Aldehydes, Ketones and Carboxylic Acids

1. Which of the following compounds will give a ketone on oxidation with chromic anhydride (CrO_3) ? (2024)

(A) $(CH_3)_2CH — CH_2OH$

(B) $CH_3CH_2CH_2OH$

(C) $(CH_3)_3C — OH$

(D) $CH_3 — CH_2 — CH — CH_3$
with OH on CH (|OH)

Ans. (D) $CH_3 — CH_2 — CH — CH_3$
with OH on CH (|OH)

2. Acetic acid reacts with PCl_5 to give : (2024)

(A) $Cl — CH_2 — COCl$

(B) $Cl — CH_2 — COOH$

(C) $CH_3 — COCl$

(D) $CCl_3 — COOH$

Ans. (C) $CH_3 — COCl$

3. The formation of cyanohydrin from an aldehyde is an example of : (2024)

(A) nucleophilic addition

(B) electrophilic addition

(C) nucleophilic substitution

(D) electrophilic substitution

Ans. (A) nucleophilic addition

4. two statements are given - one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (A), (B), (C) and (D) as given below. (2024)

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

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(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is notthe correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Assertion (A) : The pK_a of ethanoic acid is lower than that of Cl - CH_2 - COOH.

Reason (R) : Chlorine shows electron withdrawing (I) effect which increases the acidic character of Cl - CH_2 - COOH.

Ans. (D) Assertion (A) is false, but Reason (R) is true.

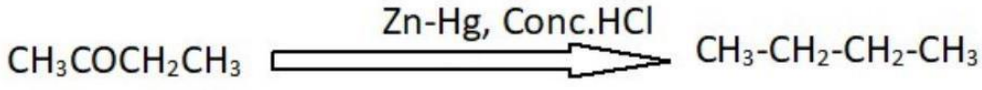
5. Write the chemical equation when : (2024)

(a) Butan-2-one is treated with Zn(Hg) and conc. HCl.

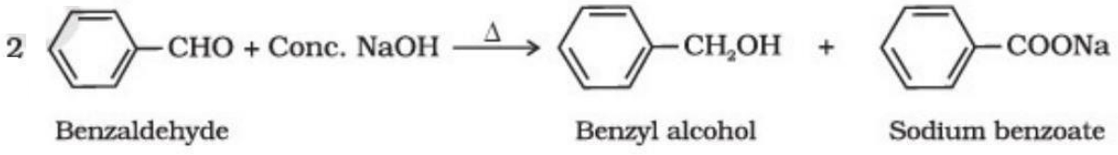
(b) Two molecules of benzaldehyde are treated with conc. NaOH.

Ans.

(a)



(b)



6. Compound (A) ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ gives two compounds (B) and (C). The compound (B) on oxidation with PCC gives compound (D) which upon treatment with dilute NaOH and subsequent heating gives compound (E). Compound (E) on catalytic hydrogenation gives compound (C). The compound (D) is oxidized further to give compound (F) which is found to be a monobasic acid (Molecular weight = 60). Identify the compounds (A), (B), (C), (D), (E) and (F). (2024)

Ans.

(A) → $CH_3\ CH_2\ CH_2\ COO\ CH_2\ CH_3$ / $CH_3\ COOCH_2CH_2\ CH_2\ CH_3$

(B) → $CH_3\ CH_2\ OH$

(C) → $CH_3\ CH_2\ CH_2\ CH_2\ OH$

(D) → $CH_3\ CHO$

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(E) → $CH_3 - CH = CH — CHO$

(F) → CH_3COOH (Either structure or name of A to F)

7. (i) Account for the following : (2024)

(1) The melting and boiling points of Zn, Cd and Hg are low.

Ans. Because of the absence of unpaired electrons in their d-orbitals resulting in weak bonding between the atoms/ due to presence of fully filled d-orbitals, weak metallic bonding takes place.

(2) Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing.

Ans.

Because Cr is more stable in +3 due to stable t_{2g}^3 configuration while Mn is more stable in +2 due to stable d^5 configuration.

(3) E^o value of Cu^{2+}/Cu is + 0·34 V.

Ans.

Because of high ΔaH^0 and low $\Delta_{hyd}H^0$, E^O value for Cu is positive.

(ii) Complete and balance the following chemical equations :

(1) $KMnO_4 \xrightarrow{heat}$

(2) $Cr_2O_7^{2-} + 6\,I^- + 14\,H^+ \longrightarrow$

Ans.

1. $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

2. $Cr_2O_7^{2-} + 6I^- + 14\,H^+ \rightarrow 2\,Cr^{3+} + 3I_2 + 7H_2O$

8. (i) Out of Cu_2Cl_2 and $CuCl_2$, which is more stable in aqueous solution and why?

(ii) Write the general electronic configuration of f-block elements.

(iii) Predict which of the following will be coloured in aqueous solution and why?

Sc^{3+}, $Fe3^+$, Zn^{2+}

[Atomic number : Sc = 21, Fe = 26, Zn = 30]

(iv) How can you obtain potassium dichromate from sodium chromate ?

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(v) Why do transition metals and their compounds show catalytic activities ?

(2024)

Ans.

(i) $CuCl_2$ is more stable than Cu_2Cl_2 as Cu^{+2} is more stable than Cu^+ due to high $\Delta_{hyd}H^0$/ Cu^+ in aqueous solution undergoes disproportionation, i.e., $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

(ii) $(n-2)f^{1-14}(n-1)d^{o-1}ns^2$

(iii) Fe^{3+}, presence of unpaired electron leading to d-d transition.

(iv) $2Na_2CrO_4 + 2\ H^+ \rightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$

$Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$

(v) Because of their ability to show variable oxidation states and complex formation / provide large surface area.

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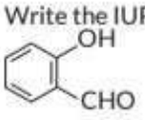
Previous Years' CBSE Board Questions

8.1 Nomenclature and Structure of Carbonyl Group

VSA (1 mark)

1. Write the structure of 2-methylbutanal. *(1/5, AI 2015)*
2. Draw the structure of 3-methylpentanal. *(Delhi 2015C)*
3. Write the IUPAC name of the following :
   $CH_3—CH_2—CHO$ *(AI 2015C)*
4. Write the IUPAC name of the compound :
   $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-\overset{\overset{O}{||}}{C}-CH_3$ *(Delhi 2014)* Ap
5. Write the structure of 4-chloropentan-2-one. *(AI 2014)*
6. Write the IUPAC name of the following compound :
   

   (Foreign 2014)

SA I (2 marks)

7. Draw the structures of the following :
   (i) *p*-Methylbenzaldehyde
   (ii) 4-Methylpent-3-en-2-one *(2/5, AI 2015C)*

8.2 Preparation of Aldehydes and Ketones

VSA (1 mark)

8. What happens when benzene is treated with CH_3COCl in presence of anhydrous $AlCl_3$? *(1/2, 2020)* U
9. How can you convert the following : Benzene to acetophenone? *(1/3, 2020)*
10. Complete the following reaction :
    $(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow$ *(1/3, Delhi 2019)*
11. Write chemical equation for the following reaction:
    Benzoyl chloride is hydrogenated in presence of $Pd/BaSO_4$. *(1/3, Delhi 2019, 1/5, 2018C)*
12. Write the equation involved in the following reaction:
    Etard reaction. *(1/2, Delhi 2017)* R
13. Write the reaction involved in the following :
    Stephen reduction. *(1/5, AI 2017)*
14. Write the product in the following reaction :
    $CH_3-CH=CH-CN \xrightarrow[(b)\ H_2O]{(a)\ DIBAL\text{-}H}$? *(1/5, AI 2017)*

    OR

    Write the product in the following reaction :
    $CH_3-CH=CH-CH_2CN \xrightarrow[(ii)\ H_2O]{(i)\ DIBAL\text{-}H}$ *(1/5, Delhi 2016)*
15. How do you convert the following :
    Ethyne to ethanal *(1/3, Foreign 2015)* An

SA I (2 marks)

16. Write the major product(s) in the following :
    (i) $CH_3-CH=CH-CH_2-CN \xrightarrow[(ii)\ H_3O^+]{(i)\ DIBAL\text{-}H}$
    (ii) $CH_3-CH_2-OH \xrightarrow{CrO_3}$ *(2/5, 2020)*
17. Write the equations involved in the following reactions :
    (i) Stephen reaction
    (ii) Etard reaction *(2/3, Foreign 2015)*

8.4 Chemical Reactions

MCQ

18. **Assertion :** The final product in Aldol condensation is always α, β-unsaturated carbonyl compound.
    Reason : α, β-unsaturated carbonyl compounds are stabilised due to conjugation.
    (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A)
    (b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A)
    (c) Assertion (A) is true, but Reason (R) is False.
    (d) Assertion (A) is false, but Reason (R) is true. *(2023)*
19. Iodoform test is not given by
    (a) ethanol (b) ethanal
    (c) pentan-2-one (d) pentan-3-one *(2020)* Ap
20. **Assertion (A) :** Reactivity of ketones is more than aldehydes.
    Reason (R) : The carbonyl carbon of ketones is less electrophilic as compared to aldehydes.
    (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
    (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
    (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
    (d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*
21. **Assertion (A) :** Oxidation of ketones is easier than aldehydes.
    Reason (R) : C-C bond of ketones is stronger than C-H bond of aldehydes.
    (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
    (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
    (c) Assertion (A) is correct, but Reason (R) is wrong statement.
    (d) Assertion (A) is wrong, but Reason (R) is correct statement. *(2020)* An

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VSA (1 mark)

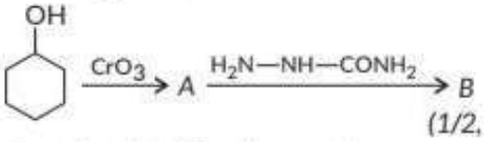
22. What happens when,
propanone is treated with methyl magnesium iodide and then hydrolysed? *(1/2, 2020)*

23. How can you convert the following : Acetone to propene ? *(1/3, 2020)* An

OR

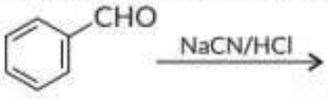
Do the following conversion in not more than two steps:
Propanone to propene *(1/3, Delhi 2017)*

24. Write structures of compounds *A* and *B* in the following reaction :



(1/2, Delhi 2019)

25. Complete the following reaction :



(1/3, Delhi 2019)

26. How do you convert the following :
Ethanal to propanone *(1/2, 2018)*

27. Give simple chemical tests to distinguish between the following pair of compounds :
Ethanal and propanal *(1/5, 2018C)*

28. Give chemical tests to distinguish between the following pair of compounds :
Benzaldehyde and acetophenone.
(1/5, AI 2017C, 1/5, Delhi 2015C)

OR

Distinguish between the following :
$C_6H_5—COCH_3$ and $C_6H_5—CHO$
(1/2, AI 2016, 1/5, AI 2015)

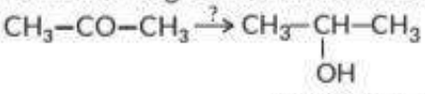
29. Write the structures of *A* and *B* in the following reaction :
$CH_3COCl \xrightarrow{H_2, Pd-BaSO_4} A \xrightarrow{H_2N—OH} B$ *(1/5, AI 2016)*

30. Give a simple chemical test to distinguish between the following pair of compounds :
CH_3CH_2CHO and $CH_3CH_2COCH_3$
(1/2, AI 2016, 1/5, AI 2015)

OR

Give simple chemical tests to distinguish between the following pair of compounds :
Propanal and butan-2-one *(1/5, Foreign 2014)*

31. Name the reagent used in the following reaction :



(Delhi 2015, 1/2, Foreign 2015)

32. Give simple chemical tests to distinguish between the following pairs of compounds :
(i) Benzaldehyde and benzoic acid
(ii) Propanal and propanone. *(1/5, Delhi 2014)* An

OR

Give simple chemical tests to distinguish between the following pair of compounds :
Propanal and propanone *(1/5, AI 2014)*

33. Account for the following :
CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. *(Delhi 2014)*

SA I (2 marks)

34. Write the products formed when benzaldehyde reacts with the following reagents (Any two) :
(i) CH_3CHO in presence of dilute NaOH
(ii) $H_2N—OH$ in presence of weak acid
(iii) Tollens' reagent *(Term II, 2021-22)* R

35. Explain the following reactions:
(a) Wolff-Kishner reduction
(b) Cannizzaro reaction *(Term II, 2021-22)*

36. Write chemical equations for the following reactions:
(i) Propanone is treated with dilute $Ba(OH)_2$.
(ii) Acetophenone is treated with Zn(Hg)/Conc. HCl
(2/3, Delhi 2019)

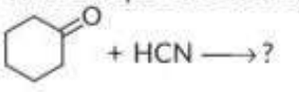
37. Write the structure of major product(s) in the following:

(i) $CH_3—CH_2—\underset{\underset{O}{\|}}{C}—H \xrightarrow[\text{(b) KOH, glycol/heat}]{\text{(a) } H_2N—NH_2}$

(ii) $CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CHO \xrightarrow{\text{conc. NaOH}}$

(2/5, AI 2019)

38. (a) Write the product in the following reaction :



(b) Give simple chemical test to distinguish between the following pair of compounds :
Butanal and Butan-2-one *(2/5, AI 2017)*

39. Write the equations involved in the following reactions :
(i) Clemmensen reduction
(ii) Cannizzaro reaction *(Delhi 2017)*

40. Predict the products of the following reactions :

(i) $CH_3—\underset{\underset{CH_3}{|}}{C}=O \xrightarrow[\text{(ii) KOH/Glycol, } \Delta]{\text{(i) } H_2N—NH_2} ?$

(ii) $C_6H_5—CO—CH_3 \xrightarrow{NaOH/I_2} ? + ?$ *(2/3, Delhi 2015)*

41. A compound 'A' of molecular formula C_2H_3OCl undergoes a series of reactions as shown below. Write the structures of *A*, *B*, *C* and *D* in the following reactions :
$(C_2H_3OCl)A \xrightarrow{H_2/Pd\text{-}BaSO_4} B \xrightarrow{\text{dil. NaOH}} C \xrightarrow{\text{Heat}} D$
(AI 2015) Ap

42. Describe the following reactions :
(i) Acetylation
(ii) Aldol condensation *(2/5, Delhi 2015C)*

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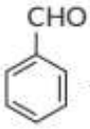
43. Write the main product in the following equations :

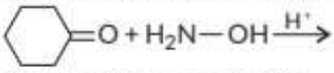
(i) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} ?$

(ii)  $\xrightarrow[273\text{-}283K]{HNO_3/H_2SO_4} ?$ *(2/5, Delhi 2015C)*

44. Draw the structures of the following derivatives :

(i) Propanone oxime

(ii) Semicarbazone of the CH_3CHO *(2/5, AI 2015C)*

45. (i) 

(ii) $2C_6H_5CHO + \text{conc. NaOH} \longrightarrow$ *(2/5, Delhi 2014)*

46. Account for the following :

(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.

