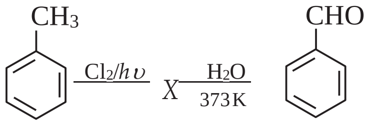
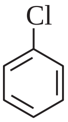
CHAPTER
12

Aldehydes, Ketones and Carboxylic Acids

12.2 Preparation of Aldehydes and Ketones

1. Identify compound X in the following sequence of reactions :



(a)


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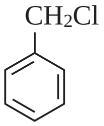
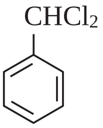


(c)


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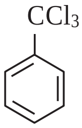
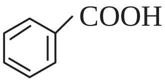


(NEET 2020)

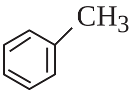
2. Reaction by which benzaldehyde cannot be prepared

(a)

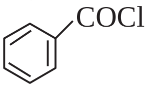
+ CO + HCl in presence of anhydrous $AlCl_3$

(b)


+ Zn/Hg and conc. HCl

(c)


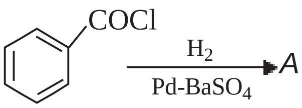
+ CrO_2Cl_2 in CS_2 followed by H_3O^+

(d)


+ H_2 in presence of Pd-$BaSO_4$

(NEET 2013)

3. Consider the following reaction,



The product A is

(a) C_6H_5CHO (b) C_6H_5OH

(c) $C_6H_5COCH_3$ (d) C_6H_5Cl *(Mains 2012)*

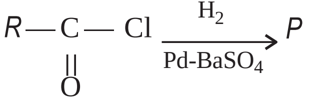
4. Which one of the following can be oxidised to the corresponding carbonyl compound?

(a) 2-Hydroxypropane (b) *ortho*-Nitrophenol

(c) Phenol

(d) 2-Methyl-2-hydroxypropane *(2004)*

5. In the following reaction, product P is

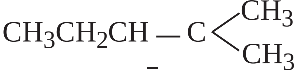


$$R-\underset{\underset{O}{\parallel}}{C}-Cl \xrightarrow[\text{Pd-BaSO}_4]{H_2} P$$

(a) RCH_2OH (b) $RCOOH$

(c) $RCHO$ (d) RCH_3 *(2002)*

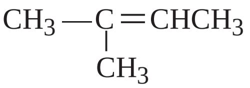
6. Which alkene on ozonolysis gives CH_3CH_2CHO and CH_3COCH_3?

(a)


$$CH_3CH_2CH-C\begin{matrix}CH_3\\CH_3\end{matrix}$$

(b) $CH_3CH_2CH\ CHCH_2CH_3$

(c) $CH_3CH_2CH\ CHCH_3$

(d)


$$CH_3-\underset{\underset{CH_3}{|}}{C}=CHCH_3$$

(2001)

7. In the reaction, $CH_3CN + 2H \xrightarrow[\text{Ether}]{HCl} X \xrightarrow{\text{Boiling } H_2O} Y$; the term Y is

(a) acetaldehyde (b) ethanamine

(c) acetone (d) dimethylamine.

(1999)

8. Ketones [$RCOR_1$] where $R = R_1$ = alkyl group. It can be obtained in one step by

(a) oxidation of tertiary alcohol

(b) reaction of acid halide with alcohols

(c) hydrolysis of esters

(d) oxidation of primary alcohol. *(1997)*

9. The oxidation of toluene to benzaldehyde by chromyl chloride is called

(a) Etard reaction

(b) Riemer–Tiemann reaction

(c) Wurtz reaction

(d) Cannizzaro's reaction. *(1996)*

12.4 Chemical Reactions

10. Reaction between benzaldehyde and acetophenone in presence of dilute NaOH is known as

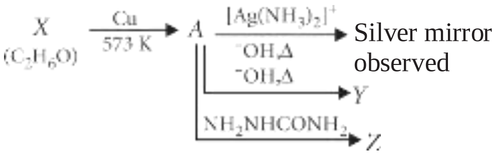
(a) Aldol condensation

(b) Cannizzaro's reaction

(c) Cross Cannizzaro's reaction

(d) Cross Aldol condensation. *(NEET 2020)*

11. Consider the reactions,



Identify *A, X, Y* and *Z*.

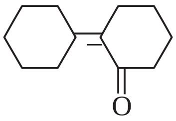
(a) *A*-Methoxymethane, *X*-Ethanol, *Y*-Ethanoic acid, *Z*-Semicarbazide.

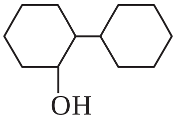
(b) *A*-Ethanal, *X*-Ethanol, *Y*-But-2-enal, *Z*-Semicarbazone.

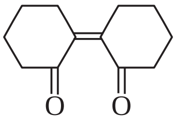
(c) *A*-Ethanol, *X*-Acetaldehyde, *Y*-Butanone, *Z*-Hydrazone.

(d) *A*-Methoxymethane, *X*-Ethanoic acid, *Y*-Acetate ion, *Z*-Hydrazine. *(NEET 2017)*

12. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating?

(a)


(b)


(c)


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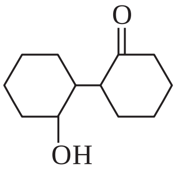
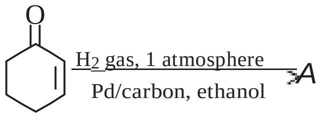
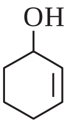


(NEET 2017)

13. The correct structure of the product '*A*' formed in the reaction

 is

(a)


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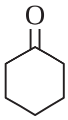

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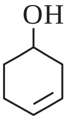

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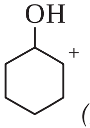


(NEET-II 2016)

14. Which of the following reagents would distinguish *cis*-cyclopenta-1,2-diol from the *trans*-isomer?

(a) MnO_2

(b) Aluminium isopropoxide

(c) Acetone

(d) Ozone *(NEET-I 2016)*

15. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is

(a) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation

(b) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism

(c) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol

(d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.

(NEET-I 2016)

16. The product formed by the reaction of an aldehyde with a primary amine is

(a) carboxylic acid	(b) aromatic acid
(c) Schiff 's base	(d) ketone. *(NEET-I 2016)*

17. Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is

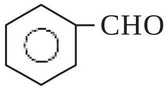
(a) hydrazine in presence of feebly acidic solution

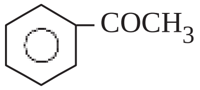
(b) hydrocyanic acid

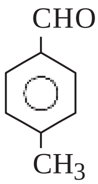
(c) sodium hydrogen sulphite

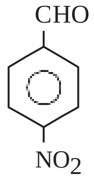
(d) a Grignard reagent. *(2015)*

18. Which one is most reactive towards nucleophilic addition reaction?

(a)


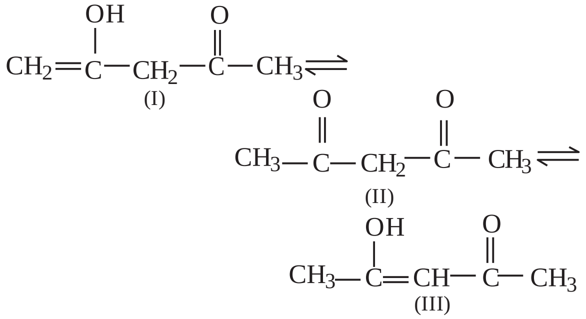
(b)


(c)


(d)


(2014)

19. The order of stability of the following tautomeric compounds is

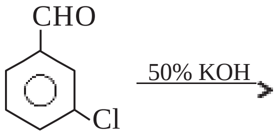


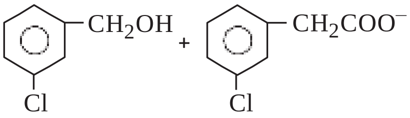
$$\underset{\text{(I)}}{CH_2{=}\overset{\overset{OH}{|}}{C}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_3} \rightleftharpoons \underset{\text{(II)}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_3} \rightleftharpoons \underset{\text{(III)}}{CH_3{-}\overset{\overset{OH}{|}}{C}{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3}$$

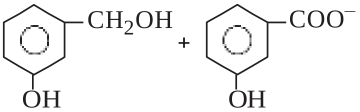
(a) II > I > III (b) II > III > I
(c) I > II > III (d) III > II > I

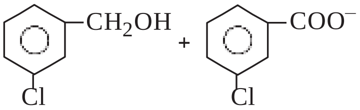
(NEET 2013)

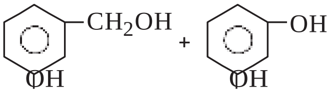
20. Predict the products in the given reaction.



(a) 

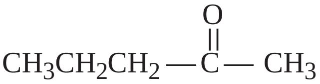
(b) 

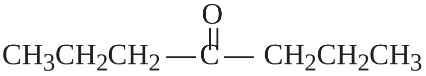
(c) 

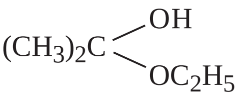
(d) 

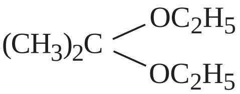
(2012)

21. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is

(a) 
$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(b) 
$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$

(c) 

(d) 

(2012)

22. CH_3CHO and $C_6H_5CH_2CHO$ can be distinguished chemically by

(a) Benedict's test
(b) iodoform test
(c) Tollens' reagent test
(d) Fehling's solution test. *(2012)*

23. Consider the reaction :

$RCHO + NH_2NH_2 \rightarrow RCH{=}N-NH_2$

What sort of reaction is it?

