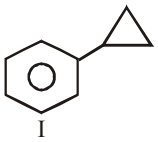
II



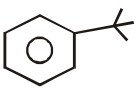
III

(a) III > II > I (b) III = II > I
(c) III > II = I (d) III = II = I

24. Which statement is true regarding oxidation of the following two compounds



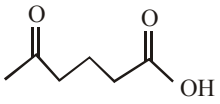
I

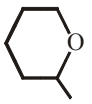


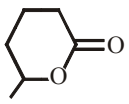
II

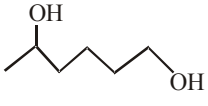
(a) Both are oxidisable to benzoic acid under similar conditions
(b) It is very difficult to oxidise either of the two
(c) Compound I is oxidisable to benzoic acid easily while compound II is oxidisable only under vigorous conditions to benzoic acid
(d) Compound I is oxidisable to benzoic acid, while II is oxidisable only under vigorous conditions to 2,2-dimethylpropanoic acid.

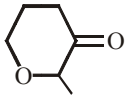
25. Predict the nature of end product in the following reaction.

 $\xrightarrow[(ii)\ H_3O^+]{(i)\ NaBH_4}$ Product

(a) 

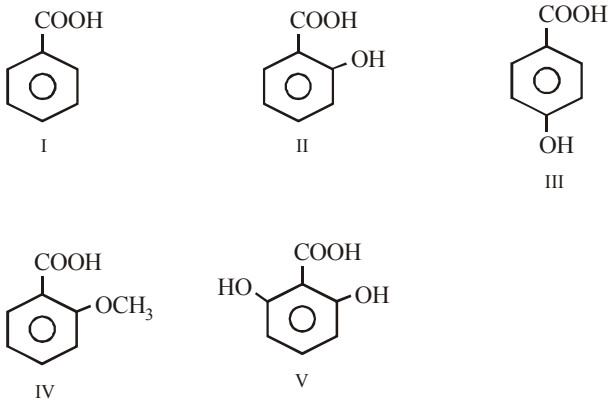
(b) 

(c) 

(d) 

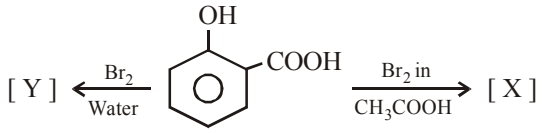
MARK YOUR RESPONSE	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ
	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ			

26. The correct order for the acidic character of the following carboxylic acids is

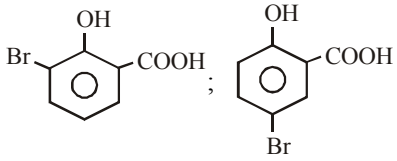


(a) IV > I > II > III > V (b) V > II > III > I > IV
(c) V > II > IV > III > I (d) V > II > IV > I > III

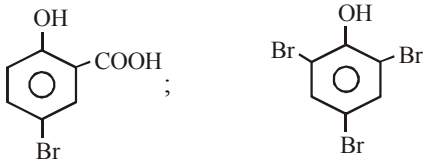
27. Salicylic acid is treated with bromine under two different conditions.



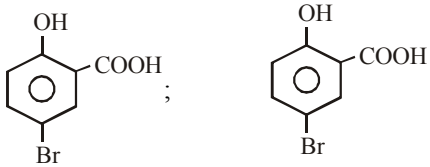
Predict the nature of [X] and [Y] in the above reactions

(a) 

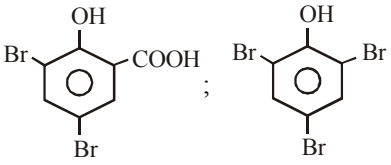
[X] [Y]

(b) 

[X] [Y]

(c) 

[X] [Y]

(d) 

[X] [Y]

28. Which of the following statement is true ?

(a) Hydrogen bonding always increases the acidic character of a species.

(b) Hydrogen bonding always decreases the acidic character of a species

(c) Hydrogen bonding may increase or decrease the acidic character of a species

(d) Hydrogen bonding plays no role in determining the acidity of a species

29. Choose the correct statement regarding acidic character of acetic acid, CH_3COOH and peroxyacetic acid, CH_3COOOH.

(a) Peroxyacetic acid is stronger acid than acetic acid since the former has one extra oxygen, an electronegative element

(b) Peroxyacetic acid is stronger than acetic acid because its conjugate base is a weaker base than acetate

(c) Peroxyacetic acid is weaker than acetic acid because its conjugate base is less stable than that of acetate ion.

(d) Both are equally strong

30. A carboxylic acid can best be converted into acid chloride by using

(a) PCl_5 (b) $SOCl_2$
(c) HCl (d) ClCOCOCl

31. The yield of acid amide in the reaction, $RCOCl + NH_3 \rightarrow RCONH_2$, is maximum when

(a) acid chloride and ammonia are treated in equimolar ratio

(b) acid chloride and ammonia are treated in 1 : 2 molar ratio

(c) acid chloride and ammonia are treated in 2 : 1 molar ratio

(d) All the three gives nearly similar result

MARK YOUR RESPONSE	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ
	31. ⓐⓑⓒⓓ				

32. Which of the following statement is not upto the mark?

(a) $R-\overset{\overset{O}{\|}}{C}-OR' \xrightarrow{OH^-} R-\overset{\overset{O}{\|}}{C}-O^- + R'OH$

(A base-catalysed reaction)

(b) $CH_3COOC_2H_5 \xrightarrow{OH^-} CH_3COOH + C_2H_5OH$

(reaction involves acyl-oxygen fission)

(c) $C_6H_5COOH + CH_3OH \xrightarrow{H^+} C_6H_5COOCH_3 + H_2O$

(reaction involves acyl-oxygen fision)

(d) $CH_3COOCH(CH_3)C_2H_5 \xrightarrow{OH^-} CH_3COO^- + HOCH(CH_3)C_2H_5$ (configuration of the reactant is retained)

33. The products in the following reaction are

$$C_6H_5COOCH_2C_6H_5 \xrightarrow{H_2-Pd/C}$$

(a) $C_6H_5CH_2OH + C_6H_5CH_2OH$

(b) $C_6H_5CH_3 + C_6H_5CH_3$

(c) $C_6H_5CH_2OH + C_6H_5CH_3$

(d) $C_6H_5COOH + C_6H_5CH_3$

34. Pyrolysis of $CH_3COO\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$ gives

(a) 1-butene and 2-butene in equimolar ratio
(b) 1-butene and 2-butene in 1 : 2 molar ratio
(c) 1-butene and 2-butene in 3 : 2 molar ratio
(d) 1-butene and 2-butene in 2 : 3 molar ratio

35. The relative stability of the four acid derivatives towards nucleophiles is

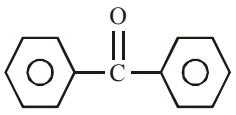
(a) Amide > Ester > Acid anhydride > Acid chloride
(b) Amide > Acid anhydride > Ester > Acid chloride
(c) Acid Chloride > Acid anhydride > Ester > Amide
(d) Acid Chloride > Ester > Acid anhydride > Amide

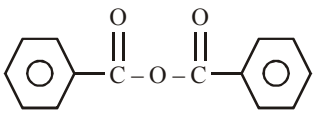
36. Which of the following statement is true about the hydrolysis of acetic anhydride ?

(i) It is more easily hydrolysed in acidic medium than in neutral
(ii) It is more easily hydrolysed in alkaline medium than in neutral
(iii) It is equally hydrolysed in all the three medium
(iv) It is more easily hydrolysed in neutral than in acidic medium
(v) It is more easily hydrolysed in neutral than in alkaline medium

(a) (i) and (ii) (b) (iii)
(c) (iv) and (v) (d) (i) and (v)

37. Which of the following compounds can undergo nucleophilic substitution easily ?


I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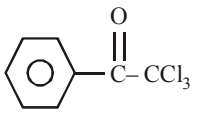
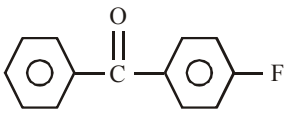
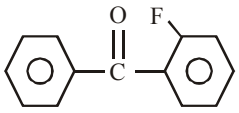
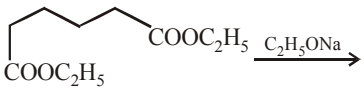
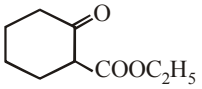
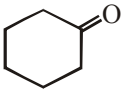
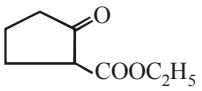
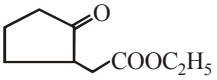

III


IV


V

(a) Only II (b) I, II, III and IV
(c) II, III and V (d) II, III and IV

38.  Z. Here Z is

(a) 
(b) 
(c) 
(d) 

39. β-Keto acids on heating easily undergo decarboxylation because

(a) it is a very storng acid
(b) it is a very weak acid
(c) its carboxylate ion is highly stable.
(d) it involves the formation of a cyclic six-membered transition state.

MARK YOUR RESPONSE					
	32. ⓐⓑⓒⓓ	33. ⓐⓑⓒⓓ	34. ⓐⓑⓒⓓ	35. ⓐⓑⓒⓓ	36. ⓐⓑⓒⓓ
	37. ⓐⓑⓒⓓ	38. ⓐⓑⓒⓓ	39. ⓐⓑⓒⓓ		

40. Which of the following intermediate is most likely to be formed during addition of HBr on crotonic acid?

$$CH_3CH=CHCOOH + HBr\ (g) \rightarrow CH_3\underset{\underset{Br}{|}}{CH} - CH_2COOH$$

(a) $CH_3CH_2-\overset{+}{C}HCOOH$

(b) $CH_3\overset{+}{C}H-CH_2COOH$

(c) $CH_3CH=CH-\underset{+}{\overset{\overset{OH}{|}}{C}}-OH$

(d) None of the three

41. Which of the following statement is true regarding esterification of a carboxylic with an alcohol ?

(i) It is carried out in presence of a strong acid which acts as a catalyst.

(ii) The strong acid makes the carbonyl carbon more electrophilic, and hence causes the alcohol, a strong nucleophile to attack on the carbonyl carbon.

(iii) The strong acid makes the carbonyl group more electrophilic which is thus attacked easily by an alcohol, a weak nucleophile.

(iv) Esterification can be done even in absence of a strong acid.

(a) (i) and (ii) (b) (i) and (iii)
(c) (i) (d) (iv)

42. The reason for greater reactivity of acetyl chloride for nucleophilic substitution than methyl chloride is due to

(i) capability of oxygen to acquire electrons

(ii) difference in the nature of carbon of the intermediate: a tetrahedral in case of acetyl chloride and a pentavalent in case of methyl chloride

(iii) difference in attack of nucleophile on the compound

(iv) better leavability of –COCl than –Cl

(a) (i) and (ii) (b) (i) and (iii)
(c) (i), (ii) and (iii) (d) (iv)

43. Esterification of acid chloride with ethanol is usually carried out in the presence of pyridine. The function of pyridine is

(a) to remove HCl formed in the reaction

(b) to react with acid chloride to form an acylpyridinium ion

(c) both (a) and (b)

(d) as a catalyst

44. The driving force for the completion of Claisen condensation between ethyl acetate and sodium ethoxide to ethyl acetoacetate is

(a) the presence of reactive methylene group in ethyl acetoacetate

(b) the phenomenon of keto enol tautomerism

(c) the presence of at least α-hydrogen atom in ester

(d) all the three factors

45. Both aldol and Claisen condensations are given by compounds having α-hydrogen atom to a C = O group. Pick up the compound which responds aldol condensation but not Claisen condensation.

$\underset{I}{CH_3CH_2COOC_2H_5}$

$\underset{II}{(CH_3)_2CHCOOC_2H_5}$ $\underset{III}{(CH_3)_3CCOOC_2H_5}$

(a) II (b) III
(c) II and III (d) None of the three

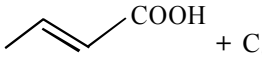
46. Which statement is true regarding reaction of an acid chloride (RCOCl) and ammonia when taken in 1 : 1 molar ratio?