(ii) There are two $-NH_2$ groups in semicarbazide ($H_2NNHCONH_2$).
However, only one is involved in the formation of semicarbazone. *(2/5, Foreign 2014)* Ev

47. Write the chemical equation to illustrate each of the following name reactions :

(i) Rosenmund reduction

(ii) Cannizzaro reaction *(2/5, Foreign 2014)*

SA II (3 marks)

48. An organic compound '*A*' having the molecular formula C_3H_8O on treatment with Cu at 573 K, gives '*B*'. '*B*' does not reduce Fehling's solution but gives a yellow precipitate of the compound '*C*' with I_2/NaOH. Deduce the structures of *A*, *B* and *C*. *(2023)*

49. Write the equation involved in the following reactions :

(i) Rosenmund reduction

(ii) Etard reaction

(iii) Stephen reaction *(Term-II, 2021-22)*

50. (i) Which will undergo faster nucleophilic addition reaction – Acetaldehyde or propanone?

(ii) What is the composition of Fehling's reagent ?

(iii) Draw structure of the semicarbazone of ethanal
(Term II, 2021-22) R

51. What happens when

(i) Propanone is treated with CH_3MgBr and then hydrolysed ?

(ii) Ethanal is treated with excess ethanol and acid?

(iii) Methanal undergoes Cannizzaro reaction ?
(Term II, 2021-22) Ev

52. An organic compound '*X*' with the molecular formula $C_5H_{10}O$ forms 2,4-DNP derivative, does not reduce Tollens' reagent but gives positive iodoform test on heating with I_2 in the presence of NaOH. Compound '*X*' gives ethanoic acid and propanoic acid on vigorous oxidation. Write the

(i) Structure of the compound '*X*'.

(ii) Structure of the product obtained when compound '*X*' reacts with 2,4-DNP reagent.

(iii) Structures of the products obtained when compound '*X*' is heated with I_2 in the presence of NaOH. *(Term II, 2021-22)* Ap

53. Write the products formed when $(CH_3)_3C-CHO$ reacts with the following reagents :

(i) CH_3COCH_3 in the presence of dilute NaOH

(ii) HCN

(iii) Conc. NaOH *(2020)*

54. (a) How can you distinguish between propanal and propanone?

(b) Draw structures of the following derivatives :

(i) Cyanohydrin of cyclobutanone

(ii) Hemiacetal of ethanal *(3/5, 2020)*

55. An alkene *A* with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds, *B* and *C*. Compound *B* gives positive Fehling's test and also reacts with iodine and NaOH solution. Compound *C* does not give Fehling solution test but forms iodoform. Identify the compounds *A*, *B* and *C*.
(3/5, AI 2019) Ap

56. (*A*), (*B*) and (*C*) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (*A*) and (*C*) give positive Tollens' test whereas isomer (*B*) does not give Tollens' test but gives positive iodoform test. Isomers (*A*) and (*B*) on reduction with Zn(Hg)/conc. HCl give the same product (*D*).

(a) Write the structures of (*A*), (*B*), (*C*) and (*D*).

(b) Out of (*A*), (*B*) and (*C*) isomers, which one is least reactive towards addition of HCN?
(2018) Ev

57. (a) Write the chemical equation for the reaction involved in Cannizzaro reaction.

(b) Draw the structure of the semicarbazone of ethanal.

(c) How can you distinguish between propanal and propanone? *(3/5, Delhi 2016)*

58. (a) Write the chemical reaction involved in Wolff-Kishner reduction.

(b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction.
$C_6H_5COCH_3$, CH_3CHO, CH_3COCH_3

(c) *A* and *B* are two functional isomers of compound C_3H_6O. On heating with NaOH and I_2, isomer *B* forms yellow precipitate of iodoform whereas isomer *A* does not form any precipitate. Write the formulae of *A* and *B*. *(3/5, AI 2016)*

59. Write the structures of the main products when acetone ($CH_3-CO-CH_3$) reacts with the following reagents :

(i) $Zn-Hg$/conc. HCl

(ii) $H_2N-NHCONH_2/H^+$

(iii) CH_3MgBr and then H_3O^+ *(3/5, AI 2015)*

60. How will you convert ethanal into the following compounds? Give the chemical equations involved.

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(i) $CH_3—CH_3$

(ii) $CH_3—\underset{\underset{OH}{|}}{CH}—CH_2—CHO$

(iii) CH_3CH_2OH *(3/5, Delhi 2015C)*

61. Write the chemical equations to illustrate the following name reactions :
(i) Wolff-Kishner reduction
(ii) Aldol condensation
(iii) Cannizzaro reaction *(3/5, Delhi 2014)*

62. Write the products formed when CH_3CHO reacts with the following reagents :
(i) HCN (ii) $H_2N—OH$
(iii) CH_3CHO in the presence of dilute NaOH
(3/5, AI 2014)

63. (a) Write the chemical equations to illustrate the following name reactions :
(i) Rosenmund reduction
(ii) Cannizzaro reaction
(b) Out of $CH_3CH_2—CO—CH_2—CH_3$ and $CH_3CH_2—CH_2—CO—CH_3$, which gives iodoform test? *(3/5, AI 2014)*

64. Write the products formed when ethanal reacts with the following reagents :
(i) CH_3MgBr and then H_3O^+
(ii) Zn-Hg/conc. HCl
(iii) C_6H_5CHO in the presence of dilute NaOH
(3/5, Foreign 2014) Ap

LA (5 marks)

65. (i) Carry out the following conversions :
(1) Ethanal to But-2-en-1-al
(2) Propanoic acid to 2-chloropropanoic acid
(ii) An alkene with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling test and also reacts with iodine and NaOH solution. Compound 'C' does not give Fehling solution test but forms iodoform. Identify the compounds 'A', 'B' and 'C'. *(2023)*

66. (i) Write the reaction involved in Cannizzaro's reaction.
(ii) Why are the boiling point of aldehydes and ketones lower than that of corresponding carboxylic acids?
(iii) An organic compound 'A' with molecular formula $C_5H_8O_2$ is reduced to *n*-pentane with hydrazine followed by heating with NaOH and glycol. 'A' forms a dioxime with hydroxylamine and gives a positive iodoform and Tollen's test. Identify 'A' and give its reaction for Iodoform and Tollen's test. *(2023)*

67. A compound 'A' (C_2H_4O) on oxidation gives 'B' ($C_2H_4O_2$). 'A' undergoes iodoform reaction to give yellow precipitate and reacts with HCN to form the compound 'C'. 'C' on hydrolysis gives 2-hydroxypropanoic acid. Identify the compounds 'A', 'B' and 'C'. Write down equations for the reactions involved.
(Term II, 2021-22) An

68. (a) An organic compound (A) having molecular formula C_4H_8O gives orange red precipitate with 2, 4-DNP reagent. It does not reduce Tollens' reagent but gives yellow precipitate of iodoform on heating with NaOH and I_2. Compound (A) on reduction with $NaBH_4$ gives compound (B) which undergoes dehydration reaction on heating with conc. H_2SO_4 to form compound (C). Compound (C) on ozonolysis gives two molecules of ethanal. Identify (A), (B) and (C) and write their structures. Write the reactions of compound (A) with (i) $NaOH/I_2$ and (ii) $NaBH_4$.
(b) Give reason :
(i) Oxidation of propanal is easier than propanone.
(ii) α-Hydrogen of aldehydes and ketones is acidic in nature. *(2020)* An

8.6 Nomenclature and Structure of Carboxyl Group

MCQ

69. What is the correct IUPAC name of the given compound?

$$CH_3—\underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2—CH_3$$

(a) 2,2-Dimethylbutanoic acid
(b) 2-Carboxyl-2-methylbutane
(c) 2-Ethyl-2-methylpropanoic acid
(d) 3-Methylbutanecarboxylic acid *(2020)*

VSA (1 mark)

70. Write the IUPAC name of the compound :

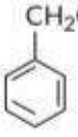
$$CH_3—\underset{\underset{OH}{|}}{CH}—CH_2—COOH$$

(Delhi 2014)

8.7 Methods of Preparation of Carboxylic Acids

VSA (1 mark)

71. Write structures of compounds A and B in each of the following reaction.



$$\xrightarrow[\Delta]{KMnO_4—KOH} A \xrightarrow{H_3O^+} B$$

(1/2, Delhi 2019) An

72. How do you convert the following :
Toluene to benzoic acid? *(1/2, 2018)*

73. Do the following conversion in not more than two steps :
Ethyl benzene to benzoic acid *(1/3, Delhi 2017)*

74. Name the reagent used in the following reaction :

$$C_6H_5—CH_2—CH_3 \xrightarrow{?} C_6H_5—COO^-K^+$$

(1/2, Delhi 2015)

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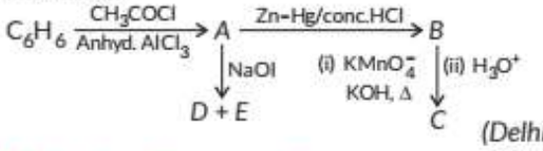
LA (5 marks)

75. Write the structures of A, B, C, D and E in the following reactions :



(Delhi 2016)

8.8 Physical Properties

VSA (1 mark)

76. Arrange the following in the increasing order of their boiling points.
CH_3CHO, CH_3COOH, CH_3CH_2OH
(1/5, AI 2016, 2015)

8.9 Chemical Reactions

MCQ

77. Which one of the following has lowest pK_a value?
(a) CH_3-COOH
(b) O_2N-CH_2-COOH
(c) $Cl-CH_2-COOH$
(d) HCOOH *(2023)*

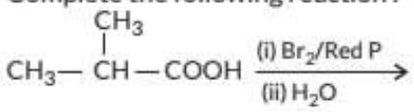
78. **Assertion :** Benzoic acid does not give Friedel-Crafts reaction.
Reason : The carboxyl group is deactivating and gets bonded to Lewis acid $AlCl_3$.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2021 C)* U

79. **Assertion (A) :** Benzoic acid does not undergo Friedal-Crafts reaction.
Reason (R) : The carboxyl group is activating and undergoes electrophilic substitution reaction.
(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
(c) Assertion (A) is correct, but Reason (R) is incorrect statement.
(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

VSA (1 mark)

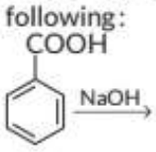
80. Arrange the following in the increasing order of the property mentioned :
(a) CH_3COOH, $ClCH_2COOH$, FCH_2COOH
(Acid strength)
(b) CH_3CHO, CH_3CH_2OH, $CH_3CH_2CH_3$
(Boiling points) *(Term II, 2021-22)*

81. Complete the following reaction :



(1/3, Delhi 2019)

82. Write the structure of major product(s) in the following :



(1/5, AI 2019)

83. Carry out the following conversions :
Propanoic acid to acetic acid. *(1/5, AI 2019)*

84. Do the following conversion in not more than two steps :
Benzoic acid to benzaldehyde.
(1/3, Delhi 2017, 1/5 Delhi 2015C)

85. Why carboxylic acid does not give reactions of carbonyl group? *(1/5, AI 2017C, 1/5, AI 2016)* An

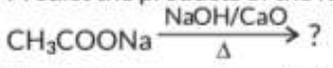
OR

Account for the following :
Carboxylic acids do not give reactions of carbonyl group. *(1/5, AI 2014)*

86. Give simple chemical tests to distinguish between the following pairs of compounds :
Benzoic acid and ethyl benzoate
(1/5, AI 2017C, 1/3, Foreign 2014)

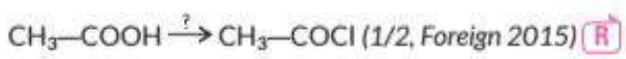
87. Distinguish between
CH_3COOH and HCOOH *(1/2, AI 2016)*

88. Predict the products of the following reaction :



(1/3, Delhi 2015)

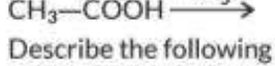
89. Name the reagent used in the following reaction :



(1/2, Foreign 2015) R

OR

Write the main product in the following equation :



(1/5, Delhi 2015C)

90. Describe the following giving chemical equation :
Decarboxylation reaction *(1/5, Delhi 2015C)*

91. Give simple chemical test to distinguish between the following pair of compounds :
Benzoic acid and phenol *(1/5, AI 2014)*

92. Write the chemical equation to illustrate the following name reaction :
Hell-Volhard-Zelinsky reaction
(1/5, Foreign 2014)

SA I (2 marks)

93. How will you carry out the following conversions : (Any two)
(i) Propanal to Propane
(ii) Ethanal to but-2-enal
(iii) Ethanoic acid to ethanamide *(Term II, 2021-22)*

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94. Predict the reagent for carrying out the following transformations: (Any two)
(i) Benzoyl chloride to benzaldehyde
(ii) Ethanal to 3-hydroxy butanal
(iii) Ethanoic acid to 2-chloroethanoic acid
(Term II, 2021-22)

95. Arrange the following compounds in the increasing order of their property indicated : (Any two)
(i) Acetaldehyde, Benzaldehyde, Acetophenone, Acetone (Reactivity towards HCN)
(ii) $(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$ (Acidic strength)
(iii) CH_3CH_2OH, CH_3CHO, CH_3COOH (Boiling point)
(Term II, 2021-22) Ap

96. Write reasons for the following statements :
(i) Benzoic acid does not undergo Friedel-Crafts reaction.
(ii) Oxidation of aldehydes is easier than that of ketones. *(Term II, 2021-22)* Ev

97. Give reasons for the following statements : (Any two)
(i) Benzaldehyde is less reactive than propanal in nucleophilic addition reactions.
(ii) Carboxylic acids do not give reactions of carbonyl group.
(iii) 4-Nitrobenzoic acid is a stronger acid than benzoic acid. *(Term II, 2021-22)*

98. (i) Which acid of the following pair would you expect to be stronger ?
$F-CH_2-COOH$ or CH_3-COOH
(ii) Arrange the following compounds in increasing order of their boiling points :
CH_3CH_2OH, CH_3-CHO, CH_3-COOH
(iii) Give simple chemical test to distinguish between benzaldehyde and acetophenone.
(Term II, 2021-22)

99. (a) Arrange the following compounds in the increasing order of their acidic strength :
$F-CH_2-COOH, NO_2-CH_2-COOH, C_6H_5-COOH$

(b) Write the IUPAC name of the given compound :

$$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$$

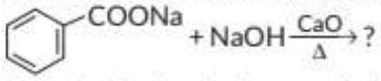
(Term II, 2021-22C)