(a) Electrophilic addition-elimination reaction
(b) Free radical addition-elimination reaction
(c) Electrophilic substitution-elimination reaction
(d) Nucleophilic addition-elimination reaction

(Mains 2012)

24. Which of the following compounds will give a yellow precipitate with iodine and alkali?

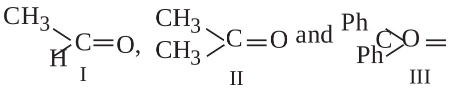
(a) Acetophenone (b) Methyl acetate
(c) Acetamide (d) 2-Hydroxypropane

(Mains 2012)

25. Clemmensen reduction of a ketone is carried out in the presence of which of the following?

(a) Glycol with KOH
(b) Zn-Hg with HCl
(c) $LiAlH_4$
(d) H_2 and Pt as catalyst *(2011)*

26. The order of reactivity of phenyl magnesium bromide (PhMgBr) with the following compounds :



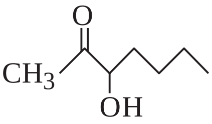
(a) III > II > I (b) II > I > III
(c) I > III > II (d) I > II > III

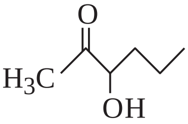
(Mains 2011)

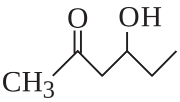
27. Which of the following reactions will not result in the formation of carbon-carbon bonds?

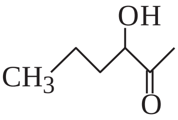
(a) Reimer–Tiemann reaction
(b) Cannizzaro reaction
(c) Wurtz reaction
(d) Friedel–Crafts acylation *(2010)*

28. Which one of the following compounds will be most readily dehydrated?

(a) 

(b) 

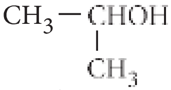
(c) 

(d) 

(Mains 2010)

29. Following compounds are given,

(i) CH_3CH_2OH (ii) CH_3COCH_3

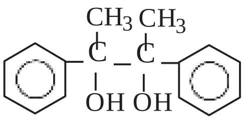
(iii) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CHOH}}$ (iv) CH_3OH

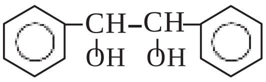
Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?

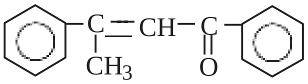
(a) (i), (iii) and (iv) (b) Only (ii)
(c) (i), (ii) and (iii) (d) (i) and (ii)

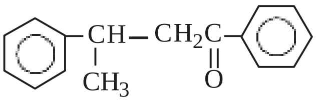
(Mains 2010)

30. Acetophenone when reacted with a base, C_2H_5ONa, yields a stable compound which has the structure

(a) 

(b) 

(c) 

(d)  *(2008)*

31. A strong base can abstract an α-hydrogen from

(a) ketone	(b) alkane
(c) alkene	(d) amine. *(2008)*

32. Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called

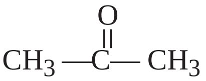
(a) Cope reduction (b) Dow reduction

(c) Wolff–Kishner reduction

(d) Clemmensen reduction. *(2007)*

33. Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid?

(a) C_6H_5CHO (b) $CH_3CH_2CH_2CHO$

(c)  $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ (d) $C_6H_5CH_2CHO$

(2007)

34. The product formed in aldol condensation is

(a) a beta-hydroxy aldehyde or a beta-hydroxy ketone

(b) an alpha-hydroxy aldehyde or ketone

(c) an alpha, beta unsaturated ester

(d) a beta-hydroxy acid. *(2007)*

35. Nucleophilic addition reaction will be most favoured in

(a) CH_3CHO

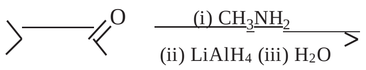
(b)  $CH_3-CH_2-CH_2\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(c) $(CH_3)_2C=O$ (d) CH_3CH_2CHO *(2006)*

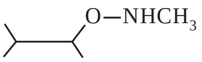
36. A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of α-hydroxy acid. The carbonyl compound is

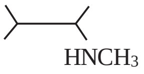
(a) formaldehyde	(b) acetaldehyde
(c) acetone	(d) diethyl ketone. *(2006)*

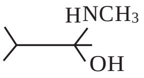
37. The major organic product formed from the following reaction :

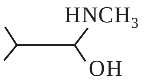


is

(a) 

(b) 

(c) 

(d) 

(2005)

38. In this reaction :

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN \xrightarrow{HOH} CH_3CH(OH)COOH$$

an asymmetric centre is generated. The acid obtained would be

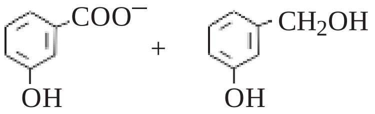
(a) *D*-isomer

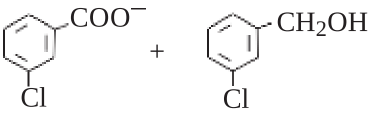
(b) *L*-isomer

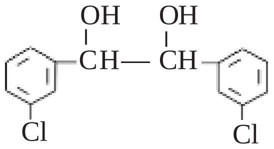
(c) 50% *D* + 50% *L*-isomer

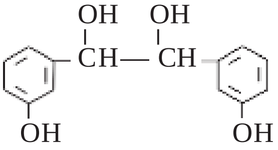
(d) 20% *D* + 80% *L*-isomer. *(2003)*

39. When *m*-chlorobenzaldehyde is treated with 50% KOH solution, the product(s) obtained is (are)

(a) 

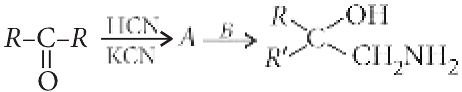
(b) 

(c) 

(d) 

(2003)

40. *A* and *B* in the following reactions are :

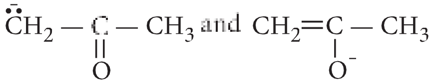


(a) $A = RR\,C\!<\!\begin{matrix}OH\\COOH\end{matrix}$, $B = NH_3$

(b) $A = RR'C\!<\!\begin{matrix}CN\\OH\end{matrix}$, $B = H_3O^+$

(c) $A = RR'CHCN$, $B = NaOH$

(d) $A = RR\,C\!<\!\begin{matrix}CN\\OH\end{matrix}$, $B = LiAlH_4$ *(2003)*

41. 
$\overset{\bullet\bullet}{\bar{C}}H_2-\underset{\underset{O}{||}}{C}-CH_3$ and $CH_2=\underset{\underset{O^-}{|}}{C}-CH_3$

are

(a) resonating structures
(b) tautomers
(c) geometrical isomers
(d) optical isomers. *(2002)*

42. Which of the following is incorrect?
(a) $FeCl_3$ is used in detection of phenol.
(b) Fehling solution is used in detection of glucose.
(c) Tollens' reagent is used in detection of unsaturation.
(d) $NaHSO_3$ is used in detection of carbonyl compound. *(2001)*

43. Polarisation in acrolein can be described as
(a) $\overset{+}{C}H_2-\overset{-}{C}H-\overset{+}{C}HO$
(b) $\overset{-}{C}H_2-\overset{-}{C}H-\overset{+}{C}HO$
(c) $\overset{-}{C}H_2-\overset{-}{C}H-CH\overset{+}{O}$
(d) $\overset{+}{C}H_2-\overset{-}{C}H-CH\overset{-}{O}$ *(2000)*

44. First product of the reaction between *R*CHO and NH_2NH_2 is
(a) $RCH=NNH_2$ (b) $RCH\ \cancel{N}H$
(c) RCH_2NH_2 (d) $RCON_3$ *(2000)*

45. An ester (*A*) with molecular formula, $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed, was treated with H_2SO_4 to give an olefin (*B*). Ozonolysis of (*B*) gave a ketone with molecular formula C_8H_8O which shows +ve iodoform test. The structure of (*A*) is
(a) $H_3CCH_2COC_6H_5$ (b) $C_2H_5COOC_6H_5$
(c) $C_6H_5COOC_2H_5$
(d) *p*-$H_3CO-C_6H_4-COCH_3$ *(1998)*

46. Iodoform test is not given by
(a) ethanal (b) ethanol
(c) 2-pentanone (d) 3-pentanone. *(1998)*

47. Phenylmethanol can be prepared by reducing the benzaldehyde with
(a) CH_3Br and Na (b) CH_3I and Mg
(c) CH_3Br (d) Zn and HCl. *(1997)*

48. The oxidation of toluene with CrO_3 in the presence of $(CH_3CO)_2O$ gives a product *A*, which on treatment with aqueous NaOH produces
(a) C_6H_5COONa (b) 2, 4-diacetyl toluene
(c) C_6H_5CHO (d) $(C_6H_5CO)_2O$ *(1995)*

49. When aniline reacts with oil of bitter almonds (C_6H_5CHO) condensation takes place and benzal derivative is formed. This is known as
(a) Schiff's base (b) Benedict's reagent
(c) Millon's base (d) Schiff's reagent. *(1995)*

50. Compound *A* has a molecular formula C_2Cl_3OH. It reduces Fehling's solution and on oxidation, it gives a monocarboxylic acid *B*. If *A* is obtained by the action of chlorine on ethyl alcohol, then compound *A* is
(a) methyl chloride
(b) monochloroacetic acid
(c) chloral
(d) chloroform. *(1994)*