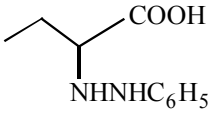
(a) Whole of acid chloride is converted into $RCONH_2$

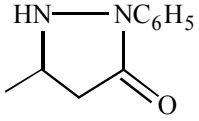
(b) One-half of acid chloride is converted into $RCONH_2$ and the other half into $RCOONH_4$

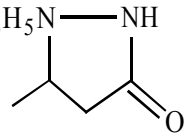
(c) One-half of acid chloride is converted into $RCONH_2$ and the remaining half remains unreacted

(d) None of the three is correct

47.  + $C_6H_5NHNH_2 \longrightarrow$ Z, Z is

(a) 

(b) 

(c) 

(d) All the three

48. Which of the following compound undergoes Claisen condensation in presence of C_2H_5ONa ?

(i) $CH_3CH_2COOC_2H_5$

(ii) $(CH_3)_2CHCOOC_2H_5$ (iii) $ClCH_2COOC_2H_5$

(a) only (i) (b) (i) and (ii)
(c) (i) and (iii) (d) all of the three

MARK YOUR RESPONSE					
	40. ⓐⓑⓒⓓ	41. ⓐⓑⓒⓓ	42. ⓐⓑⓒⓓ	43. ⓐⓑⓒⓓ	44. ⓐⓑⓒⓓ
	45. ⓐⓑⓒⓓ	46. ⓐⓑⓒⓓ	47. ⓐⓑⓒⓓ	48. ⓐⓑⓒⓓ	

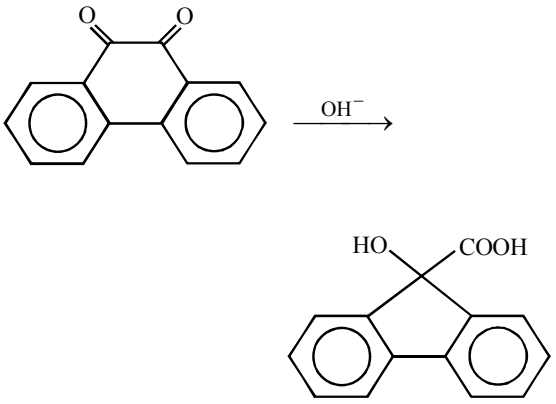
49. Which of the following can be used for introducing a ketonic group in the compound ?

(a) Claisen rearrangement (b) Claisen reaction
(c) Pinacol rerarrangement (d) All the three

50. Which reaction is used for converting a lower carboxylic acid into its next higher homologue ?

(a) Curtius reaction
(b) Baeyer – Villiger reaction
(c) Darzen glycidic ester synthesis
(d) Arndt – Eistert synthesis

51.



The above reaction is an example of

(a) Baeyer - Villiger rearrangement
(b) Benzilic acid rearrangement
(c) Cannizzaro reaction
(d) Pinacol - pinacolone rearrangement

52. Which of the following is not involved as an intermediate in the HVZ reaction?

$$CH_3CH_2COOH + Br_2 \xrightarrow{\text{red P}} CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCOOH + HBr$$

(a) $CH_3-CH=\underset{\displaystyle OH}{\underset{|}{C}}-Br$ (b) $CH_3\underset{\displaystyle Br}{\underset{|}{C}}H-COBr$

(c) Both (d) None

53. Ester + CH_3MgBr (excess) $\xrightarrow{H_3O^+}$ $C_4H_{10}O$ (Alcohol)

The alcohol formed gives white ppt. with $ZnCl_2/HCl$ immediately, the ester may be

$HCOOC_3H_7$ (I) $CH_3COOC_5H_{11}$ (II)

CH_3COOCH_3 (III) $C_2H_5COOCH_3$ (IV)

(a) II (b) II and III
(c) II and IV (d) I

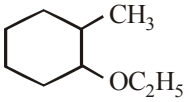
54.

$+ CH_3COOC_2H_5 \rightarrow [\ ] \xrightarrow{H_3O^+}$ A . Compound A is

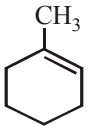
(a)

(b)

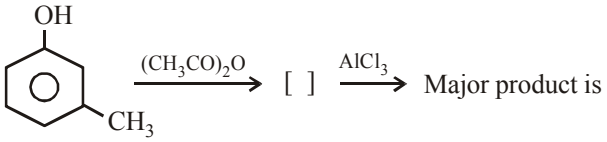
(c)



(d)

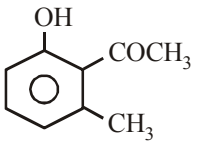


55.

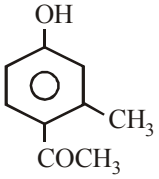


Major product is

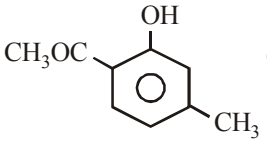
(a)



(b)



(c)



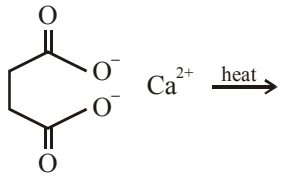
(d) All the three

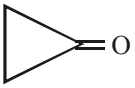
56. An organic compound A on heating with ethanol gives compounds B and C, of which compound C is again a derivative of the compound B. The compound A is

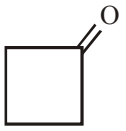
(a) CH_3COOH (b) $(CH_3CO)_2O$
(c) $CH_3COOC_2H_5$ (d) CH_3CH_2OH

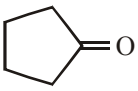
MARK YOUR RESPONSE					
	49. ⓐⓑⓒⓓ	50. ⓐⓑⓒⓓ	51. ⓐⓑⓒⓓ	52. ⓐⓑⓒⓓ	53. ⓐⓑⓒⓓ
	54. ⓐⓑⓒⓓ	55. ⓐⓑⓒⓓ	56. ⓐⓑⓒⓓ		

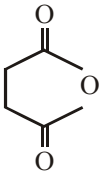
57. Identify the product in the following reaction

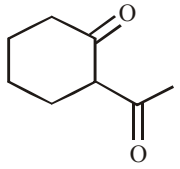


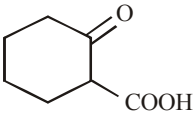
(a) 

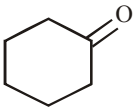
(b) 

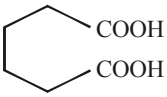
(c) 

(d) 

58.  P. The product P should be

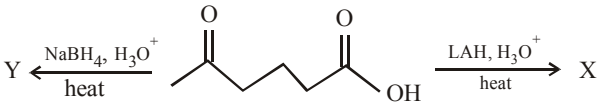
(a) 

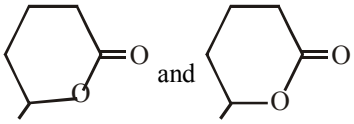
(b) 

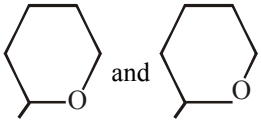
(c) 

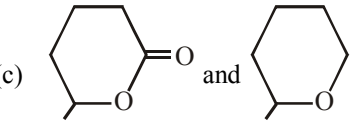
(d) A mixture of (a), (b) and (c)

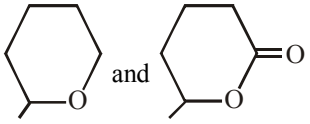
59. The products X and Y are respectively



(a) 

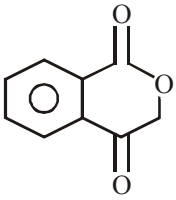
(b) 

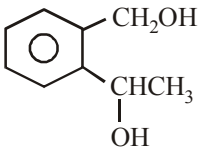
(c) 

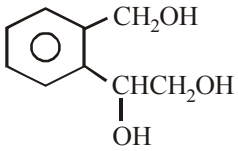
(d) 

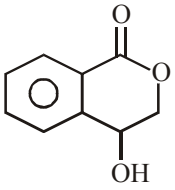
60. The following reaction can be carried out by

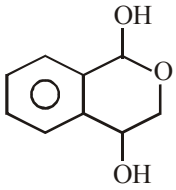
(a) $KMnO_4/H^+$
(b) CrO_3 in HCl/pyridine, Tollen's reagent
(c) MnO_2, Ag_2O
(d) (b) or (c)

61.  Product P is

(a) 

(b) 

(c) 

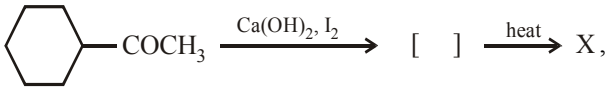
(d) 

62. $CH_3COOH \xrightarrow[(ii)\ 2CH_2N_2]{(i)\ SOCl_2} CH_3COCHN_2 \xrightarrow[Ag_2O]{H_2O} CH_3CH_2COOH$

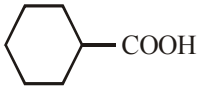
The above set of reactions is named as

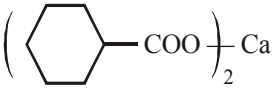
(a) Wolf reaction (b) Darzen reaction
(c) Arndt-Eistert reaction (d) Dakin reaction

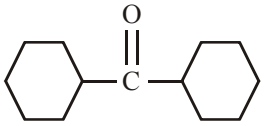
MARK YOUR RESPONSE	57. ⓐⓑⓒⓓ	58. ⓐⓑⓒⓓ	59. ⓐⓑⓒⓓ	60. ⓐⓑⓒⓓ	61. ⓐⓑⓒⓓ
	62. ⓐⓑⓒⓓ				

63. 

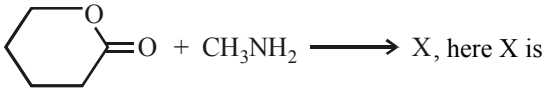
Compound X is

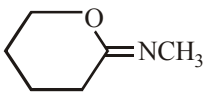
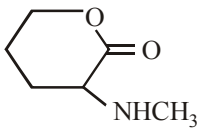
(a) 

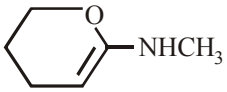
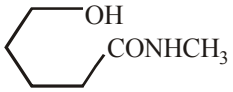
(b) 

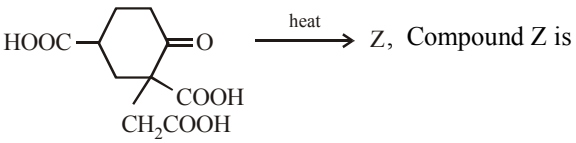
(c) 

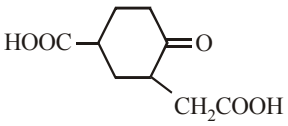
(d) $CH \equiv CH$

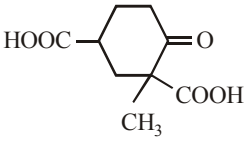
64. 

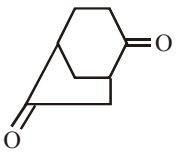
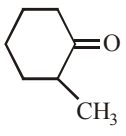
(a)  (b) 

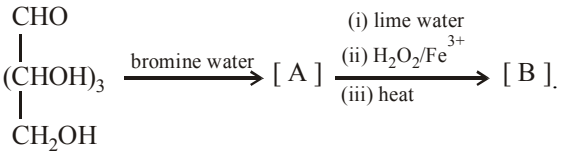
(c)  (d) 

65. 

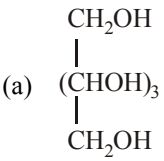
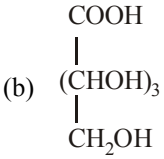
(a) 

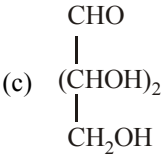
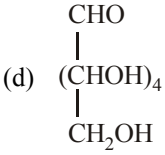
(b) 

(c)  (d) 

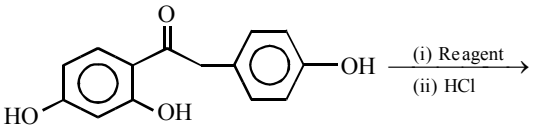
66. 