100. Arrange the following in the increasing order of their property indicated :
(a) Ethanal, Propanone, Propanal, Butanone (reactivity towards nucleophilic addition)
(b) 4-Nitrobenzoic acid, benzoic acid, 3, 4-Dinitrobenzoic acid
4-Methoxy benzoic acid (Acid strength)
(Term II, 2021-22)

101. Account for the following :
(a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.
(b) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid. *(2018)*

102. Write the reactions involved in the following :
(i) Hell–Volhard–Zelinsky reaction
(ii) Decarboxylation reaction *(Delhi 2017)*

103. (a) Write the product in the following reaction :



(b) Give simple chemical test to distinguish between the following pair of compounds :
Benzoic acid and phenol *(2/5, AI 2017)*

104. How will you convert the following in not more than two steps :
(i) Acetophenone to benzoic acid
(ii) Ethanoic acid to 2-hydroxyethanoic acid
(2/5, AI 2017)

105. (a) Write the product of the following reaction :

(b) Give simple chemical test to distinguish between the following pair of compounds :
Benzaldehyde and benzoic acid *(2/5, Delhi 2014)*

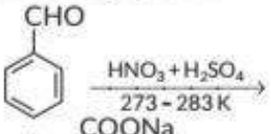
106. Account for the following :
$Cl-CH_2COOH$ is a stronger acid than CH_3COOH.
(2/5, AI 2014)

SA II (3 marks)

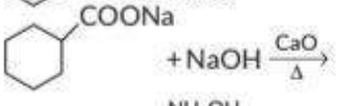
107. Explain why :
(i) Carboxyl group in benzoic acid is *meta* directing.
(ii) Sodium bisulphite is used for the purification of aldehydes and ketones.
(iii) Carboxylic acids do not give characteristic reactions of carbonyl group. *(2023)*

108. Write the major products in the following :

(i)



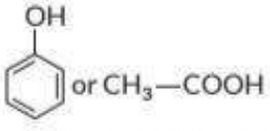
(ii)



(iii)

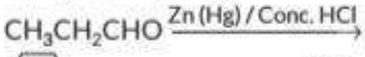
(Term II, 2021-22)

109. (i) Which acid of each pair would you expect to be stronger ? Give reason.
(I) CH_3COOH or $F-CH_2-COOH$
(II)

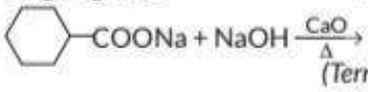


(ii) Distinguish between Pentan-2-one and Pentan-3-one. *(Term II, 2021-22)*

110. Write the main product in the following reactions:
(i) $2CH_3COCl + (CH_3)_2Cd \rightarrow$
(ii)



(iii)



(Term II, 2021-22) Ap

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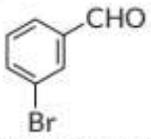
111. (a) Complete the following :

(i) $CH_3CN \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} 'A' \xrightarrow[H^+]{H_2N\text{-}OH} 'B'$

(ii) Write IUPAC name of the following compound :



(iii) Write chemical test to distinguish between the following compounds : Phenol and Benzoic acid

OR

(b) Convert the following :

(i) Benzoic acid to benzaldehyde

(ii) Propan-1-ol to 2-bromopropanoic acid

(iii) Acetaldehyde to but-2-enal

(Term II, 2021-22) Ap

112. Write the structures of compounds *A*, *B* and *C* in each of the following reactions :

(i) $C_6H_5Br \xrightarrow{Mg/dry\ ether} A \xrightarrow[(b)\ H_3O^+]{(a)\ CO_{2(g)}} B \xrightarrow{PCl_5} C$

(ii) $CH_3CN \xrightarrow[(b)\ H_3O^+]{(a)\ SnCl_2/HCl} A \xrightarrow{dil.\ NaOH} B \xrightarrow{\Delta} C$

(Delhi 2017)

LA (5 marks)

113. (i) Distinguish with a suitable chemical test :

(1) $CH_3COCH_2CH_3$ and $CH_3CH_2CH_2CHO$

(2) Ethanal and Ethanoic acid

(ii) Write the structure of oxime of acetone.

(iii) Identify *A* to *D*.

$$CH_3COOH \xrightarrow{PCl_5} A \xrightarrow{H_2/Pd\text{-}BaSO_4} B \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} C$$

$$B \xrightarrow{LiAlH_4} D$$

(2023)

114. (i) Give a chemical test to distinguish between ethanal and ethanoic acid.

(ii) Why is the α-hydrogen of aldehydes and ketones acidic in nature?

(iii) An organic compound '*A*' with molecular formula $C_4H_8O_2$ undergoes acid hydrolysis to form two compounds '*B*' and '*C*'. Oxidation of *C* with acidified potassium permanganate also produces '*B*'. Sodium salt of '*B*' on heating with soda lime gives methane.

(1) Identify '*A*', '*B*' and '*C*'.

(2) Out of '*B*' and '*C*', which will have higher boiling point? Give reason. *(2023)*

115. **Read the passage given below and answer the questions that follow :**

Aldehydes, ketones and carboxylic acids are some of the important classes of organic compounds containing carbonyl group. These are highly polar molecules due to higher electronegativity of oxygen relative to carbon in the carbonyl group. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled reduction of acyl halides. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes.

Aldehydes and ketones undergo nucleophilic addition reaction onto the carbonyl group but carboxylic acid does not undergo nucleophilic addition reaction. The alpha (α) -hydrogens of aldehydes and ketones are acidic. Therefore aldehydes and ketones having at least one α-hydrogen undergo Aldol condensation.

Aldehydes are easily oxidised by mild oxidising agents such as Tollens' reagent and Fehling's reagent. Carboxylic acids are prepared by the oxidation of primary alcohols, aldehydes and by hydrolysis of nitriles. Aromatic carboxylic acids are prepared by side-chain oxidation of alkyl benzenes. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols.

(a) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction. :

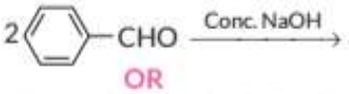
CH_3COCH_3, CH_3CHO, HCHO, $C_6H_5COCH_3$

(b) Give a simple chemical test to distinguish between Ethanal and Propanone.

(c) Why carboxylic acid does not give nucleophilic addition reactions like aldehydes and ketones?

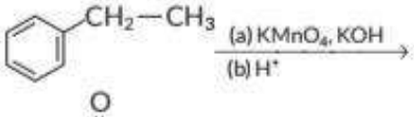
(d) (i) Why α-hydrogen of aldehydes and ketones are acidic in nature?

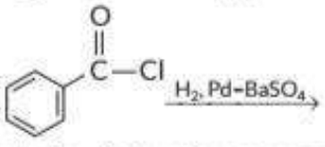
(ii) Write the products in the following:



OR

Write the major products of the following reactions:

(i) 

(ii) 

(Term II, 2021-22)

116. **Read the following passage and answer the questions that follow :**

A class of organic molecules which contain a carbon atom connected to an oxygen atom by a double bond are called Aldehydes and Ketones. It is called as carbonyl group. Aldehydes are prepared by the oxidation of alcohols. Formaldehyde is sold in an aqueous solution called formalin. Propanone, a simplest ketone is commercially prepared by fermenting corn or by oxidation of propan-2-ol. Carboxylic acids also have carbonyl carbon. They can be prepared by the oxidation of alcohols and aldehydes.

Formic acid was first isolated by the distillation of red ants. It is partially responsible for the pain and irritation of ant and wasp stings. Aldehydes undergo many nucleophilic addition reactions. They can be reduced to primary alcohols. The aldehydes with α-hydrogen undergo aldol condensation and the

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aldehydes without α-hydrogen undergo Cannizzaro reaction.

Ketones are highly reactive, although less so than aldehydes. Ketones are obtained by oxidation of secondary alcohols. Ketones possessing α-hydrogens also undergo aldol condensation. Carboxylic acids occur widely in nature and are used in the production of plastics, esters, etc. Aspirin is prepared from acetic acid. Similar to aldehydes and ketones, carboxylic acids can be halogenated at the α-carbon by reacting with a halogen in presence of phosphorus.

(a) Which of the following compounds would undergo aldol condensation?
Methanal, Benzaldehyde, Ethanal

(b) Write the chemical test to distinguish between propanal and propanone.

(c) Write the reagent required in the following reaction:

$CH_2=CH-CH_2OH \xrightarrow{?} CH_2=CH-CHO$

(d) (i) An alcohol 'A', (C_3H_8O) on oxidation gives compound 'B'. 'B' gives negative Tollens' test and reacts with hydrazine to give compound 'C'. 'B' reacts with NaOH and I_2 to give yellow precipitate of 'D'. Identify 'A', 'B', 'C' and 'D'.

OR

(ii) Write the chemical reactions for the following:
(I) Clemmensen reduction
(II) HVZ reaction *(Term II, 2021-22C)*

117. (i) Identify A, B and C in the following reactions:

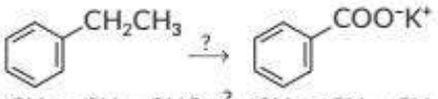
(I) 

$\xrightarrow{Mg,\ dry\ ether} A \xrightarrow[(ii)\ H_2O]{(i)\ CO_2} B \xrightarrow{PCl_5} C$

(II) $CH_3-CH_2OH \xrightarrow{CrO_3} A \xrightarrow{dil.\ NaOH} B \xrightarrow{\Delta} C$

(ii) By what tests will you distinguish between:
(I) Ethanol and Benzaldehyde
(II) Acetone and Acetic acid *(2021C)*

118. (i) Name the reagents used in the following reactions:

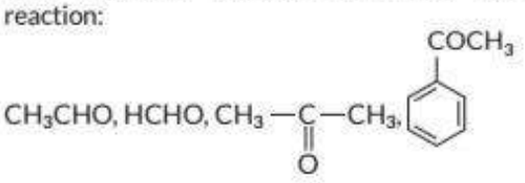
(I) 

(II) $CH_2=CH-CHO \xrightarrow{?} CH_2=CH-CH_2-OH$

(ii) Write the structure of oxime of propanal.

(iii) Why does carboxylic acid not give reactions of aldehydes and ketones?

(iv) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction:



(2021C)

119. (a) Write the products formed when benzaldehyde reacts with the following reagents :
(i) CH_3CHO in presence of dilute NaOH
(ii) H_2N-NH- 
(iii) Conc. NaOH

(b) Distinguish between following :
(i) $CH_3-CH=CH-CO-CH_3$ and $CH_3-CH_2-CO-CH=CH_2$
(ii) Benzaldehyde and Benzoic acid. *(2020)* An

CBSE Sample Questions

8.2 Preparation of Aldehydes and Ketones

MCQ

1. The oxidation of toluene to benzaldehyde by chromyl chloride is called
(a) Etard reaction
(b) Riemer-Tiemann reaction
(c) Stephen's reaction
(d) Cannizzaro's reaction. *(2022-23)*

8.4 Chemical Reactions

MCQ

2. Which of the following tests/ reactions is given by aldehydes as well as ketones?
(a) Fehling's test (b) Tollens' test
(c) 2,4-DNP test (d) Cannizzaro reaction
(2022-23)

SA I (2 marks)

3. Write the reaction and IUPAC name of the product formed when 2-methylpropanal (*iso*-butyraldehyde) is treated with ethyl magnesium bromide followed by hydrolysis. *(2022-23)*

4. Give reasons to support the answer :
(a) Presence of alpha hydrogen in aldehydes and ketones is essential for aldol condensation.
(b) 3-Hydroxypentan-2-one shows positive Tollens' test. *(Term II, 2021-22)*

SA II (3 marks)

5. An alkene 'A' (Mol. formula C_5H_{10}) on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling's test and also forms iodoform on treatment with I_2 and NaOH. Compound 'C' does not give Fehling's test but forms iodoform. Identify the compounds A, B and C. Write the reactions for ozonolysis and formation of iodoform from B and C. *(Term II, 2021-22)*

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LA (5 marks)

6. A hydrocarbon (*A*) with molecular formula C_5H_{10} on ozonolysis gives two products (*B*) and (*C*). Both (*B*) and (*C*) give a yellow precipitate when heated with iodine in presence of NaOH while only (*B*) gives a silver mirror on reaction with Tollen's reagent.
   (a) Identify (*A*), (*B*) and (*C*).
   (b) Write the reaction of *B* with Tollen's reagent.
   (c) Write the equation for iodoform test for *C*.
   (d) Write down the equation for aldol condensation reaction of *B* and *C*.

   OR

   An organic compound (*A*) with molecular formula $C_2Cl_3O_2H$ is obtained when (*B*) reacts with red P and Cl_2. The organic compound (*B*) can be obtained on the reaction of methyl magnesium chloride with dry ice followed by acid hydrolysis.
   (a) Identify *A* and *B*.
   (b) Write down the reaction for the formation of *A* from *B*. What is this reaction called?
   (c) Give any one method by which organic compound *B* can be prepared from its corresponding acid chloride.
   (d) Which will be the more acidic compound (*A*) or (*B*)? Why?
   (e) Write down the reaction to prepare methane from the compound (*B*). *(2022-23)*

7. An organic compound '*A*' C_8H_6 on treatment with dilute H_2SO_4 containing mercuric sulphate gives compound '*B*'. This compound '*B*' can also be obtained from a reaction of benzene with acetyl chloride in presence of anhy. $AlCl_3$. '*B*' on treatment with I_2 in *aq.* KOH gives '*C*' and a yellow compound '*D*'. Identify '*A*', '*B*', '*C*' and '*D*'. Give the chemical reactions involved.