51. Which of the following compounds will undergo self aldol condensation in the presence of cold dilute alkali?
(a) $CH\equiv C-CHO$ (b) $CH_2=CHCHO$
(c) C_6H_5CHO (d) CH_3CH_2CHO *(1994)*

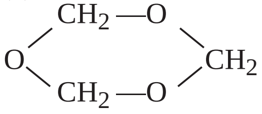
52. Which of the following compounds will give positive test with Tollens' reagent?
(a) Acetic acid (b) Acetone
(c) Acetamide (d) Acetaldehyde *(1994)*

53. $(CH_3)_2C\ \cancel{C}HCOCH_3$ can be oxidised to $(CH_3)_2C\ \cancel{C}HCOOH$ by
(a) chromic acid (b) NaOI
(c) Cu at 300°C (d) $KMnO_4$ *(1993)*

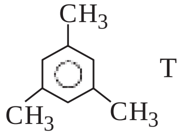
54. In which of the following, the number of carbon atoms does not remain same when carboxylic acid is obtained by oxidation?
(a) CH_3COCH_3 (b) CCl_3CH_2CHO
(c) $CH_3CH_2CH_2OH$ (d) CH_3CH_2CHO *(1992)*

55. Acetaldehyde reacts with
(a) electrophiles only (b) nucleophiles only
(c) free radicals only
(d) both electrophiles and nucleophiles. *(1991)*

56. The reagent which can be used to distinguish acetophenone from benzophenone is
(a) 2,4-dinitrophenylhydrazine
(b) aqueous solution of $NaHSO_3$
(c) Benedict reagent
(d) I_2 and NaOH. *(1990)*

57. 

The above shown polymer is obtained when a carbonyl compound is allowed to stand. It is a white solid. The polymer is
(a) trioxane (b) formose
(c) paraformaldehyde (d) metaldehyde. *(1989)*

58. 

The given compound describes a condensation polymer which can be obtained in two ways : either treating 3 molecules of acetone (CH_3COCH_3) with conc. H_2SO_4 or passing propyne ($CH_3C\equiv CH$) through a red hot tube. The polymer is
(a) phorone (b) mesityl oxide
(c) deacetonyl alcohol (d) mesitylene. *(1989)*

59. $$\underset{(A)}{3CH_3COCH_3}\xrightarrow[-3H_2O]{HCl}\underset{(B)}{(CH_3)_2C=CH-CO-CH=C(CH_3)_2}$$

This polymer (*B*) is obtained when acetone is saturated with hydrogen chloride gas, *B* can be
(a) phorone (b) formose
(c) diacetone alcohol (d) mesityl oxide. *(1989)*

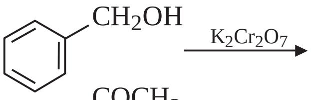
60. If formaldehyde and KOH are heated, then we get
(a) methane (b) methyl alcohol
(c) ethyl formate (d) acetylene. *(1988)*

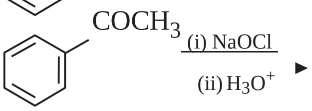
12.5 Uses of Aldehydes and Ketones

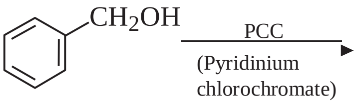
61. Formalin is an aqueous solution of
(a) fluorescein (b) formic acid
(c) formaldehyde (d) furfuraldehyde.
(1988)

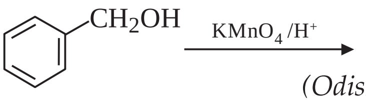
12.7 Methods of Preparation of Carboxylic Acids

62. The reaction that does not give benzoic acid as the major product is

(a) 

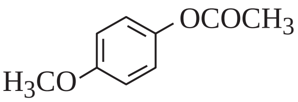
(b) 

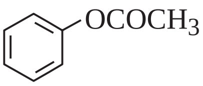
(c) 

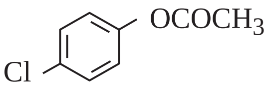
(d) 

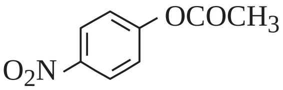
(Odisha NEET 2019)

63. Which one of the following esters gets hydrolysed most easily under alkaline conditions?

(a) 

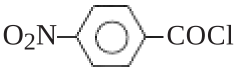
(b) 

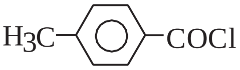
(c) 

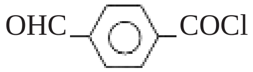
(d) 

(2015)

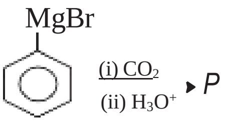
64. Consider the following compounds :
(i) C_6H_5COCl

(ii) 

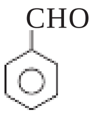
(iii) 

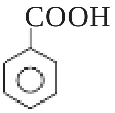
(iv) 

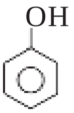
The correct decreasing order of their reactivity towards hydrolysis is
(a) (i) > (ii) > (iii) > (iv)
(b) (iv) > (ii) > (i) > (iii)
(c) (ii) > (iv) > (i) > (iii)
(d) (ii) > (iv) > (iii) > (i) *(2007)*

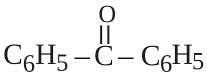
65. 

In the above reaction product *P* is

(a) 

(b) 

(c) 

(d) 
$C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$
(2002)

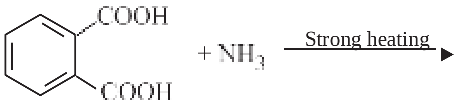
66. Which of the following compounds gives benzoic acid on hydrolysis?
(a) Chlorobenzene (b) Benzoyl chloride
(c) Chlorophenol (d) Chlorotoluene *(1996)*

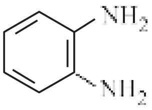
12.8 Physical Properties

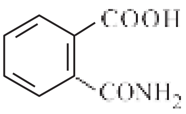
67. Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their
(a) formation of intramolecular H-bonding
(b) formation of carboxylate ion
(c) more extensive association of carboxylic acid *via* van der Waals' forces of attraction
(d) formation of intermolecular H-bonding.
(NEET 2018)

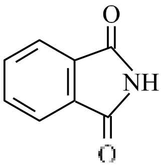
12.9 Chemical Reactions

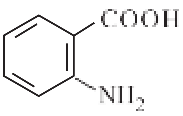
68. The major product of the following reaction is



(a)


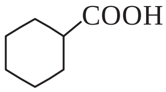
(b)


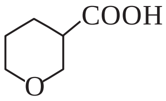
(c)


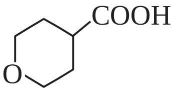
(d)


(NEET 2019)

69. The correct order of strengths of the carboxylic acids


I


II


III

is

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

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

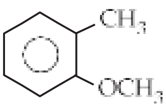
(NEET-II 2016)

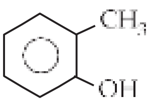
70. The correct order of decreasing acid strength of trichloroacetic acid (*A*), trifluoroacetic acid (*B*), acetic acid (*C*) and formic acid (*D*) is

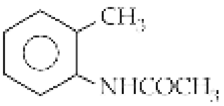
(a) B > A > D > C (b) *B* > *D* > *C* > *A*

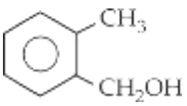
(c) *A* > *B* > *C* > *D* (d) *A* > *C* > *B* > *D* (2012)

71. Which one of the following is most reactive towards electrophilic reagent?

(a)


(b)


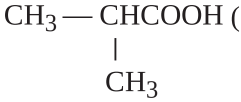
(c)


(d)


(2011, 2010)

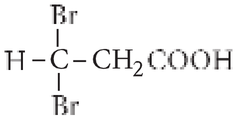
72. An organic compound *A* on treatment with NH_3 gives *B*, which on heating gives *C*. *C* when treated with Br_2 in the presence of KOH produces ethyl amine. Compound *A* is

(a) CH_3COOH (b) $CH_3CH_2CH_2COOH$

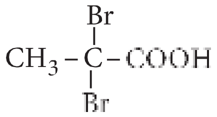
(c)

$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH$
(d) CH_3CH_2COOH

(Mains 2011)

73. Propionic acid with Br_2/P yields a dibromo product. Its structure would be

(a)

$H - \overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}} - CH_2COOH$

(b) $CH_2(Br) - CH_2 - COBr$

(c)

$CH_3 - \overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}} - COOH$

(d) $CH_2(Br) - CH(Br) - COOH$ *(2009)*

74. Which of the following represents the correct order of the acidity in the given compounds?

(a) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$

(b) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$

(c) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

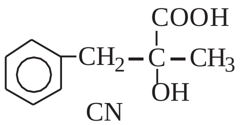
(d) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

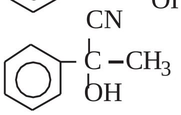
(2007)

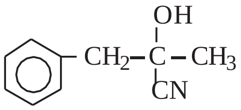
75. In a set of reactions acetic acid yielded a product *D*.