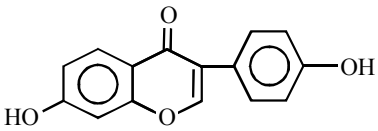
Here [B] is

(a)  (b) 

(c)  (d) 

67. Identify the reagent in the given reaction

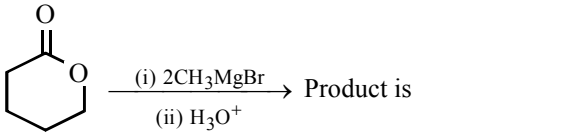


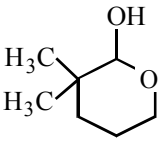
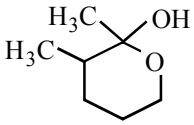


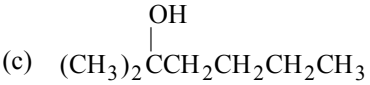
(a) $HCHO, C_2H_5ONa$ (b) CH_3CHO, OH^-

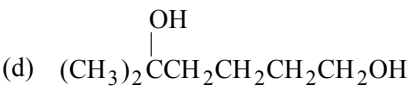
(c) $HCOOC_2H_5$

(d) $HCOOC_2H_5, C_2H_5ONa$

68. 

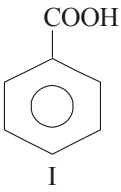
(a)  (b) 

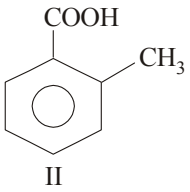
(c) 

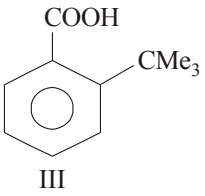
(d) 

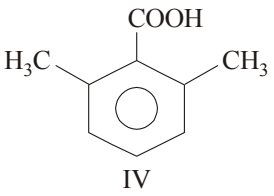
MARK YOUR RESPONSE	63. ⓐⓑⓒⓓ	64. ⓐⓑⓒⓓ	65. ⓐⓑⓒⓓ	66. ⓐⓑⓒⓓ	67. ⓐⓑⓒⓓ
	68. ⓐⓑⓒⓓ				

69. Arrange the following four acids in their decreasing order of acidity


I


II

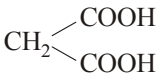

III


IV

(a) I > II > III > IV (b) IV > III > II > I

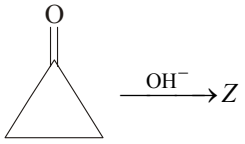
(c) II > IV > III > I (d) III > IV > II > I

70. Which of the following is least acidic in nature ?

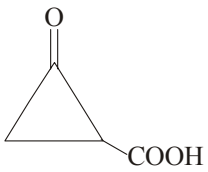
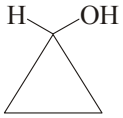
(a) CH_3COOH (b) 

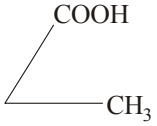
(c) CH_3CH_2COOH

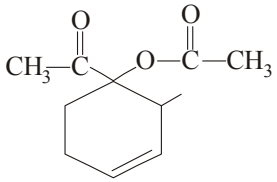
(d) $Me_3N^+CH_2CH_2CH_2COOH$

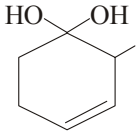
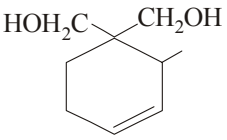
71. 

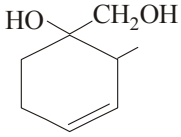
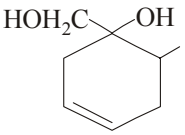
Product *Z* is

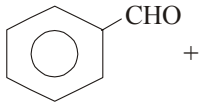
(a)  (b) 

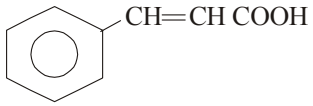
(c)  (d) None of these

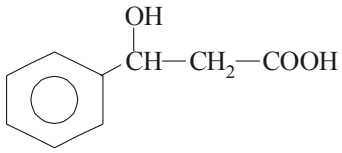
72.  $\xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4}$ Product is

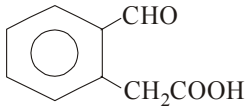
(a)  (b) 

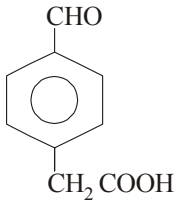
(c)  (d) 

73.  $\xrightarrow[(ii)\ H_3O^+ \\ (iii)\ heat]{(i)\ Pyridine}$ Z, Z is

(a) 

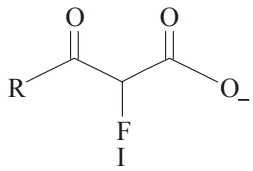
(b) 

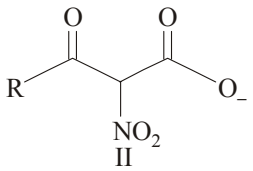
(c) 

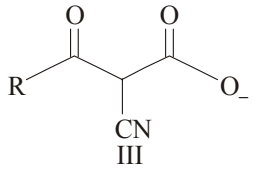
(d) 

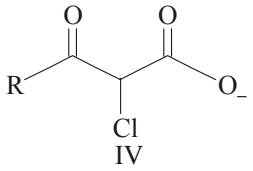
MARK YOUR RESPONSE	69. ⓐⓑⓒⓓ	70. ⓐⓑⓒⓓ	71. ⓐⓑⓒⓓ	72. ⓐⓑⓒⓓ	73. ⓐⓑⓒⓓ

74. Which of the following is the correct order of decarboxylation of β-keto carboxylate anion ?

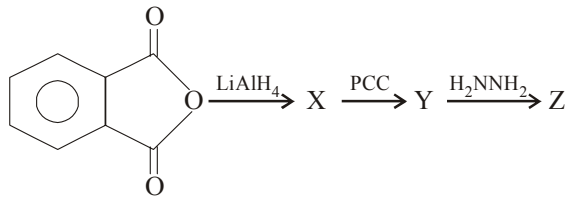

I


II

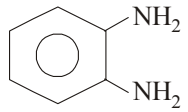
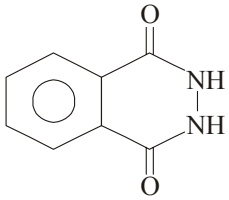

III

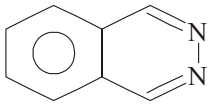
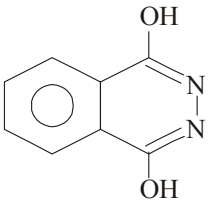

IV

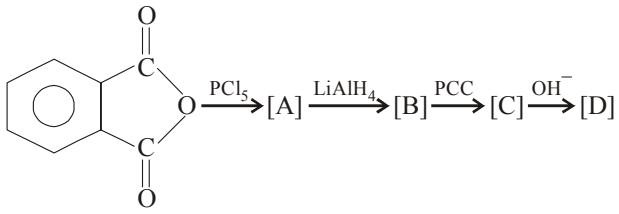
(a) I > II > III > IV (b) II > I > III > IV
(c) II > III > IV > I (d) I > IV > II > III

75. 

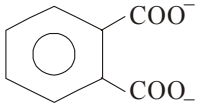
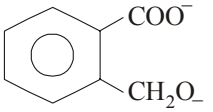
Here Z is

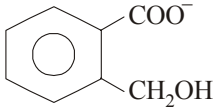
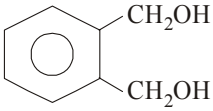
(a)  (b) 

(c)  (d) 

76. 

Compound D is

(a)  (b) 

(c)  (d) 

MARK YOUR RESPONSE	74. ⓐⓑⓒⓓ	75. ⓐⓑⓒⓓ	76. ⓐⓑⓒⓓ		

B COMPREHENSION TYPE

This section contains groups of questions. Each group is followed by some multiple choice questions based on a paragraph. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

PASSAGE-1

Amides undergo hydrolysis to yield carboxylic acids plus amines on heating in either aqueous acid or aqueous base. The conditions required for amide hydrolysis are more severe than those required for the hydrolysis of esters, anhydrides or acid chlorides, but the mechanism is similar (nucleophilic acyl substitution). Nucleophilic acyl substitutions involve a tetrahedral intermediate, hence these are quite different from alkyl substitution ($RCH_2Br \xrightarrow{NaCN} RCH_2CN$) which involves a petavalent intermediate or transition state.

One of the important reactions of esters is their reaction with two equivalent of a Grignard reagent to give tertiary alcohols.

1. The mechanism involved during the hydrolysis of acid derivatives is :

(a) elimination-addition
(b) addition-elimination
(c) nucleophilic addition elimination
(d) electrophilic addition elimination

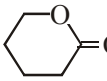
2. Which of the following constitutes the best substrate during the acidic hydrolysis of amides ?

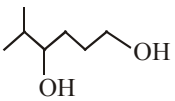
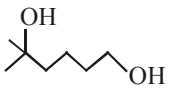
(a) $R-\overset{\overset{O}{\|}}{C}-NH_2$ (b) $R-\overset{\overset{O}{\|}}{C}-\overset{+}{N}H_3$

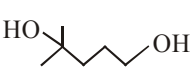
(c) $R-\overset{\overset{OH^+}{\|}}{C}-NH_2$ (d) $R-\overset{\overset{OH^+}{\|}}{C}-\overset{+}{N}H_3$

3. For which functional derivative of carboxylic acids, acidic hydrolysis is avoided?

(a) Acid chlorides (b) Acid amides
(c) Acid anhydrides (d) Esters

4. When  is treated with two equivalent of methyl magnesium iodide and the product acidified the final product will be

(a)  (b) 

(c)  (d) 

5. Which of the following methods is more general for preparing nitriles?

(a) $RCH_2Br + NaCN \longrightarrow RCH_2CN + NaBr$

(b) $RCH_2CH_2CONH_2 \xrightarrow{P_4O_{10}} RCH_2CH_2CN$

(c) Both
(d) None

PASSAGE-2

Methanoic acid, the first member of carboxylic acid series, when warmed with concentrated sulphuric acid decomposes in the following way and evolves carbon monoxide.

$$H-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{H^+} H-\overset{\overset{O}{\|}}{C}-\overset{+}{O}H_2 \xrightarrow{-H_2O}$$

$$\left[H-\overset{\overset{O}{\|}}{C}_+ \longleftrightarrow H-\overset{\overset{O^+}{\|\|}}{C} \right] \xrightarrow{-H^+} C \equiv O + H^+$$

The driving force for this reaction lies in the fact that the $HC \equiv O^+$ ion is very unstable acid and thus easily loses H^+.

6. Formic acid on heating with conc. H_2SO_4 gives

(a) $CO_2 + H_2$ (b) $CO + H_2O$
(c) CO (d) H_2O

7. What happens when acetic acid is treated with conc. H_2SO_4?

(a) $CO + H_2O$ (b) $CH_4 + CO_2$
(c) $CO + CH_4$ (d) No reaction

8. If acetic acid is replaced by triphenylacetic acid, the products formed will be

(a) $(C_6H_5)_3CH + CO$ (b) $(C_6H_5)_3CH + CO_2$
(c) $(C_6H_5)_3COH + CO$ (d) No reaction

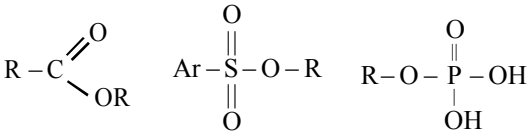
9. If formic acid is replaced by benzoylformic acid, $C_6H_5COCOOH$ the product formed will be

(a) $C_6H_5COOH + CO + CO_2$
(b) $C_6H_5COOH + CO_2$
(c) $C_6H_5COOH + CO$
(d) $C_6H_5CHO + CO_2$

MARK YOUR RESPONSE										
	1.	ⓐⓑⓒⓓ	2.	ⓐⓑⓒⓓ	3.	ⓐⓑⓒⓓ	4.	ⓐⓑⓒⓓ	5.	ⓐⓑⓒⓓ
	6.	ⓐⓑⓒⓓ	7.	ⓐⓑⓒⓓ	8.	ⓐⓑⓒⓓ	9.	ⓐⓑⓒⓓ		

PASSAGE-3

When the following three different types of esters are hydrolysed in basic medium,



Carboxylate Sulphonate Phosphate

The hydroxide anion attacks the acyl carbon in carboxylates, while it attacks the alkyl carbon in sulphonates leading to a difference in the site of cleavage. More interestingly, phosphate esters lie somewhat in between carboxylates and sulphonates in that cleavage can occur in either direction.