   OR

   (i) Write the reaction for cross aldol condensation of acetone and ethanal.
   (ii) How will you carry out the following conversions:
   (a) Benzyl alcohol to phenyl ethanoic acid
   (b) Propanone to propene
   (c) Benzene to *m*-nitroacetophenone *(2020-21)*

8.9 Chemical Reactions

MCQ

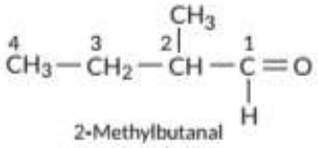
8. **Assertion :** Carboxylic acids are more acidic than phenols.
   Reason : Phenols are *ortho* and *para*-directing.
   (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
   (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
   (c) Assertion is correct statement but reason is wrong statement.
   (d) Assertion is wrong statement but reason is correct statement. *(2020-21)*

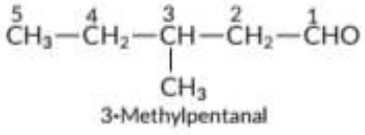
SA I (2 marks)

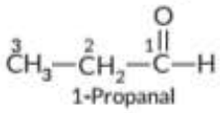
9. Arrange the following in the increasing order of their property indicated (any 2):
   (a) Benzoic acid, Phenol, Picric acid, Salicylic acid (pK_a values).
   (b) Acetaldehyde, Acetone, Methyl *tert*-butyl ketone (reactivity towards NH_2OH).
   (c) Ethanol, Ethanoic acid, Benzoic acid (boiling point) *(Term II, 2021-22)*

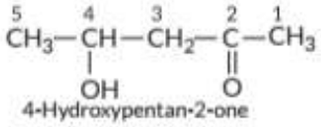
Detailed SOLUTIONS

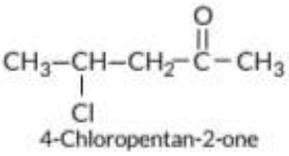
Previous Years' CBSE Board Questions

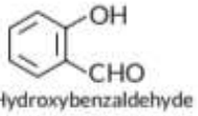
1. 
2-Methylbutanal

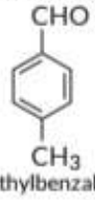
2. 
3-Methylpentanal

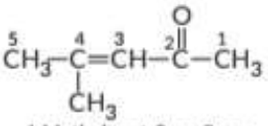
3. 
1-Propanal

4. 
4-Hydroxypentan-2-one

5. 
4-Chloropentan-2-one

6. 
2-Hydroxybenzaldehyde

7. (i) 
p-Methylbenzaldehyde

(ii) 
4-Methylpent-3-en-2-one

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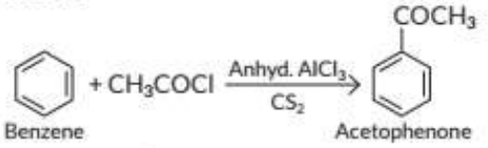
8. 

9. 

Answer Tips

- Use Friedel Crafts acylation reaction.

10. $(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-CH_2C_6H_5 + CdCl_2$

11. $\underset{\text{Benzoyl chloride}}{C_6H_5COCl} \xrightarrow[Pd\text{-}BaSO_4]{H_2} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$

12. **Etard reaction :**

13. **Stephen reduction :**

$R-CN + SnCl_2 + HCl \xrightarrow{\text{Dry ether}} R-CH=NH \xrightarrow{H_3O^+} R-CHO$

14. $CH_3-CH=CH-CN \xrightarrow{\text{(a) DIBAL-H}} CH_3-CH=CH-CH=NH \xrightarrow{\text{(b) } H_2O} CH_3-CH=CH-CHO$

OR

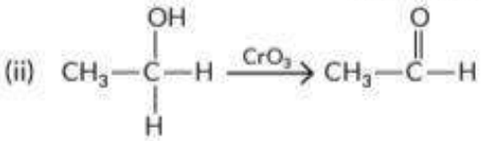
$CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} CH_3-CH=CH-CH_2CHO$

Important Part

- DIBAL-H (diisobutyl aluminium hydride) converts —CN group to —CHO in presence of H_2O. While conjugated double bond remains unaffected.

15. $\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow[HgSO_4]{\text{dil. } H_2SO_4} \underset{\text{Ethanal}}{CH_3-CHO}$

16. (i) $CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}} CH_3-CH=CH-CH_2CHO$

(ii) 

Commonly Made Mistake

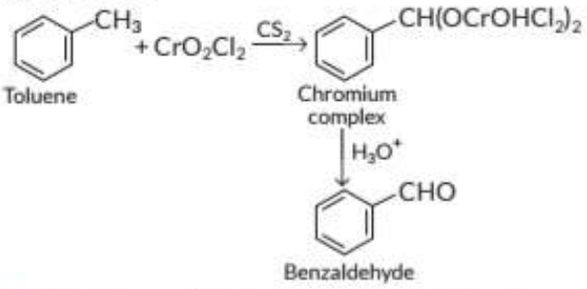
- CrO_3 is a mild oxidising agent, it oxidises alcohol to aldehyde and not to acid.

$R-CH_2OH \xrightarrow{CrO_3} R-\overset{O}{\overset{\|}{C}}-H$

17. (i) **Stephen reduction :**

$R-CN + SnCl_2 + HCl \xrightarrow{\text{Dry ether}} R-CH=NH \xrightarrow{H_3O^+} R-CHO$

(ii) **Etard reaction :**



18. (a): Aldehydes and ketones having at least one α-hydrogen atom undergo self condensation in the presence of dilute alkali to form β-hydroxyaldehydes (aldol) and β-hydroxyketones (ketol). This reaction is called aldol condensation.

The aldols and ketols readily lose water molecule to give α, β– unsaturated carbonyl compounds.

e.g., $\underset{\text{Ethanal}}{2CH_3-CHO} \rightleftharpoons[\text{dil. NaOH}] CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CHO$

3-Hydroxybutanal (Aldol)

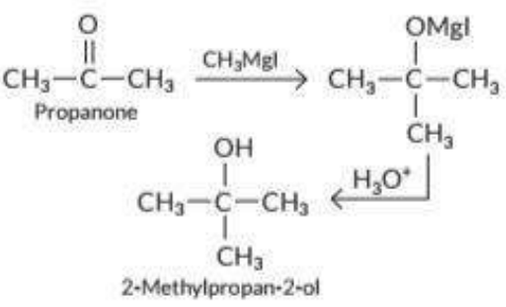
$\xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$

19. (d) : Iodoform test is given by the compound containing $CH_3-\overset{O}{\overset{\|}{C}}-$ or $CH_3-\underset{OH}{\underset{|}{CH}}-$ group thus it cannot be given by pentan-3-one, *i.e.*,

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

20. (d) : Reactivity of ketones is less than aldehydes.

21. (d) : Aldehydes are easily oxidised to carboxylic acids on treatment with mild oxidising agents. Ketones are generally oxidised under vigorous conditions *i.e.*, strong oxidising agents and at elevated temperatures.

22. 

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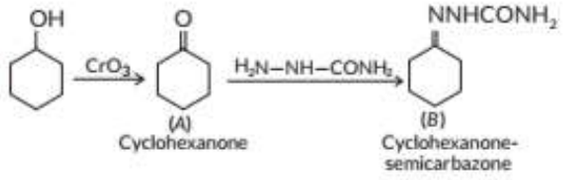
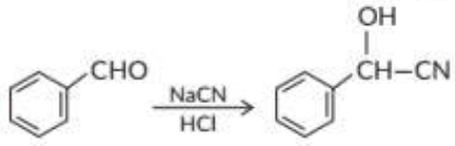
Concept Applied

➲ *RMgX* is called Grignard reagent. Its $R^-(R^-\overset{+}{M}gX)$ attacks on electrophilic centre of carbonyl compound $(\overset{+}{C}-O^-)$

23. $CH_3-\underset{\text{Propanone (Acetone)}}{\overset{O}{\overset{\|}{C}}}-CH_3 \xrightarrow{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3-\overset{OH}{\overset{|}{C}}H-CH_3}$

$\xrightarrow[443\ K]{\text{Conc. } H_2SO_4} \underset{\text{Propene}}{CH_3-CH=CH_2}$

24. 

25. 

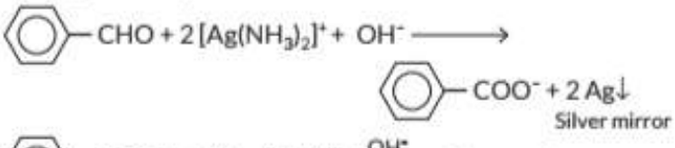
26. $\underset{\text{Ethanal}}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} \underset{\text{Propan-2-ol}}{CH_3-\overset{OH}{\overset{|}{C}}H-CH_3} \xrightarrow{Cu/\Delta} \underset{\text{Propanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$

27. Ethanal and propanal can be distinguished by iodoform test.

$\underset{\text{Ethanal}}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{NaOI} HCOONa + \underset{\text{Yellow ppt.}}{CHI_3\downarrow}$

$\underset{\text{Propanal}}{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{NaOI} \text{No reaction}$

28. Benzaldehyde and acetophenone can be distinguished by Tollens' test.



$COCH_3 + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} \text{No reaction}$

Alternative Method

➲ Acetophenone will give iodoform test whereas benzaldehyde will not.

$Ph-COCH_3 \xrightarrow{NaOI} \underset{\text{Yellow ppt.}}{CHI_3\downarrow} + PhCOONa$

$Ph-CHO \xrightarrow{NaOI} \text{No reaction}$

29. $CH_3COCl \xrightarrow{H_2,Pd\text{-}BaSO_4} \underset{\text{A (Ethanal)}}{CH_3-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{H_2N-OH} \underset{\text{B (Ethanal oxime)}}{CH_3-\overset{N-OH}{\overset{|}{C}}-H}$

30. Propanal and butan-2-one can be distinguished by their reactions with Tollens' reagent.

$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} \underset{\text{Silver mirror}}{CH_3CH_2COO^- + 2Ag\downarrow}$

$\underset{\text{Butan-2-one}}{CH_3CH_2COCH_3} + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} \text{No reaction}$

31. Lithium aluminium hydride ($LiAlH_4$).

Alternative Method

➲ Sodium borohydride ($NaBH_4$)

32. (i) Benzaldehyde and benzoic acid can be distinguished by sodium bicarbonate test.

$C_6H_5COOH + NaHCO_3 \longrightarrow \underset{\text{Effervescence}}{C_6H_5COONa + CO_2\uparrow + H_2O}$

$C_6H_5CHO + NaHCO_3 \longrightarrow \text{No reaction}$

(ii) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} \underset{\text{Silver mirror}}{CH_3CH_2COO^- + 2Ag\downarrow}$

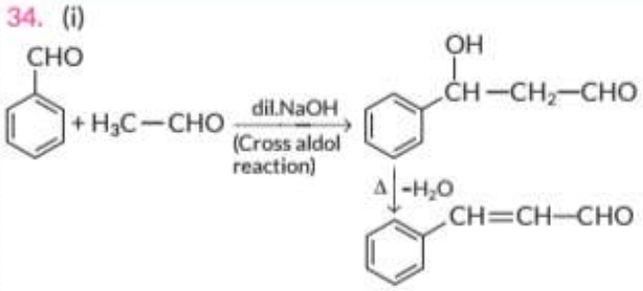
$\underset{\text{Propanone}}{CH_3COCH_3} + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} \text{No reaction}$

33. It is a nucleophilic addition reaction, in which CN^- acts as a nucleophile. CH_3CHO undergoes nucleophilic addition reactions faster than CH_3COCH_3 as in CH_3COCH_3, there are two electron releasing methyl groups attached to the carbonyl carbon that hinder the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group while in CH_3CHO, there is only one methyl group attached to the carbonyl carbon.

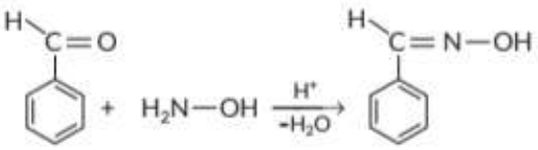
Concept Applied

➲ Order of reactivity towards nucleophilic attack : Acyl chlorides > Aldehydes > Ketones

34. (i)



(ii)



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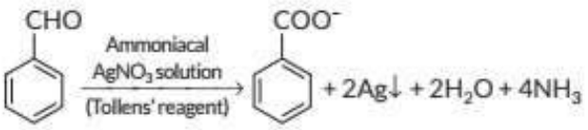
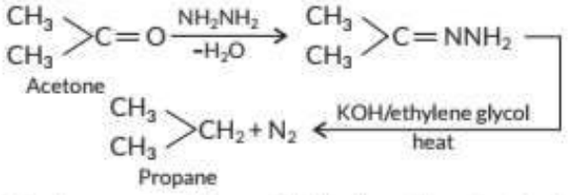
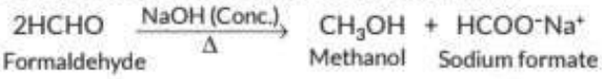
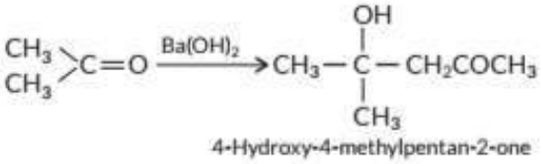
(iii) 

35. (a) **Wolff-Kishner reduction :** The carbonyl group of aldehydes and ketones is reduced to $>CH_2$ group on treatment with hydrazine followed by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol.



(b) **Cannizzaro reaction :** Aldehydes without α-hydrogen atom undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali.

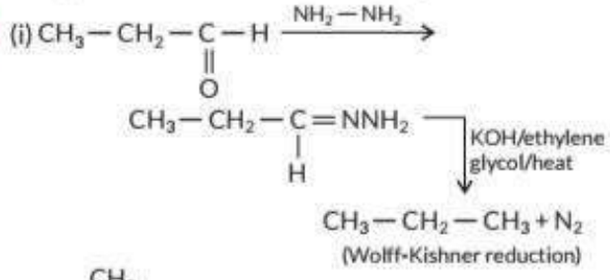


36. (i) 

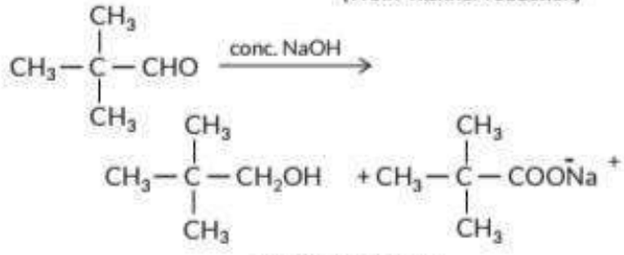
4-Hydroxy-4-methylpentan-2-one

(ii) 

Acetophenone Ethylbenzene

37. (i) 

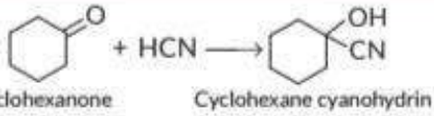
(Wolff-Kishner reduction)

(ii) 

(Cannizzaro reaction)

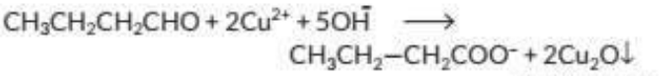
Answer Tips

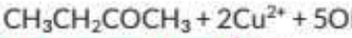
➲ Aldehydes without any α-hydrogen undergo Cannizzaro reaction.

38. (a) 

Cyclohexanone Cyclohexane cyanohydrin

(b) Butanal responds to Fehling test and silver mirror test but butan-2-one does not respond.

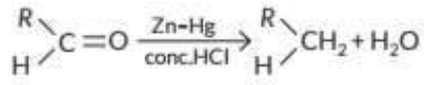




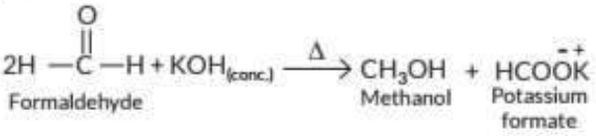
Alternative Method

➲ Butanal and butan-2-one can also be distinguished by Tollens' test (given by aldehydes) and iodoform test (given by methyl ketones, $-COCH_3$).