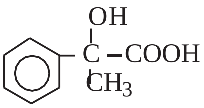
$$CH_3COOH \xrightarrow{SOCl_2} \xrightarrow[\text{anhy. } AlCl_3]{\text{benzene}} \xrightarrow{HCN} \xrightarrow{HOH}$$

The structure of *D* would be

(a)


(b)


(c)


(d)


(2005)

76. The –OH group of an alcohol or the –COOH group of a carboxylic acid can be replaced by –Cl using

(a) phosphorus pentachloride

(b) hypochlorous acid

(c) chlorine

(d) hydrochloric acid. *(2004)*

77. Which one of the following orders of acid strength is correct?

(a) *RCOOH* > *ROH* > HOH > HC≡CH

(b) *RCOOH* > HOH > *ROH* > HC≡CH

(c) *RCOOH* > HOH > HC≡CH > *ROH*

(d) *RCOOH* > HC≡CH > HOH > *ROH* *(2003)*

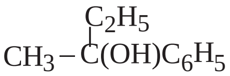
78. In a set of the given reactions, acetic acid yielded a product *C*.

$CH_3COOH + PCl_5 \rightarrow A \xrightarrow[\text{Anh. } AlCl_3]{C_6H_6} B \xrightarrow[\text{ether}]{C_2H_5MgBr} C$

Product *C* would be

(a) $CH_3CH(OH)C_2H_5$ (b) $CH_3COC_6H_5$

(c) $CH_3CH(OH)C_6H_5$

(d) 

$CH_3-\overset{C_2H_5}{\overset{|}{C}}(OH)C_6H_5$ *(2003)*

79. Ethyl benzoate can be prepared from benzoic acid by using

(a) ethyl alcohol

(b) ethyl alcohol and dry HCl

(c) ethyl chloride (d) sodium ethoxide. *(2000)*

80. Reduction by $LiAlH_4$ of hydrolysed product of an ester gives

(a) two alcohols (b) two aldehydes

(c) one acid and one alcohol

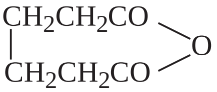
(d) two acids. *(2000)*

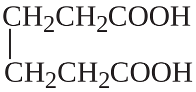
81. Which one of the following compounds will react with $NaHCO_3$ solution to give sodium salt and carbon dioxide?

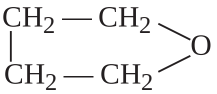
(a) Acetic acid (b) *n*-Hexanol

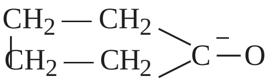
(c) Phenol (d) Both (b) and (c) *(1999)*

82. Which one of the following product is formed when adipic acid is heated?

(a) 

(b) 

(c) 

(d) 

(1995)

83. An acyl halide is formed when PCl_5 reacts with an

(a) amide (b) ester

(c) acid (d) alcohol. *(1994)*

84. Benzoic acid gives benzene on being heated with *X* and phenol gives benzene on being heated with *Y*. Therefore, *X* and *Y* are respectively

(a) soda-lime and copper

(b) Zn dust and NaOH

(c) Zn dust and soda-lime

(d) soda-lime and zinc dust. *(1992)*

85. *A* is a lighter phenol and *B* is an aromatic carboxylic acid. Separation of a mixture of *A* and *B* can be carried out easily by using a solution of

(a) sodium hydroxide (b) sodium sulphate

(c) calcium chloride (d) sodium bicarbonate. *(1992)*

86. The compound formed when malonic acid is heated with urea is

(a) cinnamic acid (b) butyric acid

(c) barbituric acid (d) crotonic acid. *(1989)*

87. Among the following the strongest acid is

(a) CH_3COOH (b) CH_2ClCH_2COOH

(c) $CH_2ClCOOH$ (d) CH_3CH_2COOH *(1988)*

88. Which of the following is the correct decreasing order of acidic strength of

(i) methanoic acid (ii) ethanoic acid

(iii) propanoic acid (iv) butanoic acid

(a) (i) > (ii) > (iii) > (iv) (b) (ii) > (iii) > (iv) > (i)

(c) (i) > (iv) > (iii) > (ii) (d) (iv) > (i) > (iii) > (ii) *(1988)*

12.A Derivatives of Carboxylic Acids

89. Match the compounds given in List-I with List-II and select the suitable option using the codes given below.

List-I	**List-II**
(A) Benzaldehyde	(i) Phenolphthalein
(B) Phthalic anhydride	(ii) Benzoin condensation
(C) Phenyl benzoate	(iii) Oil of wintergreen
(D) Methyl salicylate	(iv) Fries rearrangement

(a) (A)-(iv), (B)-(i), (C)-(iii), (D)-(ii)

(b) (A)-(iv), (B)-(ii), (C)-(iii), (D)-(i)

(c) (A)-(ii), (B)-(iii), (C)-(iv), (D)-(i)

(d) (A)-(ii), (B)-(i), (C)-(iv), (D)-(iii) *(Mains 2011)*

90. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is

(a) CH_3COOCH_3 (b) CH_3CONH_2

(c) $CH_3COOCOCH_3$ (d) CH_3COCl *(2010)*

91. The relative reactivities of acyl compounds towards nucleophilic substitution are in the order of

(a) acid anhydride > amide > ester > acyl chloride

(b) acyl chloride > ester > acid anhydride > amide

(c) acyl chloride > acid anhydride > ester > amide

(d) ester > acyl chloride > amide > acid anhydride. *(2008)*

92. Self condensation of two moles of ethyl acetate in presence of sodium ethoxide yields

(a) ethyl propionate (b) ethyl butyrate

(c) acetoacetic ester (d) methyl acetoacetate. *(2006)*

93. Which one of the following esters cannot undergo Claisen self-condensation?

(a) $C_6H_5CH_2COOC_2H_5$ (b) $C_6H_5COOC_2H_5$

(c) $CH_3CH_2CH_2CH_2COOC_2H_5$

(d) $C_6H_{11}CH_2COOC_2H_5$ *(1998)*

94. Sodium formate on heating yields

(a) oxalic acid and H_2

(b) sodium oxalate and H_2

(c) CO_2 and NaOH

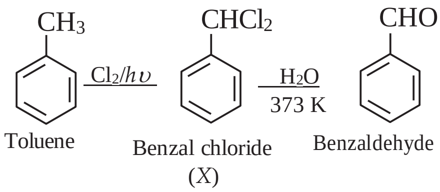
(d) sodium oxalate. *(1993)*

ANSWER KEY

1.	(c)	**2.**	(b)	**3.**	(a)	**4.**	(a)	**5.**	(c)	**6.**	(a)	**7.**	(a)	**8.**	(a)	**9.**	(a)	**10.**	(d)
11.	(b)	**12.**	(a)	**13.**	(b)	**14.**	(c)	**15.**	(b)	**16.**	(c)	**17.**	(a)	**18.**	(d)	**19.**	(d)	**20.**	(c)
21.	(d)	**22.**	(b)	**23.**	(d)	**24.**	(a,d)	**25.**	(b)	**26.**	(d)	**27.**	(b)	**28.**	(c)	**29.**	(c)	**30.**	(c)
31.	(a)	**32.**	(d)	**33.**	(a)	**34.**	(a)	**35.**	(a)	**36.**	(b)	**37.**	(b)	**38.**	(c)	**39.**	(b)	**40.**	(d)
41.	(a)	**42.**	(c)	**43.**	(d)	**44.**	(a)	**45.**	(c)	**46.**	(d)	**47.**	(d)	**48.**	(a)	**49.**	(a)	**50.**	(c)
51.	(d)	**52.**	(d)	**53.**	(b)	**54.**	(a)	**55.**	(b)	**56.**	(d)	**57.**	(a)	**58.**	(d)	**59.**	(a)	**60.**	(b)
61.	(c)	**62.**	(c)	**63.**	(d)	**64.**	(c)	**65.**	(b)	**66.**	(b)	**67.**	(d)	**68.**	(c)	**69.**	(b)	**70.**	(a)
71.	(d)	**72.**	(d)	**73.**	(c)	**74.**	(c)	**75.**	(d)	**76.**	(a)	**77.**	(b)	**78.**	(d)	**79.**	(b)	**80.**	(a)
81.	(a)	**82.**	(a)	**83.**	(c)	**84.**	(d)	**85.**	(d)	**86.**	(c)	**87.**	(c)	**88.**	(a)	**89.**	(d)	**90.**	(d)
91.	(c)	**92.**	(c)	**93.**	(b)	**94.**	(b)												

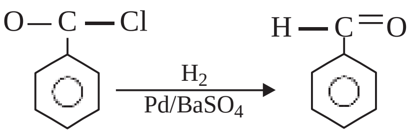
Hints & Explanations

1. (c) :



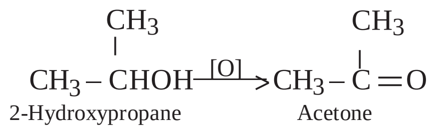
2. (b) : Clemmensen reduction in presence of Zn-Hg and conc. HCl reduces aldehydes and ketones to —CH_2 group but carboxylic acid group remains unaffected.

3. (a) :



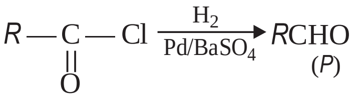
It is Rosenmund's reduction.