In acidic solution, all the three types of phosphates (monoalkyl, dialkyl and trialkyl) are hydrolysed to phosphoric acid, while in basic solution only trialkyl phosphates undergo hydrolysis and only one alkoxy group is removed.

10. Which of the following factor explains the difference in attack of the nuceophile, OH^- on carboxylates and sulphonates?

(a) Sulphonate anions are weakly basic and hence good leaving groups.

(b) Carboxylate anions are stronlgy basic and hence poor leaving groups.

(c) Both (a) and (b)

(d) None of the two

11. Competition between phosphorus and alkyl carbon to nucleophilic attack is due to the fact that

(a) Phophorus can accept an additional pair of electrons

(b) Phosphoric acid lies between carboxylic acid and sulphonic acid

(c) Both (a) and (b)

(d) None of the two

12. The rate of hydrolysis of monoalkyl phosphates tends to ..... with increase in pH.

(a) Decrease (b) Increase

(c) Remains unaffected (d) None of these

13. In an aqueous solution, a monoalkylphosphate ester can exist as

(a) A neutral ester

(b) A monoanion and dianion

(c) A monoanion, dianion and protonated ester

(d) A monoanion, dianion, protonated ester and neutral ester

PASSAGE-4

Hell-Volhard-Zelinsky (HVZ) reaction involves the reaction of aliphatic carboxylic acid with bromine in the presence a trace of PBr_3 to form α-bromocarboxylic acid.

$$CH_3CH_2COOH \xrightarrow{Br_2/PBr_3} CH_3CH_2COBr$$

$$\longrightarrow CH_3CHBrCOBr \xrightarrow{H_2O} CH_3CHBrCOOH$$

14. When two equivalents of the reagent are used, the product formed in the above reaction will be

(a) $CH_3CHBrCOBr$ (b) $CH_2BrCHBrCOOH$

(c) CH_3CBr_2COOH (d) both (b) and (c)

15. What will be the product when three equivalent of Br_2 is treated with 2,2-dimethylbutanoic acid?

(a) $CH_2Br-\underset{\displaystyle CH_2Br}{\overset{\displaystyle CH_2Br}{\underset{|}{\overset{|}{C}}}}-COOH$ (b) $Br_2CH-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2Br}{\underset{|}{\overset{|}{C}}}}-COOH$

(c) $Br_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-COOH$ (d) No reaction

16. What product will be formed when PBr_3 in the given set of reactions is replaced by PCl_3?

(a) $CH_3-\underset{|}{\overset{\displaystyle Cl}{C}}HCOOH$ (b) $CH_3-\underset{|}{\overset{\displaystyle Br}{C}}H-COOH$

(c) Both (d) Reaction not possible

MARK YOUR RESPONSE					
	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ
	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ			

17. When Br_2 in the above given set of reactions is replaced by Cl_2, the product formed will be

(a) $CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}H-COOH$ (b) $CH_3-\underset{\displaystyle Br}{\underset{|}{C}}H-COOH$

(c) $CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}H-COCl$ (d) $CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}H-COBr$

PASSAGE-5

Dicarboxylic acids are stronger than monocarboxylic acids because one –COOH group enhances the acidity of the other.

Although simple carboxylic acids are difficult to decarboxylate, β-keto acids undergo decarboxylation readily to form corresponding carboxylic acid. This is due to the formation of the resonance stabilised enolate anion from the β-keto acid.

However, dicarboxylic acids on heating form a variety of products.

(i) 1, 2 - and 1, 3-dicarboxylic acids give monocarboxylic acids.

(ii) 1, 4 - and 1, 5 - dicarboxylic acids on heating give cyclic anhydrides.

(iii) 1, 6 - and 1, 7 - dibasic acids give cyclic ketones.

18. Which of the following carboxylic acid undergoes decarboxylation easily ?

(a) CH_3CH_2COOH

(b) $CH_2=CHCOOH$

(c) $CH_2=CHCH_2COOH$

(d) $H_2NCH_2CH_2COOH$

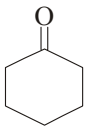
19. Which of the following is least acidic ?

(a) $CH_2(COOH)_2$

(b) $(COOH)_2$

(c) $COOHCH_2CH_2COOH$

(d) $^{-}OOC\,CH_2CH_2COOH$

20. $X \xrightarrow[(CH_3CO)_2O]{\text{distill}}$  . The compound X is

(a) $COOH(CH_2)_4COOH$

(b) $COOH(CH_2)_5COOH$

(c) $COOH(CH_2)_6COOH$

(d) $HOCH_2(CH_2)_4COOH$

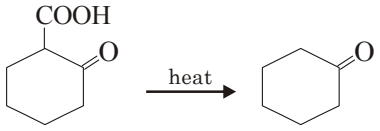
21. Which of the following is correct ?

(a) $(COOH)_2 \xrightarrow{\text{heat}} HCOOH + CO_2$

(b) $(COOH)_2 \xrightarrow{\text{heat}} CO_2 + CO + H_2O$

(c) $HOOCCH=CHCOOH \xrightarrow{\text{heat}}$

$CH_2=CHCOOH + CO_2$

(d) 

PASSAGE-6

An organic cyclic (six-membered) compound of the formula $C_7H_{11}O_2Cl$ gives usual reactions of the carboxylic group and gives white precipitate on boiling with conc HNO_3 and silver nitrate solution. On the basis of the given facts, answer the following questions.

22. How many structural isomers are possible for the compound?

(a) 3 (b) 4

(c) 5 (d) 6

23. Which of the following facts is true about the relative acidic character of the above four isomers ?

(a) All should be equally acidic

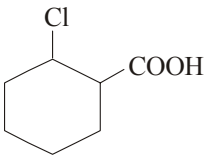
(b) One of the isomers should differ from the others

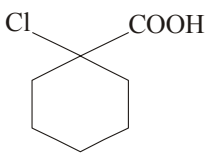
(c) Two isomers differ from the rest

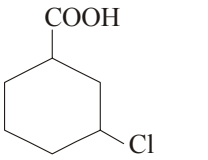
(d) Each of them has different acidic character than the others

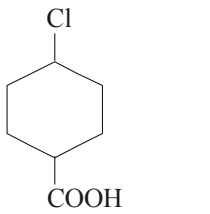
MARK YOUR RESPONSE					
	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ
	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ			

24. Which of the following is expected to be most acidic ?

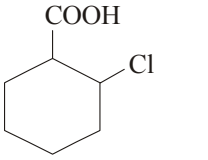
(a) 

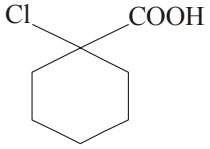
(b) 

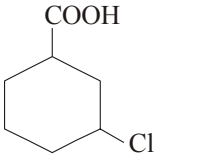
(c) 

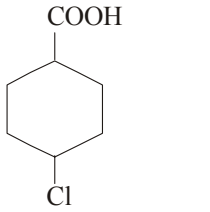
(d) 

25. Which of the following is expected to be least acidic ?

(a) 

(b) 

(c) 

(d) 

26. Which of the following factors can explain their relative acidic character ?

(a) Inductive effect (b) Mesomeric effect

(c) Both (d) None of the two

PASSAGE-7

Two moles of an ester (X) are condensed in presence of sodium ethoxide to give β-keto ester (Y) and ethanol. The compound (Y) when heated in acidic medium gives a β-keto acid (Z) along with ethanol. Compound (Z) on decarboxylation gave a C_5-ketone which did not respond haloform reaction.

27. The ketone (Z) should be

(a) $CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$ (b) $CH_3CH_2\overset{\overset{O}{\|}}{C}CH(CH_3)_2$

(c) $CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3$ (d) None of the three

28. The compound Z is

(a) $CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2COOH$

(b) $CH_3COCH_2\overset{\overset{COOH}{|}}{C}HCH_3$ (c) $CH_3CH_2\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{|}}{CHCOOH}$

(d) $CH_3\overset{\overset{O}{\|}}{C}\underset{\underset{COOH}{|}}{CHCH_2CH_3}$

29. The compound Y should be

(a) $CH_3\overset{\overset{O}{\|}}{C}CH_2COOC_2H_5$

(b) $CH_3CH_2\overset{\overset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}HCOOCH_3$

(c) $CH_3CH_2\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{|}}{CHCOOC_2H_5}$

(d) $CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}OC_2H_5$

30. On the basis of the reaction set, compound X is

(a) methyl propanoate (b) ethyl propanoate

(c) ethyl ethanoate (d) methyl butanoate

MARK YOUR RESPONSE					
	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ
	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ			

C REASONING TYPE

In the following questions two Statement-1 (Assertion) and Statement-2 (Reason) are provided. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct. Mark your responses from the following options:

(a) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(b) Both Statement-1 and Statement-2 are true and Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is true but Statement-2 is false.
(d) Statement-1 is false but Statement-2 is true.

1. **Statement-1** : Nitration of benzoic acid gives *m*-nitrobenzoic acid.
Statement-2 : Carboxyl group increases the electron-density at *meta*-position.

2. **Statement-1** : RCOCl, $(RCO)_2O$ and RCOOR' all react with Grignard reagents to form 3° alcohols.
Statement-2 : RCOCl reacts with R_2Cd to form ketones but $(RCO)_2O$ and RCOOR' do not react at all.

3. **Statement-1** : β-Keto carboxylic acids lose CO_2 when heated at about 370 K.
Statement-2 : An enol is first formed by loss of CO_2, but it readily tautomerises to the more stable ketone.

4. **Statement-1** : CH_3COCl is converted to CH_3CONH_2 on reaction with NH_3.
Statement-2 : Cl is a stronger nucleophile and better leaving group.

5. **Statement-1** : The pK_a value of acetic acid is lower than that of phenol.
Statement-2 : Phenoxide ion is more resonance stabilized

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ

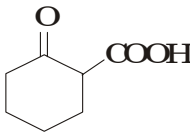
D MULTIPLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE OR MORE is/are correct.

1. RCOOH can be reduced to RCH_2OH by
(*a*) $NaBH_4$ (*b*) $LiAlH_4$
(*c*) Na/C_2H_5OH (*d*) H_2/Catalyst

2. Which of the following compound is decarboxylated on heating ?

(a) $\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}$ (b) $C_2H_5CH(COOH)_2$

(c) CH_3COCH_2COOH (d) 

3. Which of the following compounds can be used as an acylating agent ?
(*a*) CH_3COCl (*b*) $(CH_3CO)_2O$
(*c*) CH_3COOH (*d*) CH_3CH_2COCl.

4. $C_6H_5-\overset{\overset{O}{\|}}{C}-OH + H_2O^{18} \xrightarrow{H^+}$ Product

Here the product may be
(a) $C_6H_5CO^{18}OH$ (b) $C_6H_5COO^{18}H$
(c) $C_6H_5COOO^{18}H$ (d) $C_6H_5CO^{18}OOH$

5. Which of the following statement is true for the following reaction ?

$RCOOH + LiAlH_4 \longrightarrow RCH_2OH$

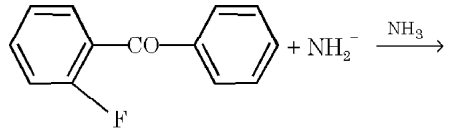
(a) The first step of the reaction is the formation of AlH_3 and H_2.
(b) A hydride ion is transferred from AlH_3 to the carboxylate carbon.
(c) An aldehyde is formed as an intermediate.
(d) Aldehyde is not the intermediate in this reaction

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ

6. Which of the following undergoes nucleophilic addition elimination ?

(a) $CH_3COCl + NH_3 \longrightarrow$

(b) $CH_3COOCH_3 + NH_3 \longrightarrow$

(c) 

(d) $CH_3COOH + NH_3$

7. An organic compound having –OH (alcoholic), –OH (phenolic), –COOH group and acetylenic hydrogen is treated with excess of sodamide. Which of the following group will react with $NaNH_2$?