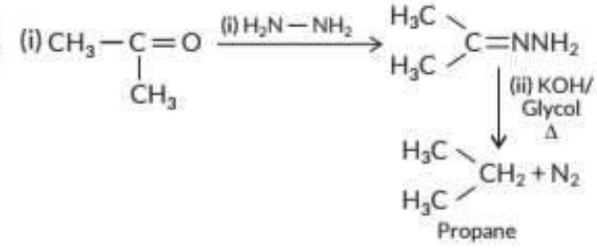
39. (i) **Clemmensen reduction :**

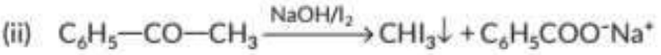


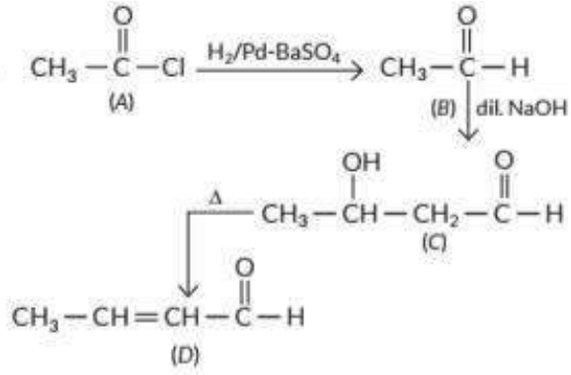
(ii) **Cannizzaro reaction :**



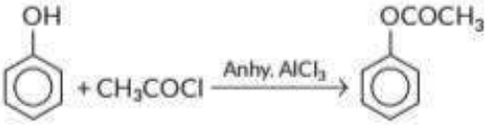
Formaldehyde

40. (i) 

(ii) 

41. 

42. (i) **Acetylation** : Introduction of acetyl group $\left(-\overset{O}{\overset{\|}{C}}-CH_3\right)$ in alcohols, phenols or amines is called acetylation.



(ii) **Aldol condensation** : Two molecules of an aldehyde or ketone having at least one α-hydrogen atom condense in the presence of a dilute alkali to give β-hydroxyaldehyde or β-hydroxyketone which upon heating gives α,β-unsaturated aldehyde or ketone.

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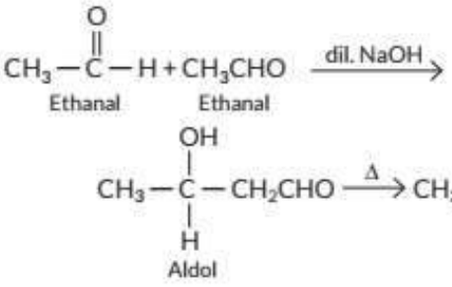
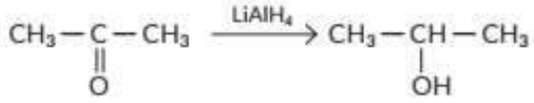
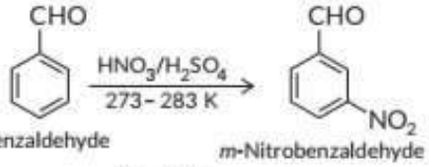
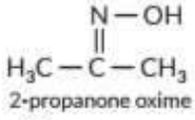
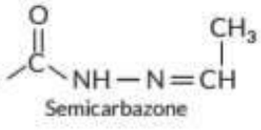
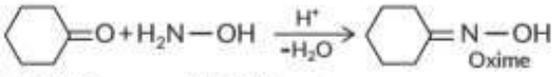


43. (i) 

(ii) 

44. (i) 

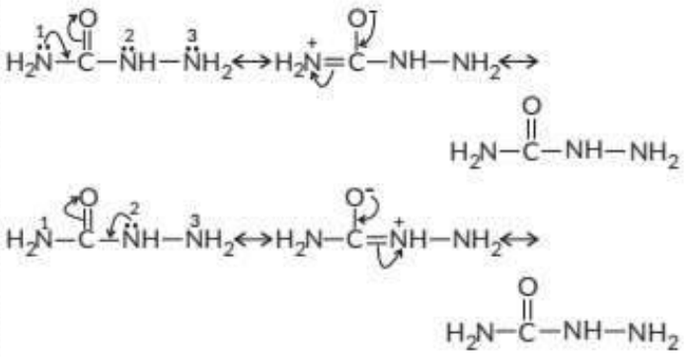
(ii) 

45. (i) 

(ii) $2C_6H_5CHO + \text{conc. } NaOH \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$

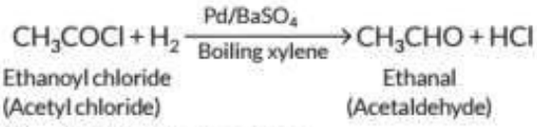
46. (i) It is a nucleophilic addition reaction, in which CN^- acts as a nucleophile. CH_3CHO undergoes nucleophilic addition reactions faster than CH_3COCH_3 as in CH_3COCH_3 there are two electron releasing methyl groups attached to the carbonyl carbon that hinder the approach of nucleophile to carbonyl carbon and reduce the electrophilicity of the carbonyl group while in CH_3CHO, there is only one methyl group attached to the carbonyl carbon.

(ii) Semicarbazide has the following resonance structures arising due to the electron withdrawing nature of the O atom.

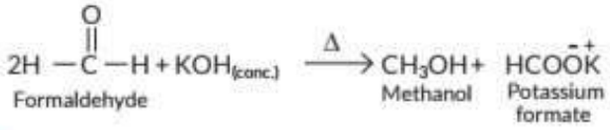


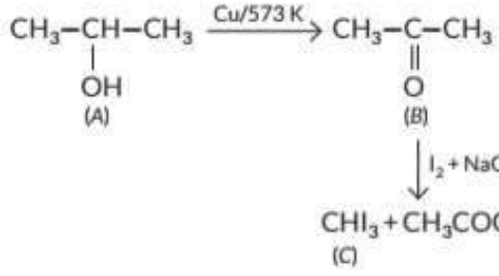
Lone pairs of N-1 and N-2 are involved in conjugation with $\rangle C=O$ group while that of N-3 is not involved in resonance thus, it is involved in the formation of semicarbazone.

47. (i) **Rosenmund's reduction :**



(ii) **Cannizzaro reaction :**



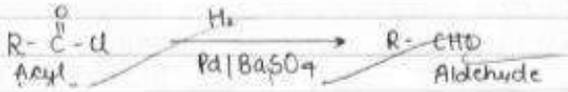
48. 

A having molecular formula (C_3H_8O) on reaction with Cu at 573 K results in formation of ketone (*B*). (*B*) does not reduce Fehling's solution but will form yellow precipitate of iodoform due to presence of $\left(CH_3-\overset{\overset{O}{\|}}{C}-\right)$ group.

49.

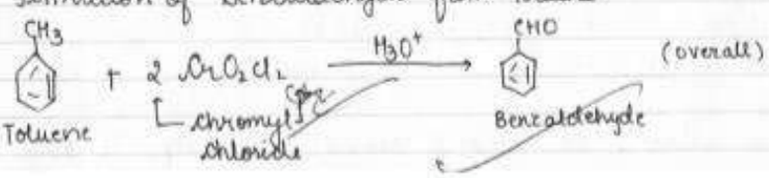
Ans 49. (a) i) Rosenmund reaction

Method for preparation of aldehydes by reducing Acyl halides



ii) Etard reaction

Formation of Benzaldehyde from Toluene



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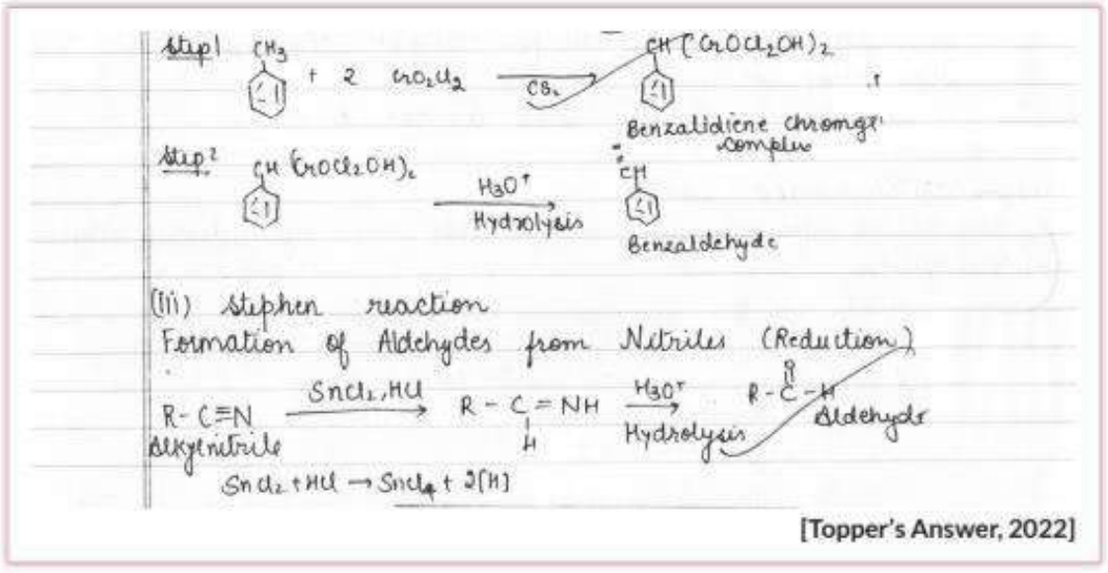


[Topper's Answer, 2022]

50. (i) Generally ketones are less reactive towards nucleophilic addition reaction because the +*I*-effect of alkyl groups makes carbonyl carbon less electrophilic as compared tos aldehydes that have only one alkyl group attached to carbonyl carbon. Moreover, the nucleophile attacks over ketones is restricted due to steric hinderance. So, acetaldehyde will undergo nucleophilic addition faster than propanone.

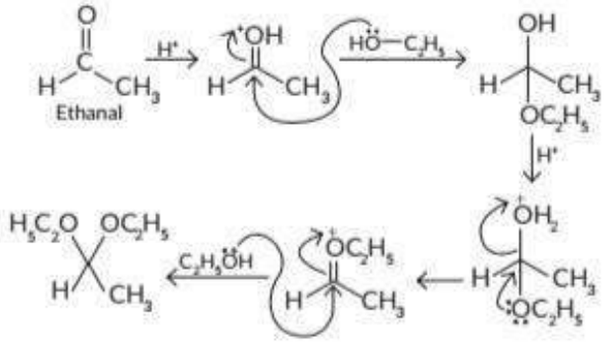
(ii) Fehling's reagent is a combination of two separate solutions, Fehling solution A and Fehling solution B. Fehling solution A is blue - coloured solution of copper sulphate, ($CuSO_4$). Fehling solution B is colourless aqueous solution of sodium potassium tartarate ($KNaC_4H_4O_6.4H_2O$), also known as Rochelle salt in alkaline medium.

(iii) $H_3C-CH(H)=O$ + $H_2N-NH-C(=O)-NH_2$ ⟶ $H_3C-C(H)=N-NH-C(=O)-NH_2$

Ethanal — Semicarbazone

51. (i) $CH_3-C(=O)-CH_3$ (Propanone) $\xrightarrow{CH_3MgBr}$ $CH_3-C(OMgBr)(CH_3)-CH_3$ $\xrightarrow{H_3O^+}$ $CH_3-C(OH)(CH_3)-CH_3$ (2-Methylpropan-2-ol)

(ii) Ethanal $\xrightarrow{H^+}$ $\xrightarrow{HO-C_2H_5}$ $\xrightarrow{H^+}$ $\xrightarrow{C_2H_5OH}$



(iii) $2H-C(=O)-H + KOH_{(conc.)} \xrightarrow{\Delta} CH_3OH + HCOO^-K^+$

Formaldehyde — Methanol — Potassium formate

52. As the compound forms 2,4-DNP derivative, hence it is an aldehyde or ketone. It does not reduce Tollens' reagent, hence it is a ketone, not aldehyde. It gives positive iodoform test, hence it is a methyl ketone, *i.e.*, it contains $CH_3-C(=O)-$ group.

(i) Therefore 'X' must be $CH_3-C(=O)-CH_2-CH_2-CH_3$ *i.e*, 2-pentanone

$CH_3-C(=O)-CH_2-CH_2-CH_3 \xrightarrow[\Delta]{\text{Conc. } HNO_3}$ CH_3COOH + CH_3CH_2COOH

Ethanoic acid — Propanoic acid

(ii) $CH_3-C(=O)-CH_2-CH_2-CH_3 + H_2NNH-C_6H_3(NO_2)_2$ $\xrightarrow{H^+}$ $CH_3-CH_2-CH_2-C(CH_3)=NNH-C_6H_3(NO_2)_2$

(iii) $CH_3-C(=O)-CH_2-CH_2-CH_3 \xrightarrow[NaOH]{I_2}$ $CHI_3\downarrow + CH_3CH_2CH_2COONa + NaOH$

53. (i) $H_3C-C(CH_3)(CH_3O)-C(=O)-H + H_3C-C(=O)-CH_3$ $\xrightarrow[H^+]{\text{dilute NaOH}}$ $H_3C-C(CH_3)(OH)-CH(H)-CH_2-C(=O)-CH_3$

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(ii) $H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{O}{||}}{C}-H + HCN \rightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-H$

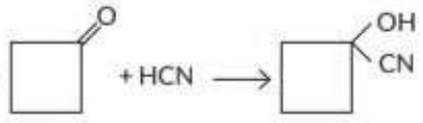
(iii) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CHO \xrightarrow{\text{conc. NaOH}} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH + CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-COO^-Na^+$

(Cannizzaro reaction)

54. (a) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} CH_3CH_2COO^- + 2Ag\downarrow$ (Silver mirror)

$CH_3COCH_3 + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-}$ No reaction (Propanone)

(b) (i) 

(ii) $\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C=O + C_2H_5OH \rightleftharpoons \begin{matrix}H_3C\\H\end{matrix}\!\!>\!C\!<\!\begin{matrix}OC_2H_5\\OH\end{matrix}$

55. As compound *B* gives positive Fehling's test so it is an aldehyde and as it gives positive iodoform test so it is acetaldehyde. Compound *C* does not give Fehling's solution test, so it is a ketone which could be acetone because acetone gives positive iodoform test.