4. (a) : Secondary alcohol on oxidation gives a ketone containing the same number of carbon atoms.



$$CH_3-\underset{\text{2-Hydroxypropane}}{\overset{CH_3}{\overset{|}{C}HOH}} \xrightarrow{[O]} \underset{\text{Acetone}}{CH_3-\overset{CH_3}{\overset{|}{C}}=O}$$

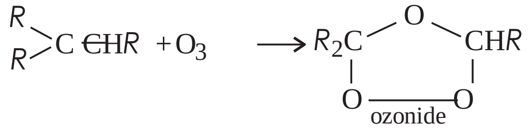
5. (c) : This is Rosenmund reduction.



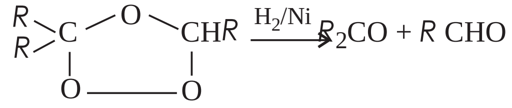
$$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[Pd/BaSO_4]{H_2} \underset{(P)}{RCHO}$$

$BaSO_4$ prevents the aldehyde from being reduced and acts as a poison to the palladium catalyst in this reaction.

6. (a) : On passing a steam of ozone through a solution of olefin in an organic solvent, an ozonide is obtained.



The ozonide on reduction with Zn and acid or H_2/Ni gives aldehydes and/or ketones.



The nature of these products helps in locating the position of the double bond in olefin.

7. (a) : $CH_3-C\equiv N + 2H \xrightarrow[\text{ether}]{HCl} \underset{(X)}{CH_3-CH=NH}$

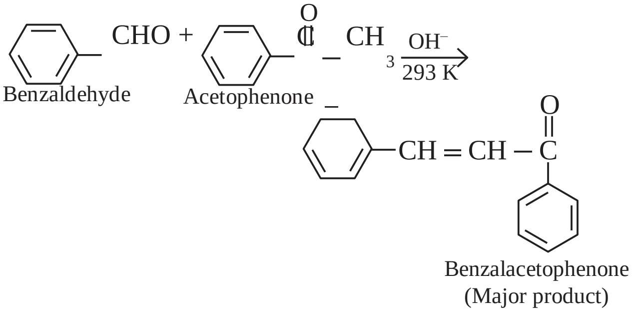
$$\underset{(X)}{CH_3-CH=NH} \xrightarrow[\Delta]{H_2O} \underset{(Y)}{CH_3-CHO + NH_3}$$

Y = Acetaldehyde

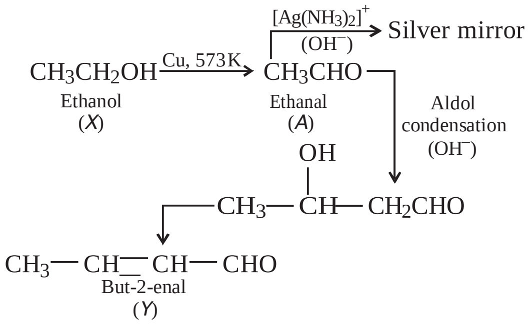
8. (a) : A tertiary alcohol is difficult to oxidise. But when it is treated with an acidic oxidising agent under some conditions, it is oxidised to ketone and then to acids. Both the ketone and acid contain the lesser number of carbon atoms than the starting alcohol.

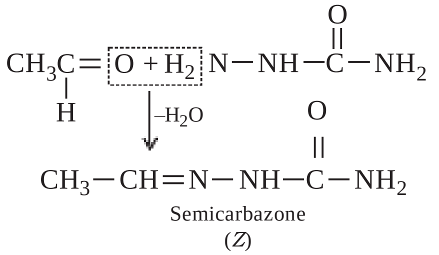
9. (a) : The oxidation of toluene ($C_6H_5CH_3$) with chromyl chloride (CrO_2Cl_2) in CCl_4 or CS_2 to give benzaldehyde is called Etard reaction. In this reaction, the chromyl chloride first forms a brown complex, which is separated and then decomposed with H_2O to give benzaldehyde (C_6H_5CHO).

10. (d) : Cross aldol condensation

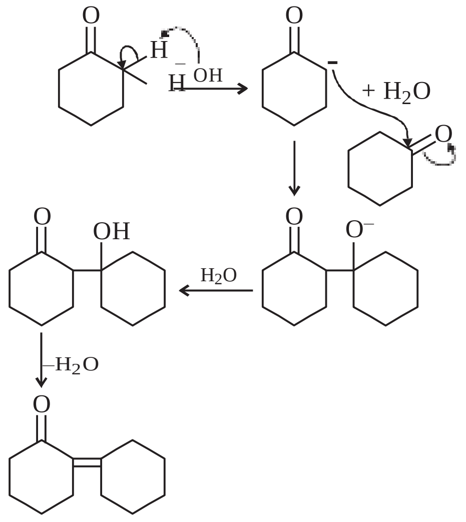


11. (b) : Since, *A* gives silver mirror test, it must be an aldehyde and aldehydes are formed by oxidation of 1° alcohols. Thus, '*X*' is a 1° alcohol, *i.e.*, CH_3CH_2OH.

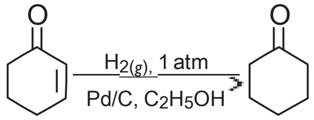




12. (a) :

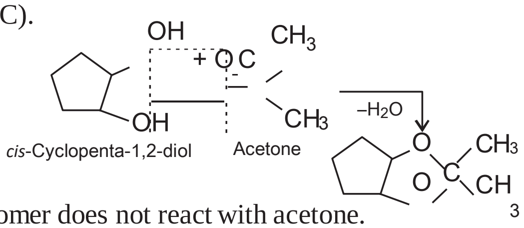


13. (b) :



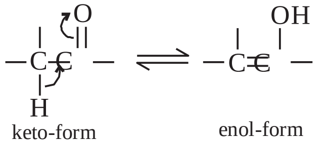
C = C bond is reduced faster than C = O bond with H_2(Pd—C).

14. (c):

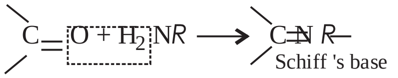


Trans-isomer does not react with acetone.

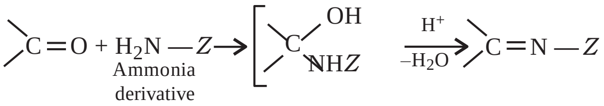
15. (b) : Keto-enol tautomerism :



16. (c) :

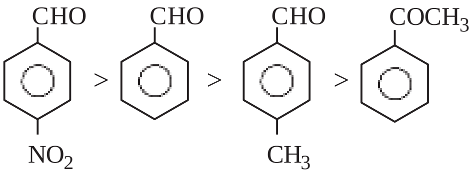


17. (a) : Carbonyl compounds react with ammonia derivatives in weakly acidic medium as follows :

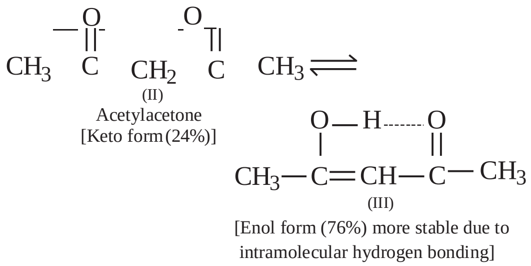


18. (d) : Aromatic aldehydes are more reactive than alkyl aryl ketones. Electron withdrawing group (—NO_2) increases the reactivity towards nucleophilic addition reactions whereas, electron donating group (—CH_3) decreases the reactivity towards nucleophilic addition reactions.

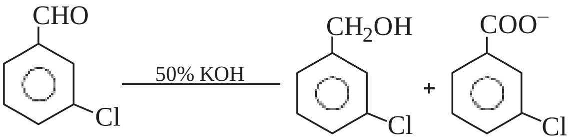
Therefore, the order is :



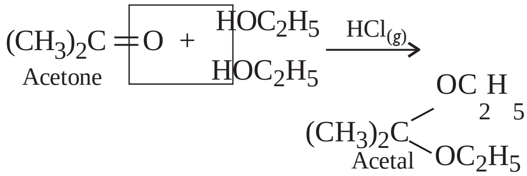
19. (d) :



20. (c) : Aldehyde having no α-hydrogen atoms on heating with concentrated alkali solution (50%) undergoes Cannizzaro's reaction.



21. (d) :

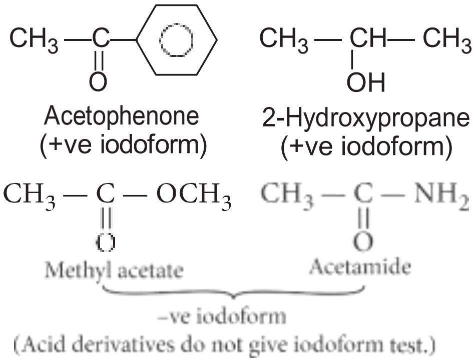


$$\underset{\text{Acetone}}{(CH_3)_2C}\boxed{=O + \begin{matrix}H\\H\end{matrix}}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} \xrightarrow{HCl_{(g)}} \underset{\text{Acetal}}{(CH_3)_2C}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$$

22. (b) : Acetaldehyde, acetone and methyl ketones having CH_3CO— group undergo haloform reaction. Thus, CH_3CHO will give yellow precipitate with I_2 and NaOH but $C_6H_5CH_2CHO$ will not.

23. (d)

24. (a, d) : This example shows iodoform reaction. The compound with $CH_3-\underset{\underset{O}{\|}}{C}-$ or $CH_3-\underset{\underset{OH}{|}}{CH}-$ group will give yellow precipitate of iodoform (CHI_3) when react with iodine and alkali.