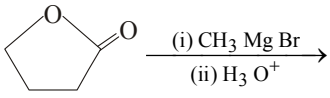
(a) alcoholic –OH group (b) phenolic –OH group

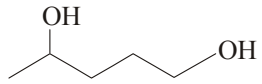
(c) acetylenic hydrogen (d) –COOH group

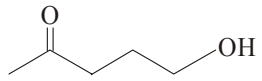
8. Acetic anhydride is prepared industrially by heating sodium acetate with

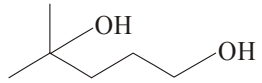
(a) $SOCl_2$ (b) PCl_5

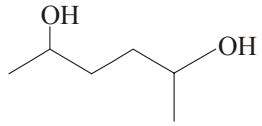
(c) CH_3COCl (d) Cl_2 and SCl_2

9.  Z, Z may be

(a) 

(b) 

(c) 

(d) 

10. Ethanoic and can't be obtained by which of the following reaction ?

(a) $C_2H_5Cl \xrightarrow[(ii)\ H_3O^+]{(i)\ KCN}$

(b) $CH_3Cl \xrightarrow[(ii)\ H_3O^+]{(i)\ AgCN}$

(c) $CH_3CH = CH_2 \xrightarrow[heat]{KMnO_4 / OH^-}$

(d) $CH_3Br \xrightarrow[(iii)\ H_3O^+]{(i)\ Mg \atop (ii)\ CO_2}$

11. Formic acid and acetic acid can be distinguished by the action of

(a) conc. H_2SO_4 (b) Tollens reagent

(c) Fehling solution (d) heat on sodium salt

12. Which of the following compounds decompose $NaHCO_3$ solution, although they do not have a –COOH group ?

(a) Carbolic acid (b) Picric acid

(c) Salicylic acid (d) Ascorbic acid

13. The possible products formed during electrolysis of $CH_3CH_2CH_2COONa$ are

(a) $CH_3CH_2CH_2CH_2CH_2CH_3$

(b) $CH_3CH_2CH_2OH$

(c) $CH_3CH_2CH_3$

(d) $CH_3CH = CH_2$

14. Kolbe's electrolytic method can be applied on

(a) $\begin{matrix} CH_2COONa \\ | \\ CH_2COONa \end{matrix}$ (b) $\begin{matrix} CHCOONa \\ \| \\ CHCOONa \end{matrix}$

(c) C_6H_5COOK (d) CH_3COOK

15. $CH_3\overset{\overset{O}{\|}}{C}-O-\underset{*}{\overset{\overset{CH_3}{|}}{C}}HCH_2CH_3 \xrightarrow{OH^-}$

$CH_3\overset{\overset{O}{\|}}{C}O^- + CH_3\underset{*}{\overset{\overset{OH}{|}}{C}}HCH_2CH_3$

Select correct statements about the above reaction.

(a) Configuration of the asterik marked C is changed

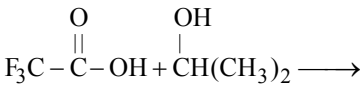
(b) Configuration of the asterik marked C is retained

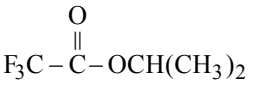
(c) The product is racemic mixture.

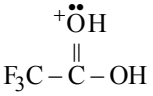
(d) The reaction is irreversible

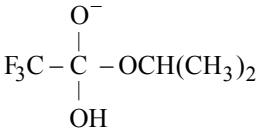
MARK YOUR RESPONSE					
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ
	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ

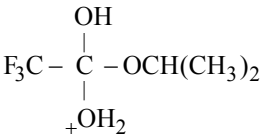
16. Which of the following is/are intermediate(s) during following esterification ?

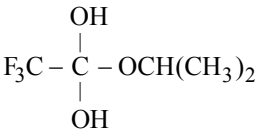




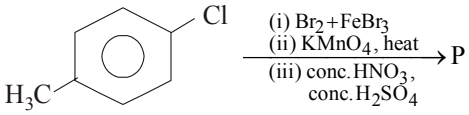
(a) 

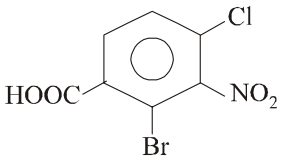
(b) 

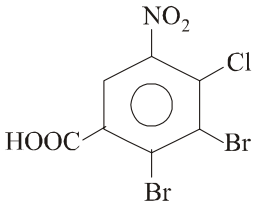
(c) 

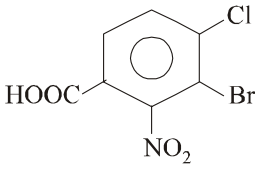
(d) 

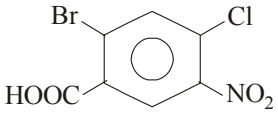
17. Identify the possible final product(s) in the following series of reactions.



(a) 

(b) 

(c) 

(d) 

MARK YOUR RESPONSE	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ			

Answerkey

A Single Correct Choice Type

1	(c)	**2**	(a)	**3**	(d)	**4**	(b)	**5**	(c)	**6**	(c)	**7**	(c)	**8**	(d)	**9**	(b)	**10**	(b)
11	(a)	**12**	(d)	**13**	(d)	**14**	(a)	**15**	(d)	**16**	(d)	**17**	(c)	**18**	(c)	**19**	(d)	**20**	(c)
21	(d)	**22**	(a)	**23**	(b)	**24**	(d)	**25**	(b)	**26**	(d)	**27**	(b)	**28**	(c)	**29**	(c)	**30**	(d)
31	(b)	**32**	(a)	**33**	(d)	**34**	(c)	**35**	(a)	**36**	(a)	**37**	(c)	**38**	(c)	**39**	(d)	**40**	(c)
41	(b)	**42**	(c)	**43**	(c)	**44**	(a)	**45**	(a)	**46**	(c)	**47**	(b)	**48**	(c)	**49**	(d)	**50**	(d)
51	(b)	**52**	(d)	**53**	(b)	**54**	(d)	**55**	(b)	**56**	(b)	**57**	(a)	**58**	(b)	**59**	(d)	**60**	(d)
61	(b)	**62**	(c)	**63**	(c)	**64**	(d)	**65**	(c)	**66**	(c)	**67**	(d)	**68**	(d)	**69**	(b)	**70**	(b)
71	(c)	**72**	(c)	**73**	(b)	**74**	(c)	**75**	(c)	**76**	(c)								

B Comprehension Type

1	(c)	**6**	(b)	**11**	(a)	**16**	(b)	**21**	(a)	**26**	(a)
2	(c)	**7**	(d)	**12**	(c)	**17**	(a)	**22**	(b)	**27**	(a)
3	(a)	**8**	(c)	**13**	(d)	**18**	(c)	**23**	(d)	**28**	(c)
4	(b)	**9**	(c)	**14**	(c)	**19**	(d)	**24**	(b)	**29**	(c)
5	(b)	**10**	(c)	**15**	(d)	**20**	(b)	**25**	(d)	**30**	(b)

C Reasoning Type

1	(c)	**2**	(b)	**3**	(b)	**4**	(c)	**5**	(b)

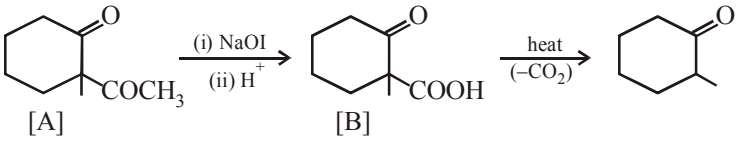
D Multiple Correct Choice Type

1	(b,d)	**2**	(b,c,d)	**3**	(a,b,d)	**4**	(a,b)	**5**	(a,b,c)	**6**	(a,b,c)	**7**	(b,c,d)
8	(a,c,d)	**9**	(b,c)	**10**	(a,b)	**11**	(a,b,c,d)	**12**	(b,d)	**13**	(a,b,c,d)	**14**	(a,b,d)
15	(b,d)	**16**	(a,c,d)	**17**	(a,d)								

Solutions

A SINGLE CORRECT CHOICE TYPE

1. **(c)** Given reagents indicate the presence of $-COCH_3$ group in the starting compound A. Further, since the –COOH group introduced in B due to iodoform reaction is absent in the final product, B should be a β–keto acid. Hence, A should have structure given in option (*c*).



[A] [B]

2. **(a)** $H-COOH \xrightarrow[\text{(dehydration)}]{\text{conc.}H_2SO_4,\text{heat}} CO + H_2O$

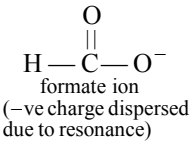
3. **(d)** $\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow[\text{(dehydration)}]{\text{conc.}H_2SO_4,\ \text{heat}} CO + CO_2 + H_2O$

4. **(b)** $HCOONa + NaOH \xrightarrow{CaO} H_2 + Na_2CO_3$

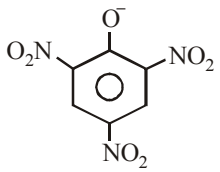
5. **(c)** $\begin{matrix}HCOONa\\+\\HCOONa\end{matrix} \xrightarrow{360^\circ} \begin{matrix}COONa\\|\\COONa\end{matrix}$

6. **(c)** An alkyl group attached to benzene ring can be oxidised only when it contains at least one α-hydrogen atom. Thus here $-CH_3$ group is oxidised and Me_3C- group not. However, Me_3C- group may cause oxidation of the benzene ring to –COOH.

7. **(c)** Conjugate bases of both of the compounds, formic acid and 2, 4, 6-trinitrophenol, are highly stable.



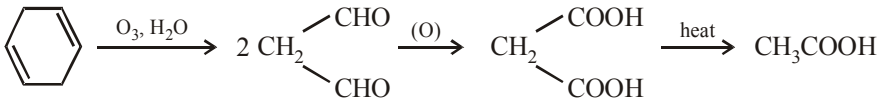
formate ion
(–ve charge dispersed due to resonance)



(–ve charge dispersed due to three electron-withdrawing $-NO_2$ groups)

8. **(d)** $C_2H_5O-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow{1.CH_3MgBr} C_2H_5O-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-OC_2H_5$

$\xrightarrow[(-CH_4)]{1.\ CH_3MgBr} CH_3-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-OC_2H_5 \xrightarrow{H_2O} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow{(-H_2O)} CH_3-\underset{\underset{CH_3}{|}}{C}=O$

9. **(b)** 

10. **(b)** Since organozinc compounds are less reactive than Grignard reagent and organolithium compounds, they do not add to the ester group of the second molecule of the reagent (difference from Grignard reagent and organolithium compounds) and hence give good yield of the hydroxy compound.

11. **(a)** This is an example of Baeyer-Villiger oxidation

12. **(d)** $CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[ZnCl_2 \text{ or } AlCl_3]{CH_3COCl} CH_3-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_2COCH_3$

13. **(d)** (a) $H-\overset{O}{\overset{||}{C}}-Cl \rightarrow CO + HCl$

(b) $CH_3CONH_2 \xrightarrow{HCl} CH_3CO\overset{+}{N}H_3Cl^-$ (Acetamide as a weak base)

$2\,CH_3CONH_2 + HgO \rightarrow (CH_3CONH)_2Hg$ (Acetamide as a weak acid)

(c) $CH_3CONH_2 \xrightarrow[\text{or } Na/C_2H_5OH]{LiAlH_4} CH_3CH_2NH_2 + H_2O$

14. **(a)** All the given reactions are examples of nucleophilic substitution at acyl carbon. Such reactions are possible when the leaving group is a weaker base than the entering group.

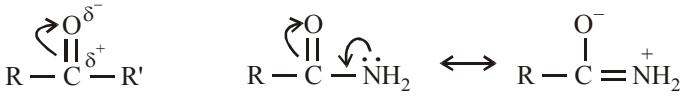
i) leaving group Cl^- is weaker than the OH^-

ii) OCH_3^- (leaving group) is stronger than Br^-

iii) NH_2^- (leaving group) is stronger than Br^-

iv) $^-OCOCH_3$ (leaving group) is weaker than OH^-

15. **(d)** Due to possibility of resonance, carbonyl carbon is no more electron deficient.