$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=CH-CH_3$ ($A(C_5H_{10})$) $\xrightarrow{O_3}$ H_3C-CHO (*B*) + $\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\!C=O$ (*C*)

Concept Applied

➲ Aldehydes give positive Fehling test while ketones do not.

56. (a) As (*A*) and (*C*) give positive Tollens' test thus these two should be aldehyde while (*B*) should be a ketone (does not give Tollens' test) with $-\overset{\overset{O}{||}}{C}-CH_3$ group (as it gives positive iodoform test).

Three isomers are

$CH_3CH_2CH_2CHO$ (*A*), $CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3$ (*B*), $CH_3-\underset{\underset{CH_3}{|}}{CH}-CHO$ (*C*)

$CH_3CH_2CH_2CHO$ (*A*) $\xrightarrow{Zn(Hg)/\text{conc. HCl}}$ $CH_3CH_2CH_2CH_3$ (*D*)

$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3$ (*B*) $\xrightarrow{Zn(Hg)/\text{conc. HCl}}$ $CH_3CH_2CH_2CH_3$ (*D*)

(b) Out of (*A*), (*B*) and (*C*) isomers, (*B*) is least reactive towards addition of HCN.

57. (a) **Cannizzaro reaction :**

$2H-\overset{\overset{O}{||}}{C}-H + KOH_{(conc.)} \xrightarrow{\Delta} CH_3OH + HCOO^-K^+$ (Formaldehyde → Methanol; Potassium formate)

(b) $H_3C-\overset{\overset{H}{|}}{C}=O + H_2N-\overset{\overset{O}{||}}{C}-NH-NH_2$ (Ethanal + Semicarbazide) → $H_3C-\overset{\overset{H}{|}}{C}=N-NH-\overset{\overset{O}{||}}{C}-NH_2$ (Semicarbazone of ethanal)

(c) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} CH_3CH_2COO^- + 2Ag\downarrow$ (Propanal → Silver mirror)

$CH_3COCH_3 + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-}$ No reaction (Propanone)

58. (a) **Wolff-Kishner reduction :** The carbonyl group of aldehydes and ketones is reduced to $>CH_2$ group on treatment with hydrazine followed by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol.

$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=O$ (Acetone) $\xrightarrow[-H_2O]{NH_2NH_2}$ $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=NNH_2$ $\xrightarrow[\text{heat}]{\text{KOH/ethylene glycol}}$ $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH_2 + N_2$ (Propane)

(b) Increasing order of reactivity towards nucleophilic addition reaction :

$C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$

(c) Formula of compounds *A* and *B* is C_3H_6O, *B* forms yellow precipitate of iodoform. Hence, *B* must contain $-COCH_3$ group. Therefore, compound '*B*' must be $CH_3-\overset{\overset{O}{||}}{C}-CH_3$.

A does not give iodoform test and it is functional isomer of *B* thus, it may be CH_3CH_2CHO.

59. (i) $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=O$ (Acetone) $\xrightarrow{Zn-Hg/\text{Conc. HCl}}$ $CH_3CH_2CH_3$ (Propane)

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(ii) $(CH_3)_2C{=}O + H_2N - NHCONH_2 \xrightarrow{H^+} (CH_3)_2C{=}N - NHCONH_2$

Acetone semicarbazone

(iii) $(CH_3)_2C{=}O + CH_3MgBr \longrightarrow (CH_3)_2C(OMgBr)CH_3 \xrightarrow{H_3O^+} (CH_3)_2C(OH)CH_3$

2-Methylpropan-2-ol

60. (i) $CH_3CHO \xrightarrow{Zn-Hg/Conc.\ HCl} CH_3-CH_3$

(ii) $2CH_3CHO \xrightarrow{dil.\ NaOH} CH_3-CH(OH)-CH_2-CHO$

(iii) $CH_3CHO \xrightarrow{H_2/Ni} CH_3-CH_2-OH$

61. (i) **Wolff-Kishner reduction :** The carbonyl group of aldehydes and ketones is reduced to $>CH_2$ group on treatment with hydrazine followed by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol.

$(CH_3)_2C{=}O \xrightarrow[-H_2O]{NH_2NH_2} (CH_3)_2C{=}NNH_2 \xrightarrow[heat]{KOH/ethylene\ glycol} (CH_3)_2CH_2 + N_2$

Acetone → Propane

(ii) **Aldol condensation :** Two molecules of an aldehyde or ketone having at least one α-hydrogen atom condense in the presence of a dilute alkali to give β-hydroxyaldehyde or β-hydroxyketone which upon heating gives α,β-unsaturated aldehyde or ketone.

$CH_3-CHO + CH_3CHO \xrightarrow{dil.\ NaOH} CH_3-CH(OH)-CH_2-CHO \xrightarrow{\Delta} CH_3-CH{=}CH-CHO$

Ethanal → Aldol → But-2-enal

(iii) **Cannizzaro reaction :**

$2HCHO + KOH_{(conc.)} \xrightarrow{\Delta} CH_3OH + HCOO^-K^+$

Formaldehyde → Methanol + Potassium formate

62. (i) $CH_3CHO + HCN \longrightarrow CH_3-CH(OH)-CN$

(ii) $CH_3CHO + H_2NOH \longrightarrow CH_3-CH{=}N-OH$

(iii) $2CH_3CHO \xrightarrow{dil.\ NaOH} CH_3-CH(OH)-CH_2-CHO$

63. (a) (i) **Rosenmund's reduction :**

$CH_3COCl + H_2 \xrightarrow[Boiling\ xylene]{Pd/BaSO_4} CH_3CHO + HCl$

Ethanoyl chloride (Acetyl chloride) → Ethanal (Acetaldehyde)

(ii) **Cannizzaro reaction :**

$2HCHO + KOH_{(conc.)} \xrightarrow{\Delta} CH_3OH + HCOO^-K^+$

Formaldehyde → Methanol + Potassium formate

(b) $CH_3CH_2CH_2-CO-CH_3$ will give iodoform test because it contains acetyl group.

$CH_3CH_2CH_2COCH_3 \xrightarrow{NaOI} CHI_3\downarrow + CH_3CH_2CH_2COONa$

Iodoform (Yellow ppt.)

64. (i) $CH_3-CHO + CH_3MgBr \xrightarrow{H_3O^+} CH_3-CH(OH)-CH_3$

(ii) $CH_3CHO \xrightarrow[Conc.\ HCl]{Zn-Hg} CH_3-CH_3$

(iii) $CH_3-CHO + C_6H_5CHO \xrightarrow{dil.\ NaOH} C_6H_5-CH(OH)-CH_2CHO$

65. (i) (1) $CH_3-CHO \xrightarrow{dil.\ NaOH} CH_3-CH(OH)-CH_2-CHO \xrightarrow{\Delta} CH_3-CH{=}CH-CHO$

Ethanal → But-2-en-1-al

(2) $CH_3CH_2COOH \xrightarrow[(ii)\ H_2O]{(i)\ Cl_2,\ Red\ P} CH_3CH(Cl)COOH$

Propanoic acid → 2-Chloropropanoic acid

(ii) As compound *B* gives positive Fehling's test so it is an aldehyde and as it gives positive iodoform test so it is acetaldehyde. Compound *C* does not give Fehling's solution test. So it is a ketone which could be acetone because acetone gives positive iodoform test.

$(CH_3)_2C{=}CH-CH_3 \xrightarrow{O_3} H_3C-CHO + (H_3C)_2C{=}O$

A (C_5H_{10}) → (B) + (C)

66. (i) Only those aldehydes which do not have an α-hydrogen atom undergo self-oxidation and reduction reaction on treatment with concentrated alkali. In this reaction, one molecule of aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

$HCHO + HCHO \xrightarrow[\Delta]{conc.\ KOH} CH_3OH + HCOOK$

Formaldehyde → Methanol + Potassium formate

(ii) The boiling points of aldehydes and ketones are lower than that of corresponding carboxylic acids because they are not associated with intermolecular hydrogen bonding, whereas carboxylic acids are associated with intermolecular H-bonding.

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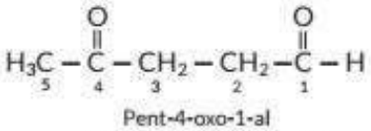
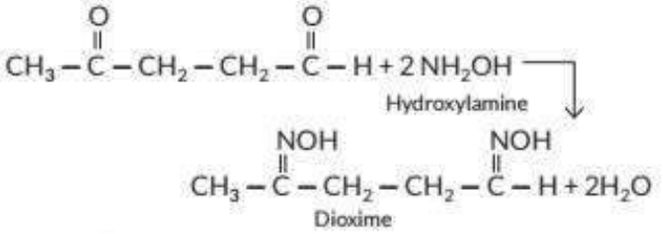
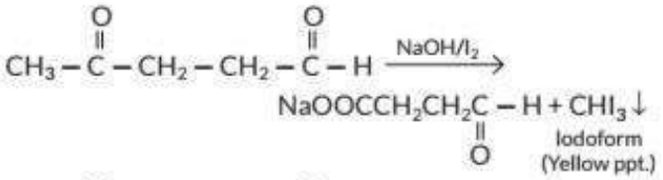
(iii) The organic compound 'A' when treated with hydrazine ($NH_2 - NH_2$) followed by heating with NaOH and glycol forms *n*-pentane. This suggests that compound 'A' must be a carbonyl compound. The molecular formula of 'A' suggests that it must have two carbonyl groups, out of which one is an aldehyde.

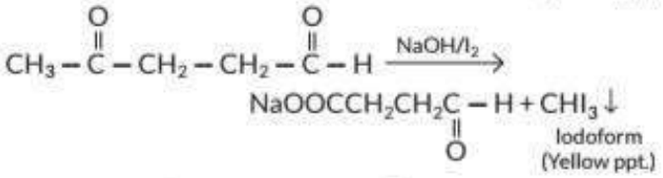
Thus, the expected structure of compound 'A' is

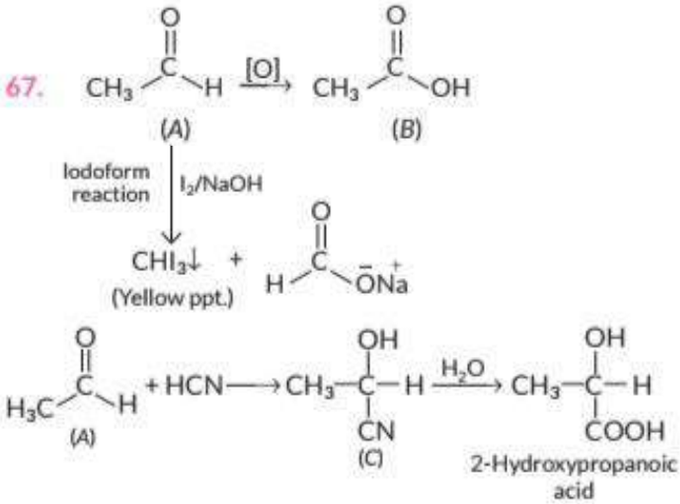


Pent-4-oxo-1-al

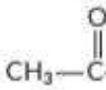


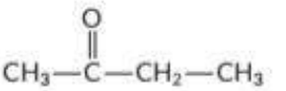


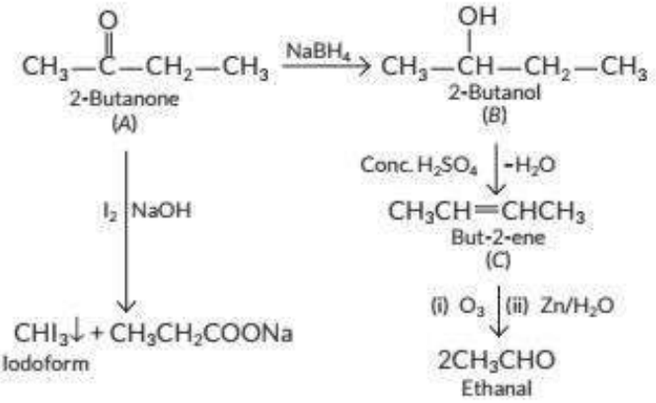


67. 

68. (a) As (A) forms 2, 4-DNP derivative, hence it is an aldehyde or ketone. Since it does not reduce Tollens' reagent, hence it is a ketone (A). As it gives iodoform reaction, hence it is a methyl ketone, *i.e.*, contains

 group.

Therefore, (A) must be  *i.e.*, 2-butanone.



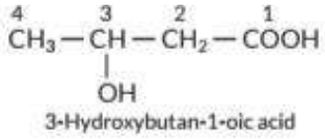
(b) (i) Unlike aldehydes, ketones do not contain any hydrogen atom attached to >C=O group and hence they cannot be oxidised without the cleavage of some carbon-carbon bonds. Thus oxidation of propanal is easier than propanone.

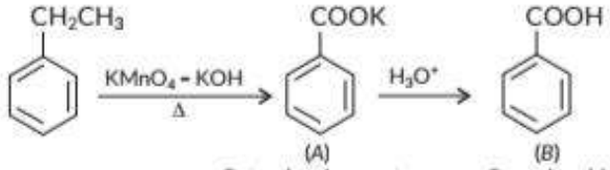
(ii) Due to –*I* effect of the carbonyl group of aldehydes and ketones, it withdraws electrons from the adjacent carbon-carbon bond. This makes α-carbon electron deficient. The α-carbon in turn, withdraws electrons from the C_α—H bonds. As a result, the electron density in C_α—H bond decreases. Hence, the α-hydrogens are weakly held and can be easily abstracted by strong bases giving enolate anions which are stabilised by resonance.

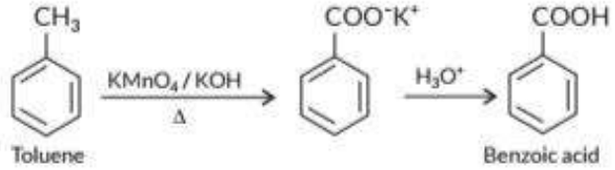
Concept Applied

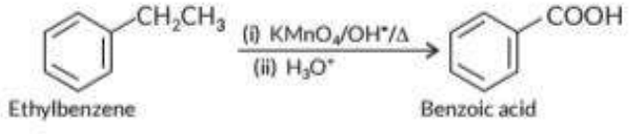
➲ Carbonyl group (>C=O) exerts –*I* effect and hence stabilise the anion formed after removal of H^+.

69. (a)

70. 
3-Hydroxybutan-1-oic acid

71. 

72. 

73. 