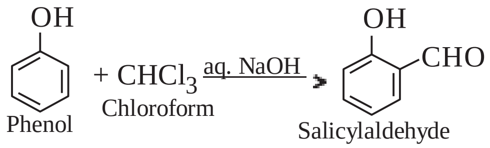
25. (b) : Carbonyl group is reduced to – CH_2 group, when treated with amalgamated zinc and conc. HCl. This process is called Clemmensen's reduction.

$$>C=O \xrightarrow{\text{Zn-Hg/HCl}} >CH_2$$

26. (d) : Greater the number of alkyl / phenyl groups attached to the carbonyl groups lower will be its reactivity I > II > III.

+*R*-effect is stronger than +*I*-effect.

27. (b) : (a) Reimer–Tiemann reaction :



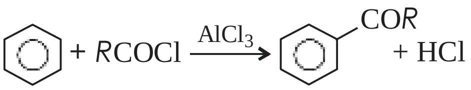
(b) Cannizzaro reaction :

$$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{50\%\ NaOH} \underset{\text{Sodium formate}}{HCOO^- Na^+} + \underset{\text{Methanol}}{CH_3OH}$$

(c) Wurtz reaction :

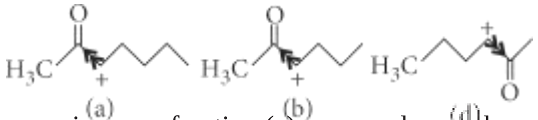
$$\underset{\text{Methyl iodide}}{H_3C-I} + 2Na + I-CH_3 \rightarrow \underset{\text{Ethane}}{CH_3-CH_3} + 2NaI$$

(d) Friedel–Crafts acylation :

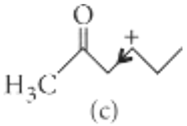


From the above examples it is evident that C—C bond formation does not take place in Cannizzaro reaction.

28. (c) : The ease of dehydration of the given compounds can be explained on the basis of the stability of the carbocation formed. In case of options (a), (b) and (d), a secondary carbocation is formed but the presence of an electron withdrawing $>C=O$ group adjacent to the positively charged carbon, intensifies the charge and hence, destabilises the species.

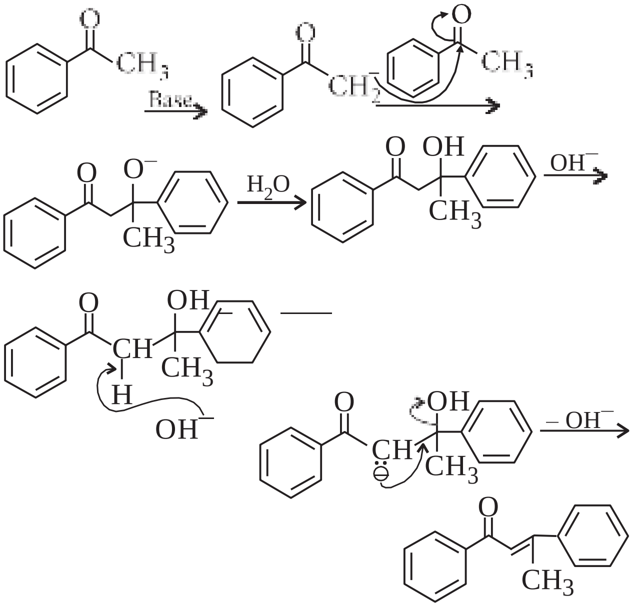


However, in case of option (c), a secondary carbocation is formed, but the electron withdrawing $>C=O$ group is present farther away, as a result, the effect of this group is diminished and hence, the carbocation is relatively more stable.


(c)
More stable

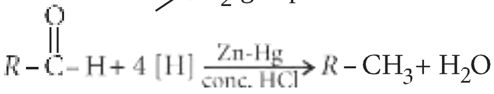
29. (c) : Compounds with $CH_3-\underset{\underset{OH}{|}}{CH}-$ or $CH_3-\underset{\underset{O}{\|}}{C}-$ give positive iodoform hence, (i), (ii) and (iii) will give positive iodoform not (iv).

30. (c) : The first step is a simple condensation reaction. The last step is an example of E1cB mechanism and the leaving group is hydroxide, which is unusual. Still this step manages to take place owing to the stability incorporated therein the product, which is a conjugated carbonyl compound.



31. (a) : The base (OH^-) ion removes one of the α-hydrogen atom (which is some what acidic) from aldehydes and ketones to form a carbanion or the enolate ion. The acidity of α-hydrogen is due to resonance stabilization of enolate anion.

32. (d) : Aldehydes and ketones are converted to alkanes when treated with zinc amalgam and conc. HCl. This is known as Clemmensen reduction. Here $>C=O$ group is reduced to $>CH_2$ group.



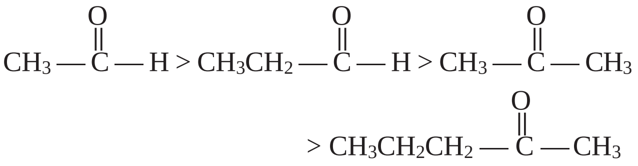
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H+4\,[H]\xrightarrow[\text{conc. HCl}]{\text{Zn-Hg}}R-CH_3+H_2O$$

33. (a) : Aldehydes which do not have α-H atom, in presence of 50% NaOH or 50% KOH undergo disproportionation reaction to produce alcohol and sodium salt of acid. This reaction is known as Cannizzaro reaction. C_6H_5CHO containing no α-H atom undergoes Cannizzaro reaction to produce benzyl alcohol and sodium benzoate.

$$C_6H_5CHO\xrightarrow{50\%\text{ NaOH}}C_6H_5CH_2OH+C_6H_5COONa$$

34. (a) : The aldehydes or ketones containing α-H atom in presence of dilute alkali undergo self condensation reaction to form β-hydroxyaldehyde or β-hydroxyketone. This reaction is known as aldol condensation.

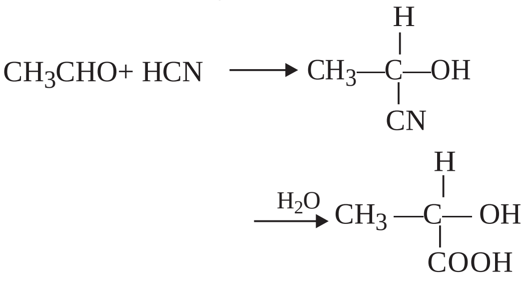
35. (a) : The reactivity of the carbonyl group towards the addition reactions depends upon the magnitude of the positive charge on the carbonyl carbon atom. The introduction of group with –*I* effect increases the reactivity while introduction of alkyl group (+*I* effect) decreases the reactivity.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H>CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H>CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3>CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

+*I*-effect increases, reactivity decreases.

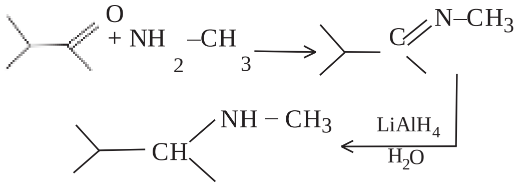
36. (b) :



$$CH_3CHO+HCN\longrightarrow CH_3-\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-OH\xrightarrow{H_2O}CH_3-\underset{\underset{\displaystyle COOH}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-OH$$

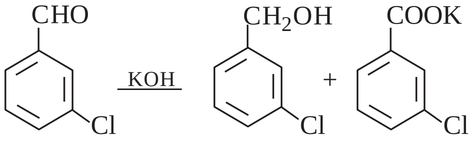
Lactic acid

37. (b) :



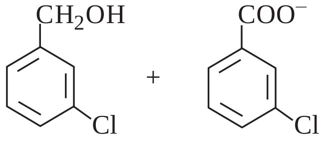
38. (c) : Lactic acid ($CH_3CH(OH)COOH$) is an optically active compound due to the presence of asymmetric carbon atom. It exists in *D*- and *L*-form, the ratio of which is found to be (1 : 1), *i.e.*, a racemic mixture is obtained.

39. (b) :



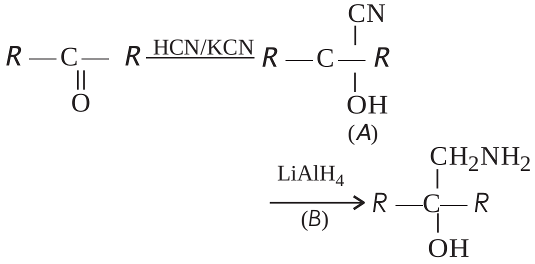
m-chlorobenzaldehyde

or



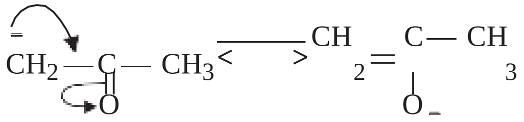
The above reaction is known as Cannizzaro's reaction.

40. (d) :



$$R-\underset{\underset{\displaystyle O}{\|}}{C}-R\xrightarrow{\text{HCN/KCN}}\underset{(A)}{R-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CN}{|}}{C}}-R}\xrightarrow[(B)]{\text{LiAlH}_4}R-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_2NH_2}{|}}{C}}-R$$

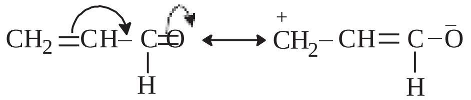
41. (a) : They are resonating forms because the position of the atomic nuclei remains the same and only electron redistribution has occurred.