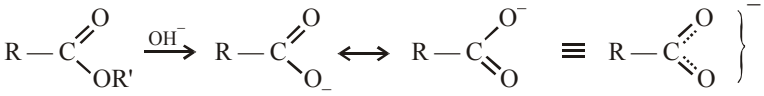


Aldehyde or Ketone (Electron deficient carbon) — Resonance in acid amides (Carbonyl carbon is not electron deficient)

16. **(d)** Hydrolysis is a nucleophilic substitution. Hence more is the electron deficiency of carbonyl carbon, more will be the ease of hydrolysis ; $-NO_2$ group is strongly electron-withdrawing due to –M and –I effects, hence it will produce electron deficiency at carbonyl carbon to the maximum extent.

17. **(c)** Phosphorus converts a little of the acid into acid chloride which is more reactive than the parent carboxylic acid. Thus it is the acid chloride, not the acid itself, that undergoes chlorination on the α-carbon.

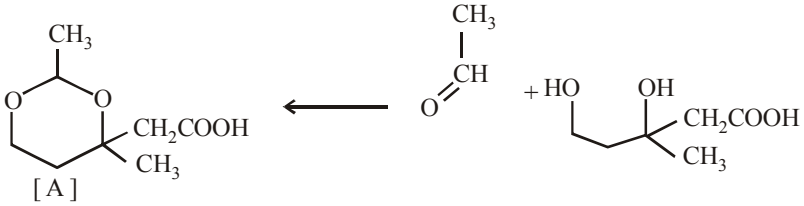
$$CH_3CH_2COOH \xrightarrow{PCl_3 \text{ from } P+Cl_2} CH_3CH_2COCl \xrightarrow{Cl_2} CH_3\overset{Cl}{\overset{|}{C}}HCOCl \xrightarrow{H_2O} CH_3\overset{Cl}{\overset{|}{C}}HCOOH$$

18. **(c)** 

Resonance stabilized carboxylate anion

Since carboxylate anion is quite stable, it has little tendency to react with an alcohol.

19. **(d)** The compound A is cyclic acetal, so it should have an aldehyde and a diol as the two starting compounds.



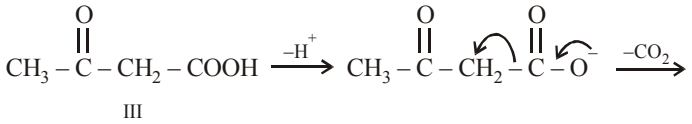
[A]

20. **(c)** 1, 6- and 1, 7-dicarboxylic acids on heating form cyclic ketones (Blanc rule)

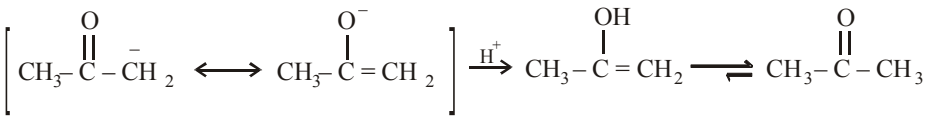
21. **(d)** The yield of product in a reversible reaction can be increased by (i) removing one of the products, (ii) taking either of the reactant in excess.

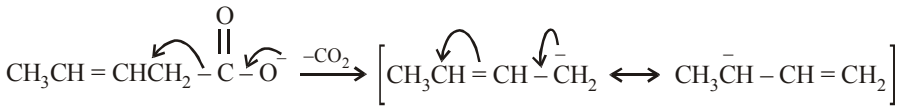
22. **(a)** N-Chloro- or N-bromo-succinimide is the latest reagent used for α-halogenation.

23. **(b)** β-Keto carboxylic acids and β, γ-unsaturated carboxylic acids undergo decarboxylation easily because the corresponding carbanion is quite stable due to resonance.

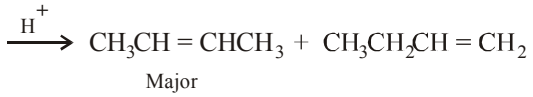


III

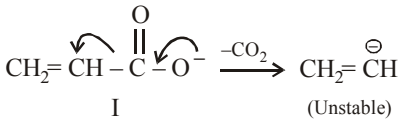




II

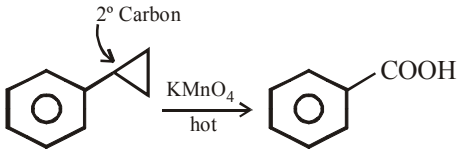


Major

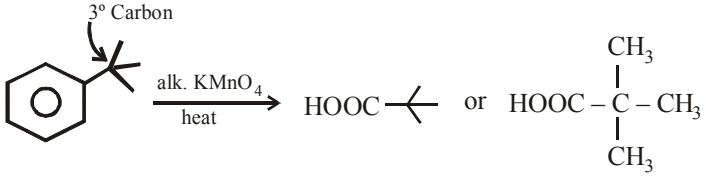


I (Unstable)

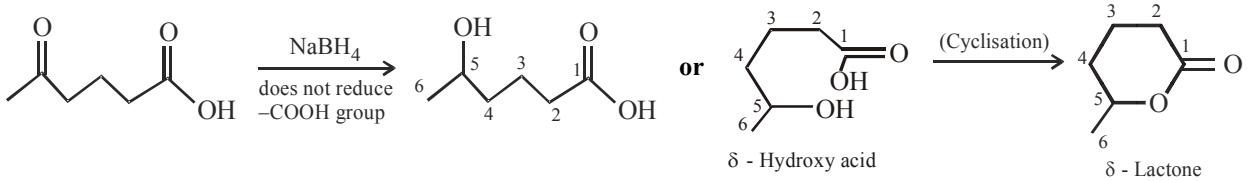
24. **(d)** If the key atom of the side chain of a benzene ring is 1º or 2º, it is oxidised to –COOH irrespective of its nature.



In case the key atom of the side chain is 3º, i.e. when it is not having any H, oxidation is very difficult. However, on vigorous oxidation, benzene ring is oxidised instead of side chain.



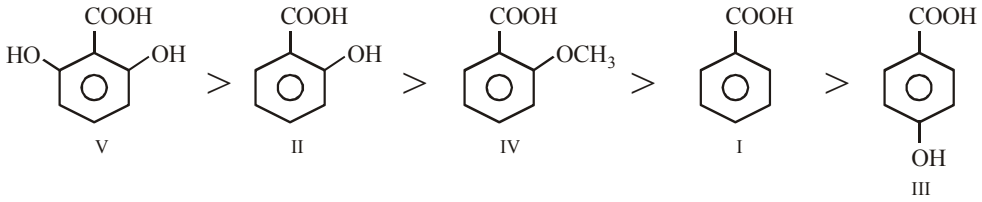
25. **(b)**



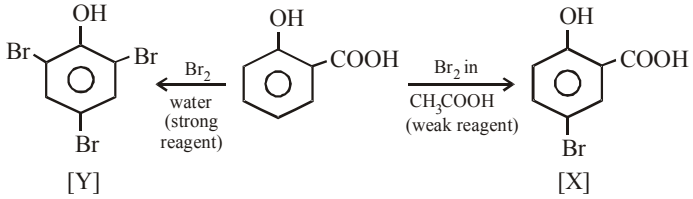
δ - Hydroxy acid

δ - Lactone

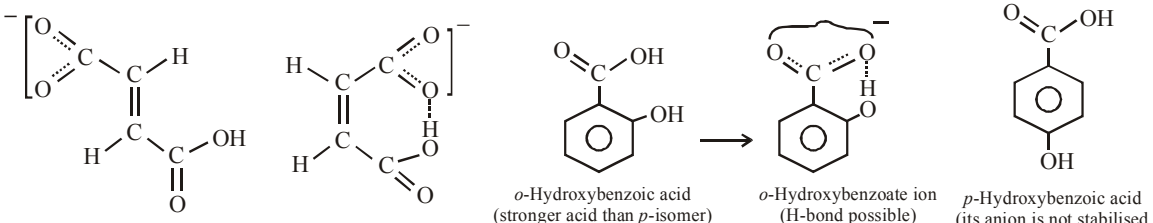
26. **(d)** V is most stable because its anion is stabilized to a greater extent through H – bonding with H atom of OH present on both *ortho*-positions ; followed by II in which one OH group is present. Compound IV comes next to II because here $-OCH_3$ group is present in *ortho* position which although is not capable of forming H–bonding yet more acidic than *p*-HOC_6H_4COOH (III) due to ortho effect. Compound III is less acidic than benzoic acid because of electron-releasing group in the para position. Thus



27. **(b)** Note that when some activating group, e.g. –OH is present along with –COOH in ortho or para position substitution occurs with respect to –OH preferably at para position due to steric factors. In case the reagent used is strong, electrophile enters at all possible positions even with the replacement of –COOH group.



28. **(c)** Hydrogen bonding may decrease or increase the acidity of a species depending upon the structure. If the H-bonding involves the dissociating hydrogen, i.e. H atom of the –COOH group it decreases the acidity as in maleate monoanion (corresponding *trans*-isomer the fumarate monoanion is stronger than maleate monoanion). In case the H-bonding involves the oxygen of the $-COO^-$ and H of other group like –OH, it stabilises the carboxylate anion and its formation will be easy as in *o*-hydroxybenzoic acid, since the carboxylate anion of benzoic acid and *p*-hydroxybenzoic acid can't form such H-bond these acids are weaker than *o*-hydroxybenzoic acid.



29. **(c)** $CH_3-\overset{\overset{O}{\|}}{C}-O-H \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O^- + H^+$;

Acetic acid → Conjugate base (Resonance possible, hence stable and weak base)

$CH_3-\overset{\overset{O}{\|}}{C}-O-O-H \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-O^-$

Peroxyacetic acid → Conjugate base (Resonance not possible, hence unstable and strong base)

30. **(d)** Use of $SOCl_2$ and ClCOCOCl forms gaseous by-products which can be easily removed, giving better yield of RCOCl. Further, oxalyl chaloride is particularly easy to use becasue any excess of it can be easily evaporated due to its low b.p. (62ºC)

$$R-\overset{\overset{O}{\|}}{C}-OH + Cl-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow R-\overset{\overset{O}{\|}}{C}-Cl + HCl\uparrow + CO\uparrow + CO_2\uparrow$$

31. **(b)** For the complete conversion of an acid chloride molecules into acid amide, ammonia should be used in 1 : 2 molar ratio; because one molecule of ammonia acts a nucleophile while the other as a Bronsted base to remove the acid formed during the reaction.

$$RCOCl + NH_3 \rightarrow RCONH_2 + HCl$$
$$HCl + NH_3 \rightarrow NH_4Cl$$
$$\overline{RCOCl + 2NH_3 \rightarrow RCONH_2 + NH_4Cl}$$

In case the two reactants are taken in 1 : 1 molar ratio, one-half of acid chloride will remain unreacted.

$$RCOCl + NH_3 \longrightarrow \frac{1}{2}RCONH_2 + \frac{1}{2}NH_4Cl + \frac{1}{2}RCOCl$$

However, the above reaction can be forced to completion if it is carried out in presence of some other base, like NaOH, which reacts with the acid formed and thus allowing the whole NH_3 a weaker base to react only with RCOCl.

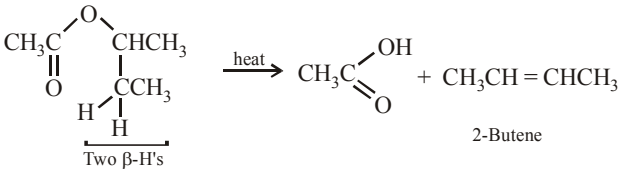
$$RCOCl + NH_3 \xrightarrow{NaOH} RCONH_2 + NaCl + H_2O$$

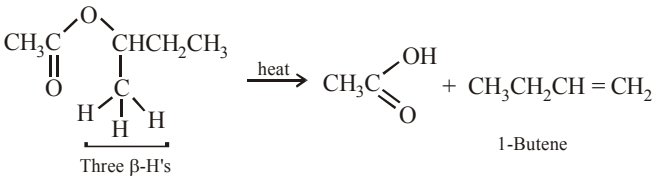
32. **(a)** During alkaline hydrolysis of an ester (saponification), base is consumed in the reaction, it is better to call this reaction as **base-promoted** rather than **base -catalysed**.