74. Alkaline potassium permanganate ($KMnO_4$, KOH)

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75. $C_6H_6 \xrightarrow[\text{Anhyd } AlCl_3]{CH_3COCl} C_6H_5COCH_3$ (A) $\xrightarrow[\text{Conc. HCl}]{\text{Zn - Hg}} C_6H_5CH_2CH_3$ (B)

(A) $\xrightarrow{NaOI}$ C_6H_5COONa (D) $+ CHI_3$ (E)

(B) $\xrightarrow[KOH, \Delta]{(i)\ KMnO_4,\ (ii)\ H_3O^+}$ C_6H_5COOH (C)

76. Increasing order of boiling point :
$CH_3CHO < C_2H_5OH < CH_3COOH$

77. (b): As $pK_a \propto \frac{1}{\text{acidity}}$

$O_2N - CH_2 - COOH$ will be most acidic due to presence of strong electron withdrawing group *i.e.*, $-NO_2$.

78. (a): Carboxylic acid does not undergo Friedel-Crafts reaction because (i) the carboxyl group is strongly deactivating and (ii) the catalyst $AlCl_3$ gets bonded to the carboxyl group strongly.

79. (c) : Due to presence of electron withdrawing group (−COOH) in aromatic carboxylic acids, they do not undergo Friedel-Crafts reaction.

80. (a) Acidic strength increases as $-I$ effect (F > Cl) of substituents increases, so the order of acidity is :
$CH_3COOH < ClCH_2COOH < FCH_2COOH$.

(b) Alcohols have higher boiling point as compared to aldehydes or alkanes of comparable molecular mass due to the presence of intermolecular hydrogen bonding in them.

Boiling point order : $CH_3CH_2CH_3 < CH_3CHO < CH_3CH_2OH$

81. $CH_3-CH(CH_3)-COOH \xrightarrow[(ii)\ H_3O^+]{(i)\ Br_2/\text{Red P}} CH_3-C(CH_3)(Br)-COOH$
2-Bromo-2-methyl propanoic acid

82. $C_6H_5COOH \xrightarrow{NaOH} C_6H_5COO^-Na^+$

83. $CH_3CH_2COOH \xrightarrow[(ii)\ CaO/\Delta]{(i)\ NaOH} CH_3-CH_3 \xrightarrow{Br_2,\ h\nu} CH_3CH_2Br \xrightarrow{KOH_{(aq)}} CH_3CH_2OH \xrightarrow{KMnO_4} CH_3COOH$
Propanoic acid → Acetic acid

84. $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow[\text{Rosenmund reduction}]{H_2/Pd\text{-}BaSO_4} C_6H_5CHO$
Benzoic acid → Benzoyl chloride → Benzaldehyde

85. The carbonyl group in −COOH is inert and does not show nucleophilic addition reaction like carbonyl compound. It is due to resonance stabilisation of carboxylate ion :

$$R-C(=O)-O^- \longleftrightarrow R-C(-O^-)=O$$

86. Benzoic acid and ethyl benzoate can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ whereas ethyl benzoate does not react.

$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2\uparrow + H_2O$ (Effervescence)

$C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow$ No reaction

87. Add Tollens' reagent to formic acid and warm. Silver mirror is formed.

$HCOOH + 2[Ag(NH_3)_2]^+ + 2OH^- \xrightarrow{\text{Warm}} 2Ag\downarrow + CO_2 + 2NH_3 + 2NH_4OH$
Formic acid → Silver mirror

Acetic acid does not give this test.

88. $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} CH_4 + Na_2CO_3$ (Methane)

89. $CH_3-COOH \xrightarrow{PCl_5} CH_3-COCl + POCl_3 + HCl$

90. **Decarboxylation** : Sodium or potassium salt of carboxylic acids on heating with soda lime (NaOH and CaO), loses a molecule of carbon dioxide and alkanes are obtained as products.

$R-C(=O)-O^-Na^+ + NaOH \xrightarrow{CaO} R-H + Na_2CO_3$

91. Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ but phenol will not react.

$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2\uparrow + H_2O$ (Effervescence)

$C_6H_5OH + NaHCO_3 \longrightarrow$ No reaction

92. **Hell-Volhard-Zelinsky reaction** : Carboxylic acids react with chlorine or bromine in the presence of phosphorous to give compounds in which α-hydrogen atom is replaced by halogen atom.

$CH_3COOH + Cl_2 \xrightarrow{\text{Red P}} ClCH_2-COOH + HCl$
Acetic acid → Chloroacetic acid

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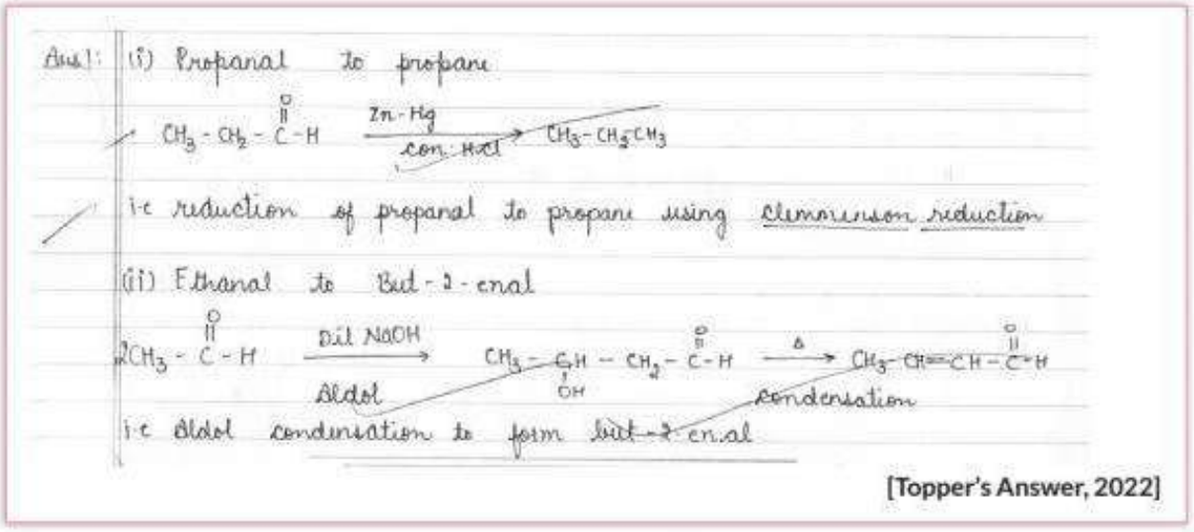
93.



[Topper's Answer, 2022]

(iii) Ethanoic acid to ethanamide

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + NH_3 \rightarrow CH_3COO\bar{N}H_4^+ \xrightarrow[-H_2O]{\Delta} \underset{\text{Ethanamide}}{CH_3CONH_2}$$

94. (i) $\underset{\text{Benzoyl chloride}}{C_6H_5COCl} \xrightarrow[Pd\text{-}BaSO_4]{H_2} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$

(ii) $CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3-\overset{OH}{\overset{|}{C}}H-CH_2CHO$

(iii) $CH_3COOH \xrightarrow[\text{Red P}]{Cl_2} ClCH_2-COOH$

95. (i) $C_6H_5COCH_3 < CH_3COCH_3 < C_6H_5CHO < CH_3CHO$

The reactivity towards nucleophilic addition reactions decreases as the steric hindrance and +*I* effect of the alkyl groups increases. Due to +*R* effect of the benzene ring, the aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones.

(ii) $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

Acidic strength of carboxylic acid is increased by the presence of electron with drawing groups while decreased by the presence of electron donating groups. Inductive effect decreases rapidly with distance.

(iii) $CH_3CHO < C_2H_5OH < CH_3COOH$

Alcohols have higher boiling points than aldehydes of similar molecular weight due to the presence of H-bonding in alcohols. Carboxylic acids have higher boiling points than alcohols because of more extensive association of carboxylic acid molecules through inter-molecular hydrogen bonding.

96. (i) Due to presence of electron withdrawing group (−COOH) in aromatic carboxylic acids, they do not undergo Friedel–Crafts reaction.

(ii) Unlike aldehydes, ketones do not contain any hydrogen atom attached to $>C=O$ group and hence, they cannot be oxidised without the cleavage of some carbon-carbon bonds. Thus, oxidation of aldehydes is easier than ketones.

97. (i) Greater the number of alkyl groups attached to the carbonyl group, greater is the electron density on the carbonyl carbon and hence, lower is its reactivity towards nucleophilic addition reactions.

The +*R* effect of the benzene ring increases the electron density on the carbonyl group thereby repelling the nucleophiles. Hence, aromatic aldehydes are less reactive than the corresponding aliphatic aldehydes.

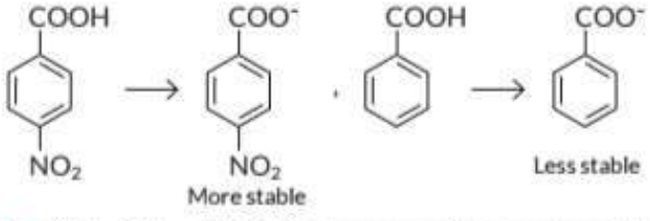
So, the increasing order of reactivity is

$\underset{\text{Benzaldehyde}}{C_6H_5CHO} < \underset{\text{Propanal}}{CH_3CH_2CHO}$

(ii) The carbonyl group in −COOH is inert and does not show nucleophilic addition reaction like carbonyl compounds. It is due to resonance stabilisation of carboxylate ion :

$$R-\overset{O^-}{\overset{|}{C}}=O \longleftrightarrow R-\overset{O}{\overset{\|}{C}}-O^-$$

(iii) 4-Nitrobenzoic acid is a stronger acid than benzoic acid because conjugate base obtained from the 4-nitrobenzoic acid is more stable in comparison of conjugate base obtained from benzoic acid. This is due to −*R* effect of electron withdrawing nitro group.



98. (i) $F-CH_2-COOH$ is stronger acid as compared to $H_3C-COOH$ due to −*I* effect of fluorine that stabilises the conjugate base formed after the loss of H^+.

(ii) Alcohols have higher boiling points than aldehydes of similar molecular weight due to the presence of H-bonding in alcohols. Carboxylic acids have higher boiling points than alcohols because of more extensive association of carboxylic acid molecules through inter-molecular hydrogen bonding.

Order of boiling point :

$CH_3-CHO < CH_3CH_2OH < H_3C-COOH$

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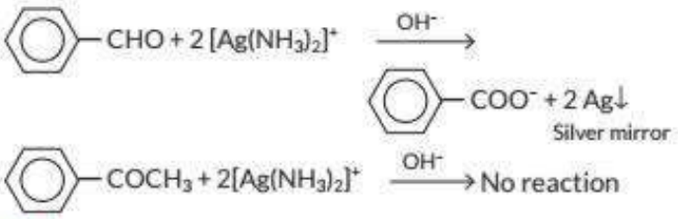
(iii) Benzaldehyde and acetophenone can be distinguished by Tollens' test. Benzaldehyde will form silver mirror, on treatment with Tollens' reagent whereas acetophenone will not show Tollens' test.



99. (a) $C_6H_5COOH < FCH_2COOH < NO_2CH_2COOH$

Electron withdrawing groups increase the stability of the carboxylate ion by dispersing the negative charge and hence increase the acidity of the substituted acid. The effect of given substituents follows the order: Ph < F < NO_2.

(b) $\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{\underset{\|}{C}}(=O)-H$

1-Butanal

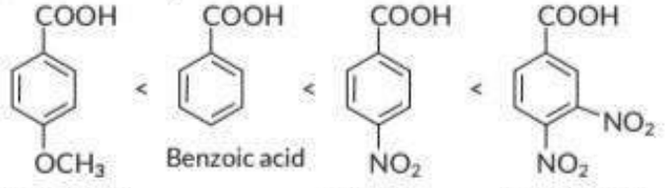
100. (a) Generally aldehydes are more reactive than ketones towards nucleophilic addition reactions because aldehydes are less sterically hindered and possess low electron density on carbonyl carbon due to the presence of single alkyl substituent with the carbonyl group.

So, order of reactivity is :

Butanone < Propanone < Propanal < Ethanal.

(b) Acidic strength of acid is increased by the presence of electron withdrawing groups at *-o* and *-p* positions of the ring, while electron donating groups decrease its acidic strength.

Order of acidity :



4-Methoxy benzoic acid | Benzoic acid | 4-Nitro-benzoic acid | 3, 4-Dinitro-benzoic acid

101. (a) Due to presence of electron withdrawing group (−COOH) in aromatic carboxylic acids, they do not undergo Friedel-Crafts reaction.

(b) Due to presence of strong electron withdrawing group (−NO_2), 4-nitrobenzoic acid is more acidic than benzoic acid and therefore, pK_a value is lower.

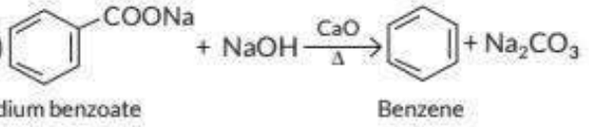
102. (i) **Hell-Volhard-Zelinsky reaction** : Carboxylic acids react with chlorine or bromine in the presence of phosphorous to give compounds in which α-hydrogen atom is replaced by halogen atom.

$$\underset{\text{Acetic acid}}{CH_3COOH} + Cl_2 \xrightarrow{\text{Red P}} \underset{\text{Chloroacetic acid}}{ClCH_2-COOH} + HCl$$

(ii) **Decarboxylation** : Sodium or potassium salt of carboxylic acids on heating with soda lime (NaOH and CaO), loses a molecule of carbon dioxide and alkanes are obtained as products.

$$R-\overset{O}{\overset{\|}{C}}-O^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} R-H + Na_2CO_3$$

103. (a)

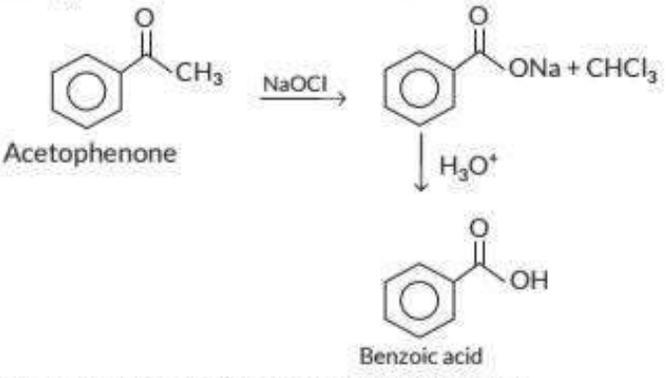


Sodium benzoate | Benzene

(b) Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution.

Benzoic acid will give effervescence with $NaHCO_3$ but phenol will not react.

104. (i) Acetophenone to benzoic acid :



Acetophenone | Benzoic acid

(ii) Ethanoic acid to 2-hydroxyethanoic acid.