42. (c) : Tollens' reagent is a solution of ammoniacal silver nitrate and used for the detection of — CHO group. Aldehydes reduce Tollens' reagent and itself gets oxidised to convert Ag^+ ions to Ag powder which forms the silver coloured mirror in the test tube. So, this test is also known as silver mirror test.

$$R-CHO+[Ag(NH_3)_2]^+\rightarrow R-COO^-+\underset{\text{(Powder)}}{Ag}$$

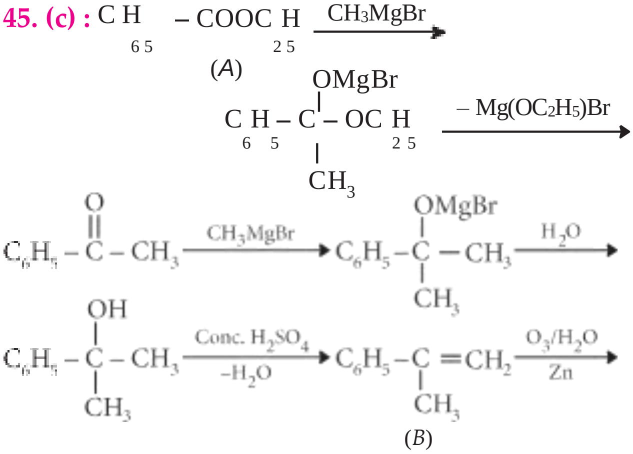
43. (d) : O-atom is more electronegative than C-atom, therefore O-atom bears partial –ve charge and C-atom to which it is attached bear partial +ve charge.



44. (a) : It is a simple condensation reaction which proceeds with elimination of water.

$$R-CH=\boxed{O+H_2}N-NH_2\xrightarrow{-H_2O}RCH=N-NH_2$$

45. (c) :



$C_6H_5-CO-CH_3 \xrightarrow{I_2/NaOH} CHI_3 + C_6H_5-COONa$

(C_8H_8O) Iodoform

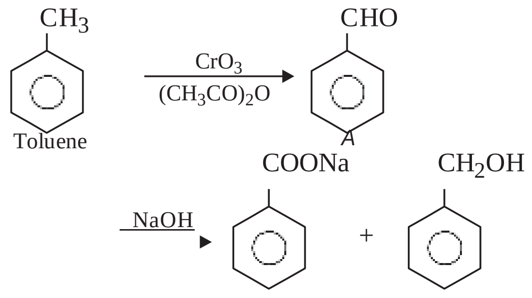
46. (d) : Compounds containing

$CH_3-\underset{\underset{O}{\|}}{C}-$ or $CH_3-\underset{\underset{OH}{|}}{CH}-$ group show iodoform test. So iodoform test is not given by 3-pentanone.

47. (d) : $C_6H_5CHO + 2[H] \xrightarrow{Zn/HCl} C_6H_5CH_2OH$

Benzaldehyde Phenylmethanol (Benzyl alcohol)

48. (a) :



(Cannizzaro product)

49. (a) : Benzaldehyde reacts with primary aromatic amines to form Schiff 's base (Benzylidene aniline).

$C_6H_5HC=O + C_6H_5NH_2 \rightarrow C_6H_5HC=NC_6H_5 + H_2O$

Benzaldehyde Aniline Benzylidene aniline

50. (c) : $CH_3CH_2OH \xrightarrow[-2HCl]{Cl_2} CH_3CHO$

(Ethyl alcohol) (Acetaldehyde)

$\xrightarrow[-3HCl]{3Cl_2} CCl_3CHO$

(Chloral)

(*A*)

$CCl_3CHO \xrightarrow{[O]} CCl_3COOH$

Monocarboxylic acid

(*B*)

The compound '*A*' reduces Fehling's solution thus, it must have free —CHO group.

Thus, the compound *A* is chloral.

51. (d) : Since CH_3CH_2CHO has α-hydrogen atom, therefore it will undergo aldol condensation in the presence of cold dilute alkali.

52. (d) : Acetaldehyde reduces Tollens' reagent to silver mirror.

$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow CH_3COO^-$

(Acetaldehyde) (Tollens' reagent)

$+ 2H_2O + 2Ag + 4NH_3$

(Silver mirror)

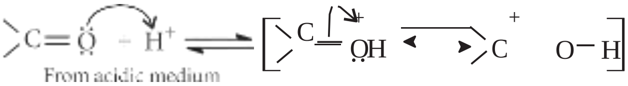
53. (b) : $(CH_3)_2C=CHCOCH_3 \xrightarrow{NaOI} (CH_3)_2C=CHCOOH + CHI_3$

$(NaOH + I_2)$/NaOI is the best suitable reagent for the given reaction.

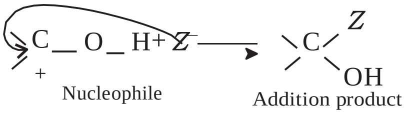
54. (a) : Ketones on oxidation give carboxylic acids with lesser number of carbon atoms *i.e,*

$CH_3COCH_3 \xrightarrow{[O]} CH_3COOH + CO_2 + H_2O$

55. (b) : Acetaldehyde reacts only with nucleophiles. Since the mobile π-electrons of carbon oxygen double bond are strongly pulled towards oxygen, carbonyl carbon is electron deficient and carbonyl oxygen is electron rich. Thus, the electron deficient carbonyl carbon is most susceptible to attack by electron rich nucleophilic reagent, *i.e.*, by base.



The nucleophile, then attacks the protonated carbonyl group to form addition product.

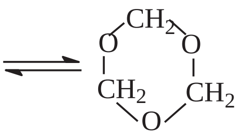


56. (d) : Acetophenone reacts with NaOH and I_2 to give yellow ppt. of CHI_3 but benzophenone ($C_6H_5COC_6H_5$) does not. Hence, it can be used to distinguish between them.

$C_6H_5COCH_3 \xrightarrow{I_2,\ NaOH} CHI_3 + C_6H_5COONa$

yellow ppt.

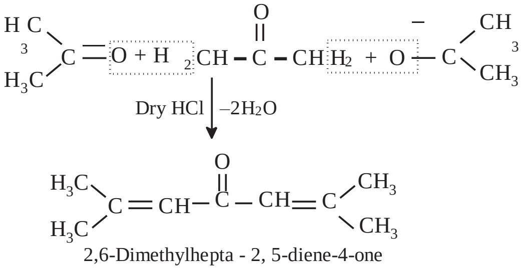
57. (a) : 3HCHO



Trioxane (metaformaldehyde)

58. (d) : Acetoneformsmesitylene (1,3,5-trimethylbenzene) on distillation with conc. H_2SO_4.

59. (a) :



2,6-Dimethylhepta - 2, 5-diene-4-one (phorone)

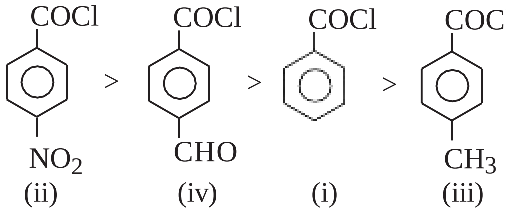
60. (b) : $HCHO + KOH \xrightarrow{50\%\ KOH} HCOOK + CH_3OH$
The above reaction is called as Cannizzaro's reaction.

61. (c) : Formula is an aqueous solution of 40% HCHO.

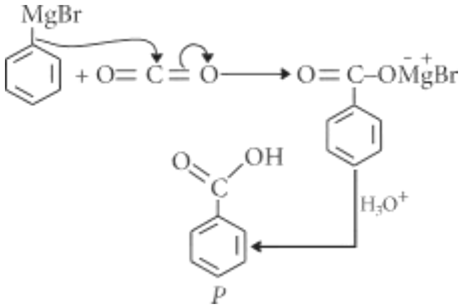
62. (c) : PCC (Pyridium chlorochromate) stops oxidation at the aldehyde stage, thereby preventing the further oxidation of aldehydes to carboxylic acids.

63. (d) : Electron withdrawing groups increase the reactivity towards nucleophilic substitution reaction and $-NO_2$ is a strong electron withdrawing group.

64. (c) : The ease of hydrolysis depends upon the magnitude of the +ve charge on the carbonyl group. Electron withdrawing groups increase the magnitude of positive charge and electron donating groups decrease the magnitude of positive charge. Hence, the decreasing order of reactivity towards hydrolysis is



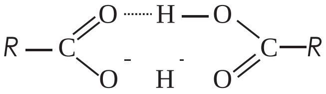
65. (b) :



The product (*P*) is benzoic acid.

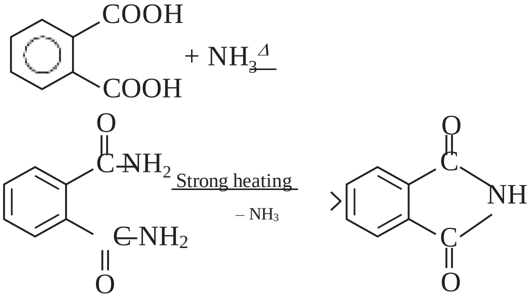
66. (b) : $C_6H_5COCl + H_2O \rightarrow C_6H_5COOH + HCl$
Benzoyl chloride Benzoic acid

67. (d) : Due to the formation of intermolecular H-bonding, association occurs in carboxylic acids.