33. **(d)** The reaction is an example of hydrogenolysis (cleavage by hydrogen)

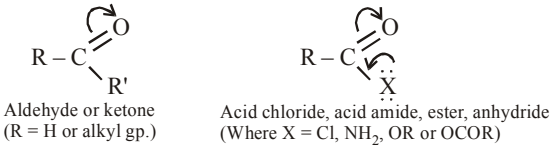
$$C_6H_5COOCH_2C_6H_5 \xrightarrow{H_2-Pd/C} C_6H_5COOH + C_6H_5CH_3$$

34. **(c)** During pyrolysis of an ester, H atom is removed from the β-position w.r.t. to the alcoholic part of the molecule. Since the molecule has 2 β-hydrogens as well as 3 β - H's leading to two butenes in 2 : 3 molar ratio.



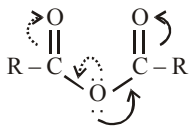


35. **(a)** Stability of acid derivative toward nucleophiles means more stability (or less reactivity) of its carbonyl group. A carbonyl group in aldehydes and ketones is higly reactive toward nucleophile because of electrophilic character of its carbonyl carbon.

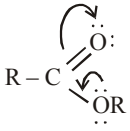


However, in acid derivatives, the electrophilic character of the carbonyl carbon decreases because the double bond of C = O is in conjugation with a lone pair of electrons. Hence acid derivatives are less reactive (more stable) toward nucleophiles. Further among acid chlorides, acid anhydrides, esters and amides the relative stability depends upon the difference in electronegativity of Cl, O and N, which follows the order Cl > O > N. Thus carbonyl group of acid chlorides are least stable while that of acid amides is most stable.

Since O of acid anhydrides and esters has intermediate - I effect, these are more stable than acid chlorides but less stable than acid amides. However, carbonyl group of ester is more stabilized than that of an anhydride because in anhydride stabilization due to lone pair of electrons on O is shared by two C = O groups.



Acid anhydride
(Each carbonyl group is less stabilised than that of an ester)



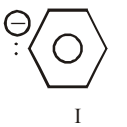
Ester
(Carbonyl group is more stable)

Thus the stability order of the carbonyl group of the four acid derivatives toward nucleophiles is

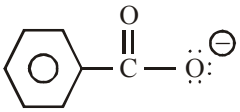
Acid amides > Esters > Acid anhydrides > Acid chlorides

36. **(a)** Hydrolysis of acetic anhydride (acyl nucleophilic substitution, in general) takes place readily in acidic medium because protonation of carbonyl oxygen makes carbon more electrophilic and hence more reactive even toward weak nucleophile, H_2O. Acid derivatives are also more readily hydrolyzed in alkaline medium because here a strong nucleophile (OH^-) is present.

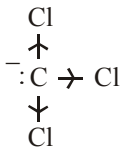
37. **(c)** Nucleophilic substitution at acyl carbon is easy when the leaving group stabilises itself and thus behaves as a weak base. Leaving group of the five compounds are



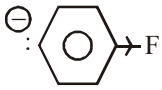
I
Strongly basic
(unstable)



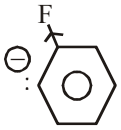
II
Weak base



III
Weak base



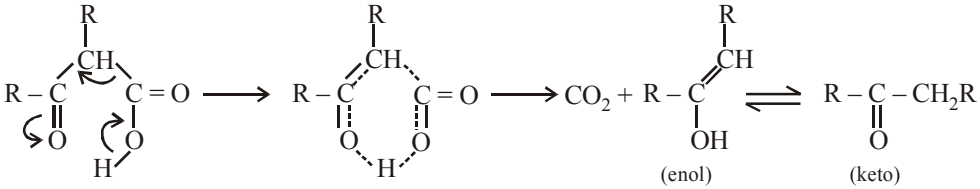
IV
Strong base
(–I effect, not much effective)



V
Weak base
(–I effect effective)

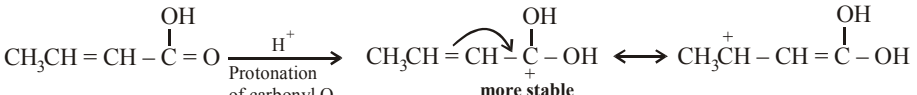
38. **(c)** It is an example of Dieckmann condensation.

39. **(d)** Decarboxylation of β-keto acids involves transfer of the acidic hydrogen to the group followed by loss of CO_2 via a cylic six-membered transition state.



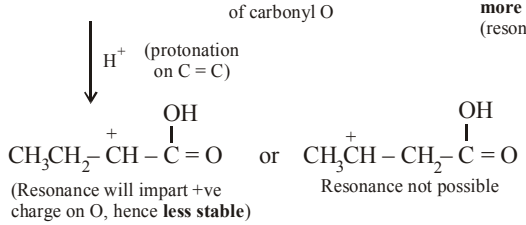
(enol) (keto)

40. **(c)** Electrophilic addition to α,β-unsaturated carbonyl compounds takes place in a way that in conjugated systems, i.e. at the ends of the conjugated system, since this yields a resonance-stabilized carbocation.



Protonation of carbonyl O

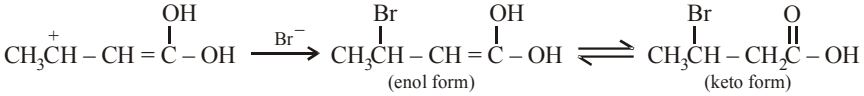
more stable
(resonance stabilized)



(Resonance will impart +ve charge on O, hence **less stable**)

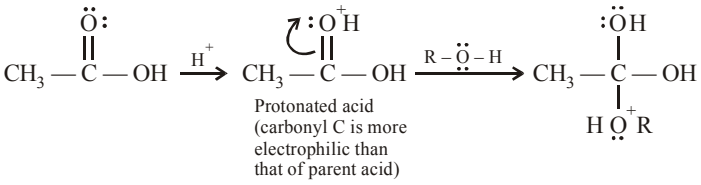
Resonance not possible

Addition of Br^- on the more stable carbocation takes place in the following manner.

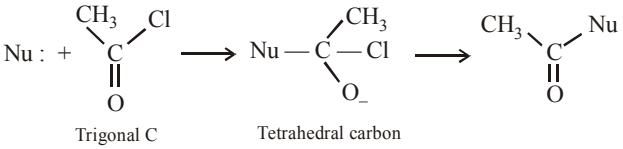


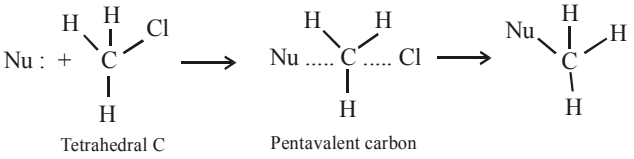
(enol form) (keto form)

41. **(b)** First two steps of the esterification make the question clear

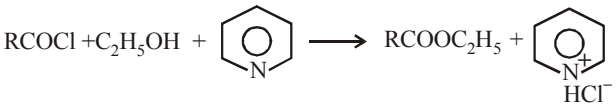


42. **(c)**

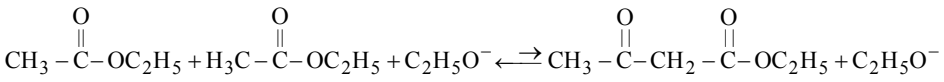




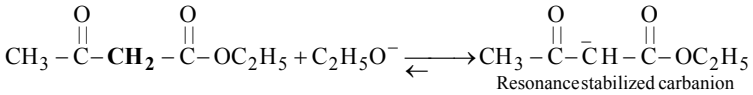
43. **(c)**



44. **(a)** The first two steps of Claisen condensation are reversible with the more tendency toward reactant and not to products.



However, due to reactive methylene group the reaction does not stop at this step but converted into carbanion, which being resonance-stabilized favours the reaction more toward right than to left.



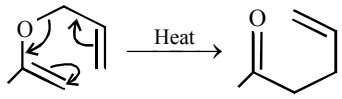
45. **(a)** For aldol condensation, the reactant should have at least one (not necessarily two) α-H, while for Claisen condensation, reactant (ester) should have two α - H's.

46. **(c)** When an acid chloride (or acid anhydride) and ammonia are taken in 1:1 molar ratio, only half of the acid chloride is converted into amide.

One half of the molecule of ammonia acts as a nucleophile to form amide, while the other half acts as a Bronsted base to remove the acid (HCl) formed during the reaction as NH_4Cl.

47. **(b)** It is an example of Michael addition. For details, consult **"Disha's Organic Chemistry" by Dr. O.P. Agarwal** .

48. **(c)** Claisen condensation is possible when esters have at least two α – hydrogen atoms. For details consult "Disha's Organic Chemistry by Dr. O. P. Agarwal".

49. **(d)** (a)  (Claisen rearrangement)

An allyl ether

(b) $2CH_3COOC_2H_5 \xrightarrow{\text{Base}} CH_3COCH_2COOC_2H_5$ (Claisen reaction)

An ester with two α – H

(c) $(CH_3)_2\underset{\underset{OH}{|}}{C}-\underset{\underset{OH}{|}}{C}(CH_3)_2 \xrightarrow{H^+} (CH_3)_2\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$ (Pinacol rearrangement)

A 1, 2-diol

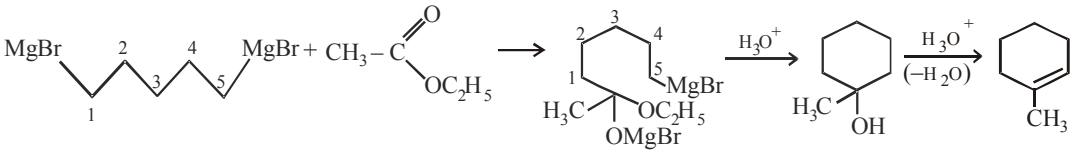
50. **(d)** $R-COOH \xrightarrow{SOCl_2} RCOCl \xrightarrow{CH_2N_2} RCOCHN_2 \xrightarrow[H_2O]{Ag_2O} RCH_2COOH$

Diazoketone

51. **(b)** Benzilic acid involves tansformaiton of α – diketones to α - hydroxy acid by means of OH^-.

52. **(d)** Both are involved in HVZ reaction.

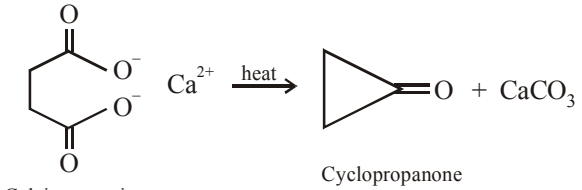
53. **(b)** Recall that esters react with excess of Grignard reagent to form 2º (in case of HCOOR) or 3º alcohols (in case of RCOOR) having two alkyl groups correspponding to Grignard reagent. Further, since alcohol responds Lucas reagent immediately, it must be 3º and thus here it should be $(CH_3)_3$ COH. As the 3º alcohol is having three methyl groups two of which are coming from CH_3MgBr, the third CH_3 methyl must be derived from R part of the ester R COOR'. Hence the ester may be any ester derived from acetic acid, i.e., it is CH_3COOR.

54. **(d)** 

55. **(b)** This is an example of Fries rearrangement, *p*-substituted product is major due to steric effect.

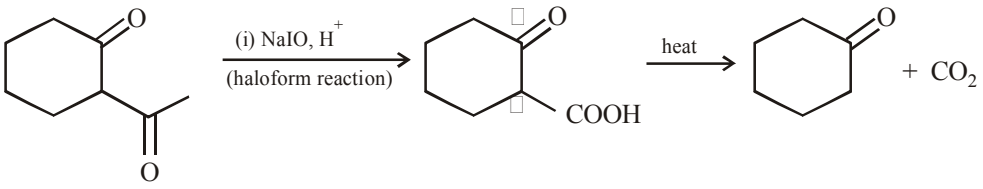
56. **(b)** $\underset{(A)}{(CH_3CO)_2O} \xrightarrow{C_2H_5OH} \underset{(B)}{CH_3COOH} + \underset{(C)}{CH_3COOC_2H_5}$

57. **(a)** Calcium salts of dicarboxylic acids, on heating, give cyclic ketones.