So, they have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass.

68. (c) :



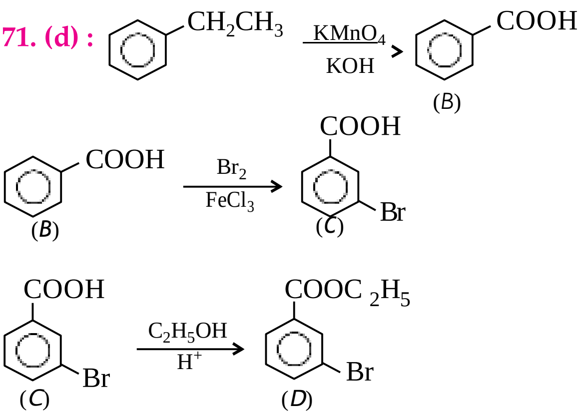
Phthalamide Phthalimide

69. (b) : Acidic strength $\propto -I$ effect
As oxygen is more electron withdrawing (II) and (III) show greater $-I$ effect than (I). Thus, (I) is least acidic. Out of (II) and (III), (II) is more acidic than (III) as distance of O increases from —COOH group and acidic strength decreases.

70. (a) : As $-I$ effect increases, —COOH group becomes more electron deficient and tendency to loose H^+ ions increases *i.e.*, acid strength increases. As $+I$ effect increases, acid strength decreases.
Thus, correct order of acid strength is

$$\underset{(B)}{CF_3COOH} > \underset{(A)}{CCl_3COOH} > \underset{(D)}{HCOOH} > \underset{(C)}{CH_3COOH}$$

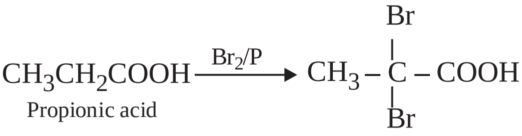
71. (d) :



72. (d) : The compound will be CH_3CH_2COOH.

$$\begin{tikzcd} \underset{A}{CH_3CH_2COOH} \arrow[r, "NH_3"] & \underset{B}{CH_3CH_2COONH_4} \arrow[d, "\Delta"] \\ \underset{\text{Ethyl amine}}{CH_3-CH_2-NH_2} & CH_3CH_2CONH_2 \arrow[l, "Br_2/KOH"'] \end{tikzcd}$$

73. (c) : This is Hell–Volhard–Zelinsky reaction. In this reaction, acids containing α-H react with X_2/red P giving product in which the α-hydrogens are substituted by X.

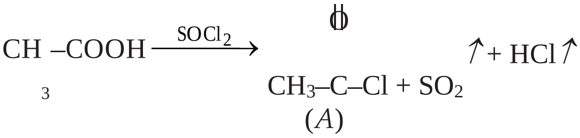


$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow{Br_2/P} CH_3-\underset{Br}{\overset{Br}{C}}-COOH$$

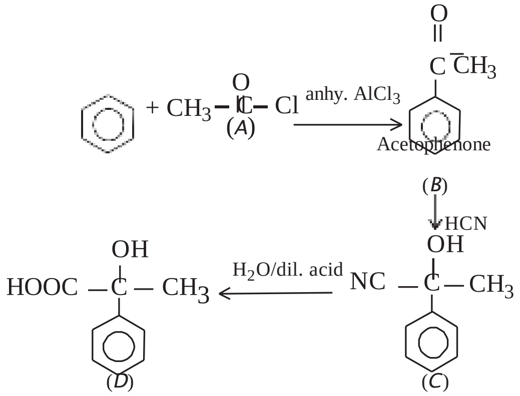
74. (c) : $FCH_2COOH > ClCH_2COOH$
$> BrCH_2COOH > CH_3COOH$

Acidity decreases as the $-I$ effect of the group decreases, F is the most electronegative atom and hence it has highest $-I$ effect among the halogens.

75. (d) :



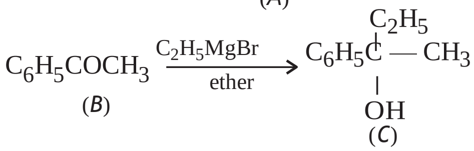
$$CH_3-COOH \xrightarrow{SOCl_2} \underset{(A)}{CH_3-\overset{O}{\overset{\|}{C}}-Cl} + SO_2\uparrow + HCl\uparrow$$



76. (a) : $ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$
$RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$

77. (b) : Carboxylic acid is much stronger than water and alcohol. Since the carboxylate ion after the removal of proton is stabilised by resonating structures. The — OH in alcohols is almost neutral. Acetylene is also weakest acid among the given examples.

78. (d) : $CH_3COOH + PCl_5 \longrightarrow \underset{(A)}{CH_3COCl} \xrightarrow[\text{anhy. }AlCl_3]{C_6H_6}$



$$\underset{(B)}{C_6H_5COCH_3} \xrightarrow[\text{ether}]{C_2H_5MgBr} \underset{(C)}{C_6H_5\overset{C_2H_5}{\underset{OH}{C}}—CH_3}$$

79. (b) : Ethyl benzoate can be prepared by heating benzoic acid with ethyl alcohol in presence of dry HCl or conc. H_2SO_4. The reaction is called as esterification reaction.

$$C_6H_5–COOH + C_2H_5–OH \xrightarrow[-H_2O]{\text{dry HCl}} \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5}$$

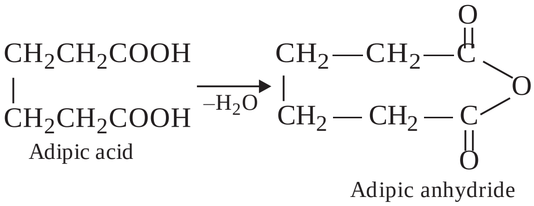
80. (a) : Reduction of hydrolysed product of ester by $LiAlH_4$ produces two alcohols.

$$R – COOR' \xrightarrow{H_2O} R – COOH + R'OH$$

$$\xrightarrow[\text{ether}]{LiAlH_4} R – CH_2OH + R'OH$$

81. (a) : $NaHCO_3$ is weakly basic, so it can only react with the acid CH_3COOH. While phenol is weakly acidic and *n*-hexanol is neutral, they do not react with $NaHCO_3$.
$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 + H_2O$

82. (a) :



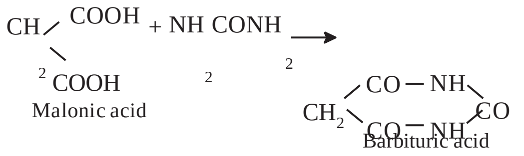
83. (c) : $\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$

84. (d) : $C_6H_5COOH \xrightarrow{\text{Soda-lime}(X)} C_6H_6 + Na_2CO_3$

$C_6H_5OH \xrightarrow{\text{Zn dust }(Y)} C_6H_6 + ZnO$

85. (d) : Carboxylic acids dissolve in $NaHCO_3$ but phenols do not.

86. (c) :



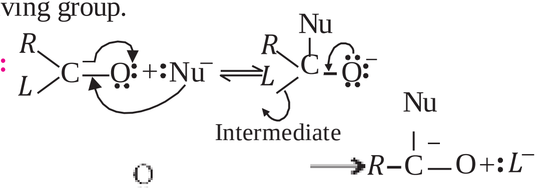
87. (c) : Strongest acid is $CH_2ClCOOH$ as –*I* effect of Cl atom decreases with the increase in distance.

88. (a) : +*I* effect of the alkyl group increases from CH_3 to CH_3CH_2 to $CH_3CH_2CH_2$ to $CH_3CH_2CH_2CH_2$, resulting in decrease of acid character. Therefore, the order is (i) > (ii) > (iii) > (iv).

89. (d)

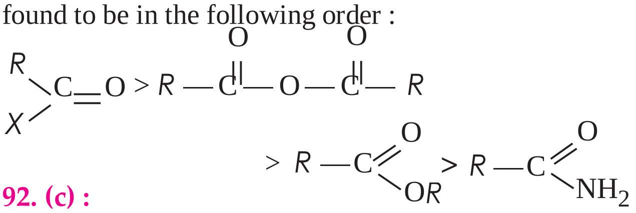
90. (d) : CH_3COCl is most susceptible to nucleophilic attack. The susceptibility of a substrate towards nucleophilic attack depends on how good a leaving group is attached to it. Cl^- is a weak base and therefore, a good leaving group.

91. (c) :



$(L = X^-, NH_2^-, O^-—\overset{O}{\overset{\|}{C}}—R \text{ or } O^-R)$

The relative reactivities of various compounds have been found to be in the following order :



92. (c) : Ethyl acetate undergoes Claisen condensation in presence of sodium ethoxide involving α-hydrogen atom in which two molecules of ethyl acetate combine together to form acetoacetic ester.

$$CH_3COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa} \underset{\text{Acetoacetic ester}}{CH_3COCH_2COOC_2H_5} + C_2H_5OH$$

93. (b) : The esters having active methylene group (– CH_2 –), show Claisen condensation reaction. As C_6H_5 – $COOC_2H_5$ has no α-hydrogen atom or active methylene group, so it cannot undergo Claisen condensation reaction.

94. (b) :

$$2HCOONa \longrightarrow \underset{\text{Sodium oxalate}}{\begin{matrix}COONa\\|\\COONa\end{matrix}} + H_2$$