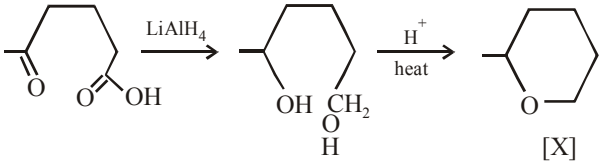


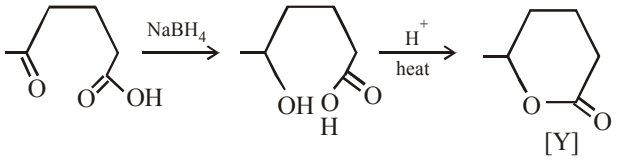
Calcium succinate

Cyclopropanone

58. **(b)** 

59. **(d)** Remember that $LiAlH_4$ reduces both >C = O as well as –COOH to alcohols, while $NaBH_4$ reduces only $\rangle C = O$ without affecting –COOH.





60. **(d)** Acidic $KMnO_4$ will also oxidise the double bond, while in other two cases ; PCC (in b) oxidises $–CH_2OH$ to –CHO and MnO_2 (in c) selectively oxidises allylic alcohol to –CHO without affecting the double bond. Tollen's reagent, being mild oxidising agent, again oxidises –CHO group to –COOH.

61. **(b)** LAH reduces both ester as well as keto group, while SBH reduces only keto group without affecting ester group.

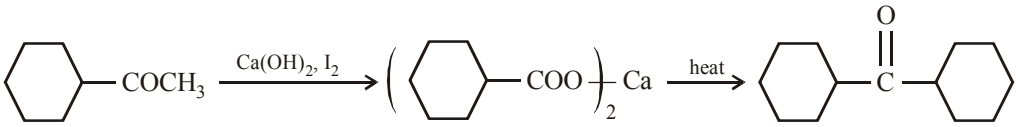
62. **(c)** $CH_3COOH \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{CH_2N_2} CH_3COCHN_2 + HCl^*$

$CH_3COCHN_2 \xrightarrow[Ag_2O\ (catalyst)]{H_2O} CH_3CH_2COOH$

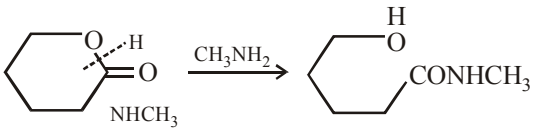
* HCl so formed is removed by second molecule of CH_2N_2($CH_2N_2 + HCl \longrightarrow CH_3Cl + N_2$) otherwise, it would react with diazoketone to form halomethyl ketone as the final product.

$CH_3COCHN_2 + HCl \longrightarrow CH_3COCH_2Cl + N_2$

63. **(c)**

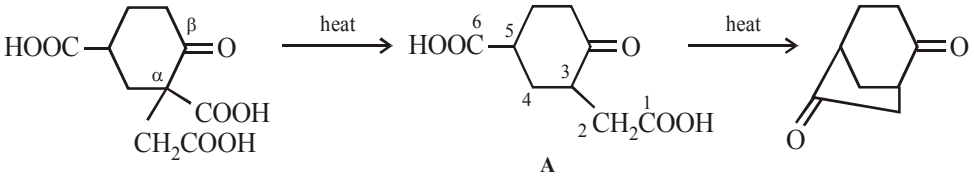


64. **(d)**



A δ-lactone
(cyclic ester)

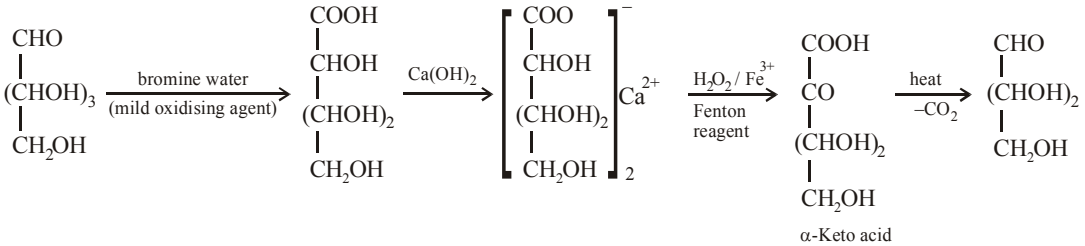
65. **(c)**



A

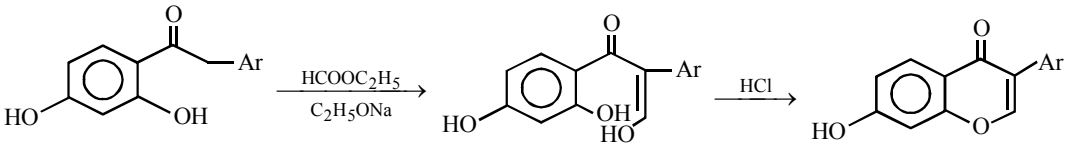
Recall that β-keto acids, on heating, lose a molecule of CO_2. Further note, that compound A is 1, 6-dicarboxylic acid which on heating forms five membered cyclic ketone.

66. **(c)**



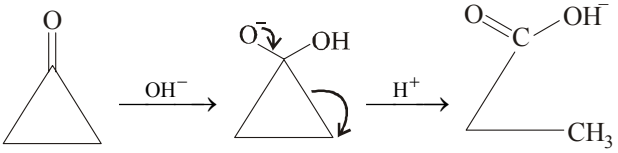
α-Keto acid

67. **(d)** This is an example of Claisen condensation



68. **(d)** Cyclic ester reacts with excess of Grignard reagent to form diols, one alcoholic group is 3° and other is 1°.

71. **(c)**



B COMPREHENSION TYPE

1. **(c)** The first step is the addition of a nucleophile on the electron-deficient carbonyl carbon, while the second step is elimination step.

2. **(c)** Protonation of the carbonyl group activates the carbonyl carbon by making it more electron-deficient and thus easily attacked by a nucleophile.

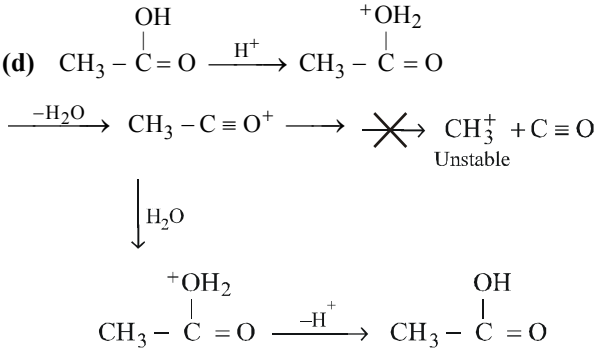
3. **(a)** Acidic hydrolysis should be avoided for acid chlorides, since HCl formed as one of the products may cause side reactions. Hence acid chlorides are best hydrolysed by water in presence of base like pyridine or OH^- to remove HCl.

4. **(b)** The substrate is a cyclic ester, recall that esters react with two equivalents of Grignard reagent to form 3º alcohols having two alkyl groups corresponding to Grignard reagent.

5. **(b)** Dehydration from amides is more geenral because nitrile synthesis through S_N2 displacement is subjected to steric hindrance particularly for the synthesis of α-substituted nitriles.

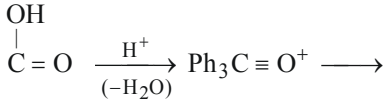
6. **(b)** $CO + H_2O$ will be formed as mentioned in the work-up.

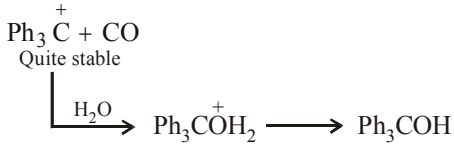
7. **(d)**



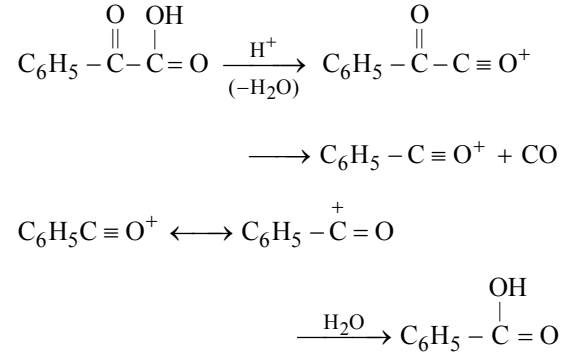
Thus acetic acid will be regenerated, i.e. there is no reaction.

8. **(c)**





9. **(c)**



10. **(c)** Carboxylates are strongly basic, while sulphonates are weakly basic.

11. **(a)** Phosphorus forms stable pentacovalent compounds because it can expand its octet.

12. **(c)** Monoalkyl and dialkyl phosphates do not undergo basic hydrolysis because they contain acidic – OH groups, which in presence of basic medium, form anions that repels OH^-.

13. **(d)** All the four forms are possible.

14. **(c)** The HVZ reaction brings about halogenation only at the α-carbon of the fatty acid. In case the acid has two α-H's, α-dihalo product will be formed when 2 equivalents of halogen are used.

15. **(d)** The acid does not have an α–H, necessary for the reaction.

16–17.(b–a)

The α-halogen comes from halogen (Cl_2 or Br_2) whatever might the nature of PX_3 which is used for converting acid to acid chloride.

C Reasoning Type

1. **(c)** **The correct reason :** Carboxyl group only marginally decreases the electron density at *m*-position relative to *o*- and *p*-positions.

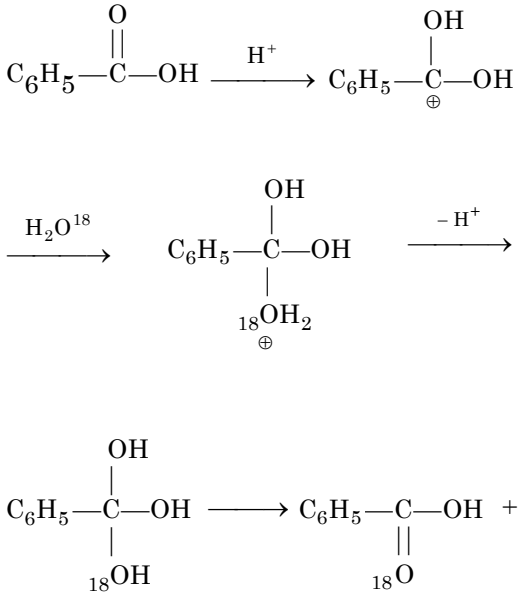
2. **(b)** **The correct explanation :** RCOCl, $(RCO)_2O$ and RCOOR' all add two molecules of Grignard reagents to give 3° alcohols.

D Multiple Correct Choice Type

2. **(b,c,d)** Dicarboxylic acids having two —COOH groups on the same carbon atom ; and β-keto acids are easily decarboxylated on heating.

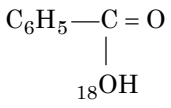
3. **(a,b,d)** Stronger the basic nature of the leaving group, weaker will be its leavability. In CH_3COOH, OH^- is a strong base so it can't be removed easily to form $CH_3\overset{+}{C}O$ required for acetylation (acylation).

4. **(a,b)**

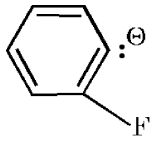


5. **(a,b,c)** Consult mechanism of the reaction in text.

6. **(a,b,c)** The first three are examples of nucleophilic addition elimination reaction, option (*c*) is although ketone, it undergoes acyl type of nucleophilic substitution, *i.e.* nucleophilic addition elimination because the leaving group here is an aryl anion having electronwithdrawing F in the *o*-position making the carbanion stable. Thus it is a weaker base and better leaving group than the ordinary Ar^-. In (*d*) –OH is a poor leaving group.



Remember that C—O^{18} bond is difficult to break than the C—O bond.



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