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[H_2O]{Cl_2/\text{Red P}} \underset{\text{2-Chloroethanoic acid}}{Cl-CH_2-COOH} \xrightarrow{NaOH} \underset{\text{2-Hydroxyethanoic acid}}{HO-CH_2-COOH}$$

105. (a) $CH_3COOH \xrightarrow{Cl_2/\text{ Red P}} \underset{Cl}{CH_2COOH}$

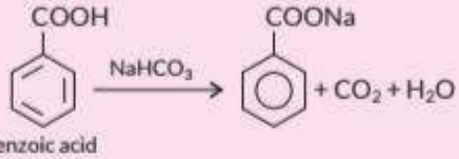
(b) Benzaldehyde when treated with ammoniacal silver nitrate gives silver mirror.

$$C_6H_5CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow \underset{\text{Silver mirror}}{C_6H_5COO^-} + 2Ag\downarrow + 4NH_3 + 2H_2O$$

Benzoic acid does not give this test.

Alternative Method

➲ **Sodium Bicarbonate test** : Benzoic acid reacts with sodium bicarbonate to liberate CO_2.



Benzoic acid

C_6H_5CHO does not give this test.

106. Chloroacetic acid has lower pK_a value than acetic acid; 'Cl' in chloroacetic acid shows *-I* effect, it creates less electron density on oxygen of carboxylic acid. Thus, release of proton becomes easier. Hence, chloroacetic acid is stronger than acetic acid.

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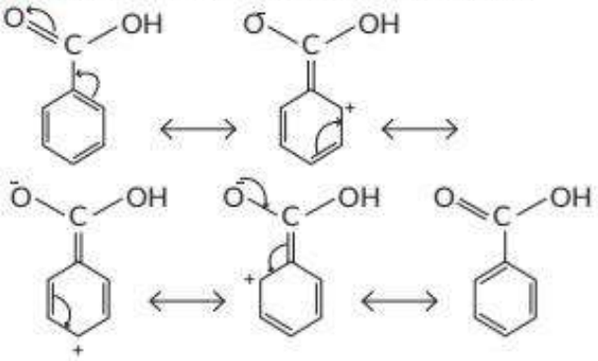
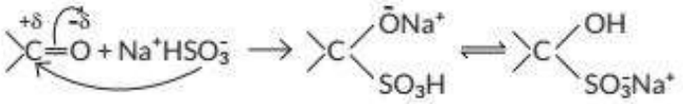
107. (i) Resonance structures of benzoic acid;



Resonance structures show that carboxylic acid group present in benzoic acid acts as a ring deactivating and *meta* directing group.

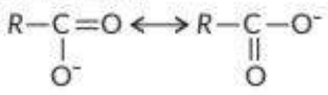
(ii) Sodium hydrogensulphite ($NaHSO_3$) adds on aldehydes and ketones to give addition products.

$$NaHSO_3 \longrightarrow Na^+ + HSO_3^-$$

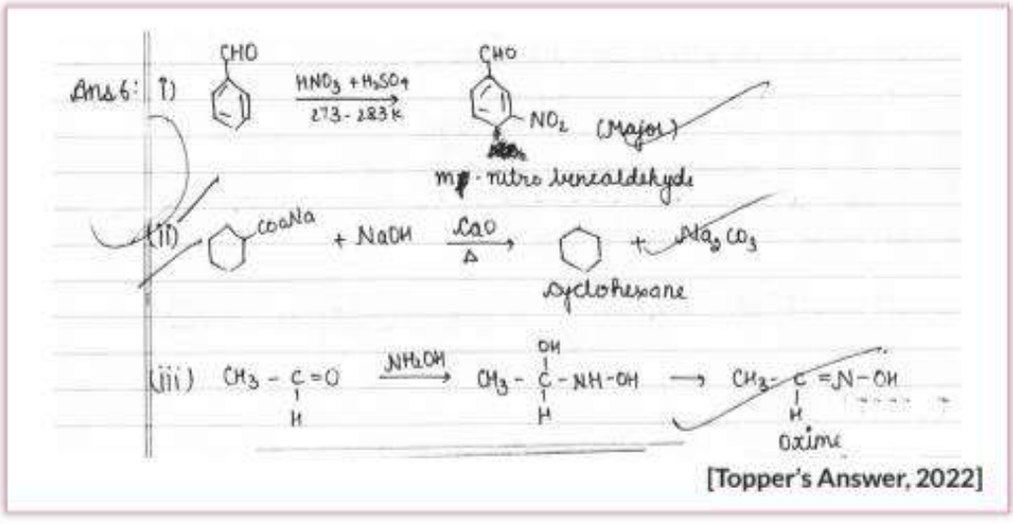


Most of the aldehydes give product in good yield. Most of the ketones give very poor yield due to steric hindrance in the crystalline solid and highly soluble in water. These can be converted back to the original carbonyl compound by reaction with dilute mineral acids or alkali. Therefore, this reaction is used for the separation and purification of aldehydes and ketones.

(iii) The carbonyl group in −COOH is inert and does not show nucleophilic addition reaction like carbonyl compounds. It is due to resonance stabilisation of carboxylate ion :

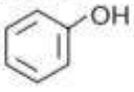


108.

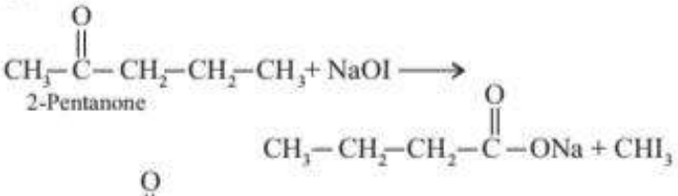


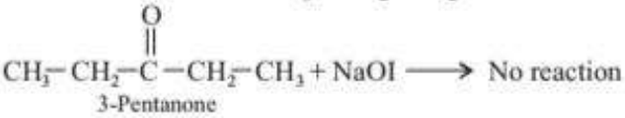
[Topper's Answer, 2022]

109. (i) (I) $F-CH_2COOH > CH_3COOH$

(II) CH_3COOH is stronger than 

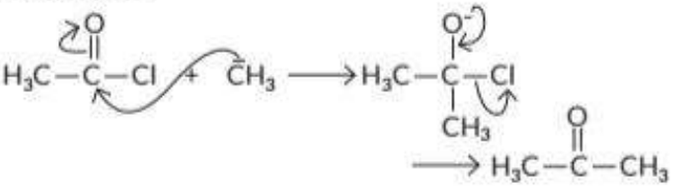
(ii) Iodoform test





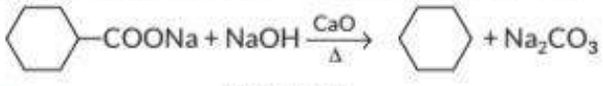
110. (i) $2H_3C-\overset{O}{\overset{\|}{C}}-Cl + (CH_3)_2Cd \longrightarrow 2H_3C-\overset{O}{\overset{\|}{C}}-CH_3$

Mechanism :



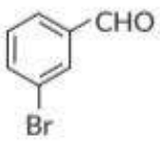
(ii) $CH_3CH_2CHO \xrightarrow[\text{Conc. HCl}]{Zn(Hg)} CH_3CH_2CH_3 + H_2O$

This reaction is an example of Clemmensen reduction.

(iii) 

111. (a) (i) $CH_3CN \xrightarrow[(2)\ H_2O]{(1)\ AlH(i\text{-}Bu)_2} CH_3CHO$ (A)

$\xrightarrow{NH_2OH/H^+}$ $H_3C-\overset{N-OH}{\overset{\|}{C}}-H$ Ethanal oxime (B)

(ii) 

IUPAC name : 3-Bromobenzaldehyde

(iii) Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give brisk effervescence of CO_2 with $NaHCO_3$ but

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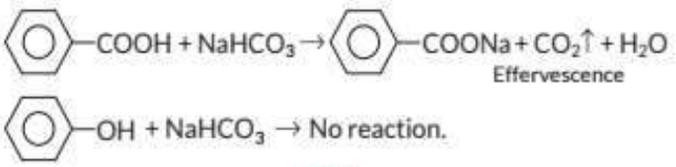
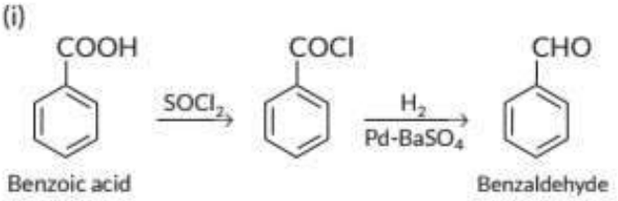
phenol will not give because it is weaker acid than benzoic acid.



OR

(b) (i)



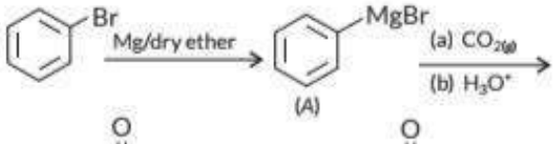
(ii) $H_3C-CH_2-CH_2-OH$ (Propan-1-ol) $\xrightarrow[\text{Oxidation}]{K_2Cr_2O_7/H_2SO_4}$ H_3C-CH_2-COOH

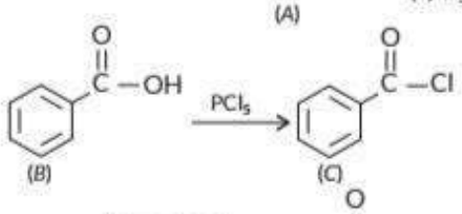
$H_3C-CH_2-COOH \xrightarrow[(ii)\ H_2O]{(i)\ Br_2/Red\ P}$ $H_3C-\underset{Br}{CH}-COOH$ (2-Bromopropanoic acid)

(iii) $CH_3-\overset{O}{\overset{\|}{C}}-H$ (Ethanal) $+ CH_3CHO$ (Ethanal) $\xrightarrow{\text{dil. NaOH}}$

$CH_3-\underset{H}{\overset{OH}{C}}-CH_2CHO$ (Aldol) $\xrightarrow{\Delta}$ $CH_3-C(H)=CH-CHO$ (But-2-enal)

112. (i)





(ii) $CH_3-C\equiv N \xrightarrow[(b)\ H_3O^+]{(a)\ SnCl_2/HCl}$ $CH_3-\overset{O}{\overset{\|}{C}}-H$ (A)

(A) $\xrightarrow{\text{dil. NaOH}}$ $CH_3-\underset{H}{\overset{OH}{C}}-\underset{H}{C}-\overset{O}{\overset{\|}{C}}-H$ (B) $\xrightarrow{\Delta}$ $CH_3CH=CH-\overset{O}{\overset{\|}{C}}-H$ (C)

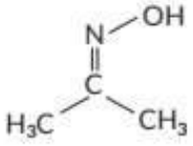
Concept Applied

$H_3C-C\equiv N \xrightarrow{SnCl_2/HCl} H_3C-CH=NH\cdot HCl$

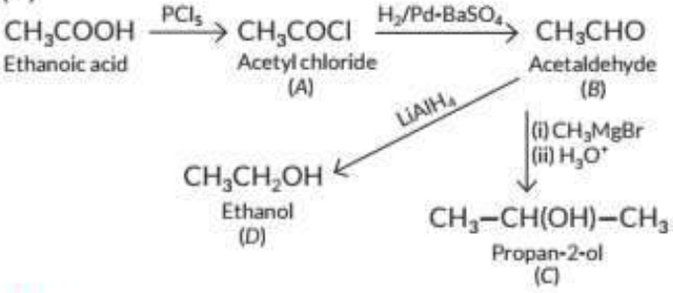
113. (i) (1) Butanone and butanal can be distinguished by Tollens' test as aldehyde will give positive Tollens' test while ketone does not give any reaction.

(2) Ethanal and ethanoic acid can be distinguished by sodium bicarbonate test. Carboxylic acid gives brisk effervescence with $NaHCO_3$ while aldehyde does not form any effervescence.

(ii) Oxime of acetone is an organic compound with formula $(CH_3)_2CNOH$. It is simplest example of ketoxime. The structure



(iii)



114. (i) Sodium bicarbonate test can be used to distinguish between ethanal and ethanoic acid as a brisk effervescence of CO_2 gas is observed when ethanoic acid reacts with $NaHCO_3$, whereas ethanal does not react with $NaHCO_3$.

$CH_3COOH_{(l)} + NaHCO_{3(s)} \rightarrow CH_3COONa_{(aq)} + CO_{2(g)}\uparrow + H_2O_{(l)}$

(ii) The α-hydrogens of aldehydes and ketones are acidic in nature due to the presence of carbonyl group that has a strong electron withdrawing effect. Another reason is the resonance stabilisation of the anion formed after the removal of α-hydrogen.

(iii) The given organic compound '*A*' with molecular formula, $C_4H_8O_2$ is an ester that undergoes acid hydrolysis to give carboxylic acid and alcohol.

$CH_3COOC_2H_5 + H_2O \xrightarrow[\text{Hydrolysis}]{aq.H_2SO_4} CH_3COOH + C_2H_5OH$

Ethyl acetate 'A' — 'B' — 'C'

$C_2H_5OH \xrightarrow[\text{alkaline } KMnO_4]{\text{acidified } K_2Cr_2O_7} CH_3COOH$

Ethanol (C) — Ethanoic acid (B)

Now, sodium salt of '*B*' is sodium acetate (CH_3COONa) which reacts with soda lime to give methane as shown:

$CH_3COONa + NaOH \xrightarrow[633\ K,\ \Delta]{CaO} CH_4 + Na_2CO_3$

Methane

(1) *A* is $CH_3COOC_2H_5$
B is CH_3COOH
C is C_2H_5OH

(2) Out of '*B*' and '*C*', *i.e.*, ethanoic acid and ethanol, the former has a higher boiling point as due to the formation of a dimer, the van der Waals force increases, causing an increase in the boiling point. The dimer is formed due to the presence of H-bonding between carbonyl oxygen and acidic hydrogen.

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115. (a) $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

The reactivity towards nucleophilic addition reactions decreases as the steric hindrance and $+I$ effect of the alkyl groups increases. Due to $+R$ effect of the benzene ring, the aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones.

(b) Tollens' reagent test :

$$CH_3CHO + [Ag(NH_3)_2]^{2+} \xrightarrow{3OH^-} CH_3COO^- + 2Ag\downarrow + 2H_2O + 4NH_3$$

$$\underset{\text{Propanone}}{CH_3COOH} \xrightarrow[\text{reagent}]{\text{Tollens'}} \text{No reaction}$$

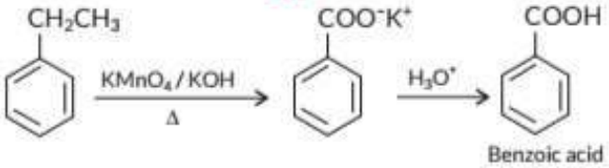
(c) The carbonyl group in $-COOH$ is inert and does not show nucleophilic addition reaction like carbonyl compound. It is due to resonance stabilisation of carboxylate ion :

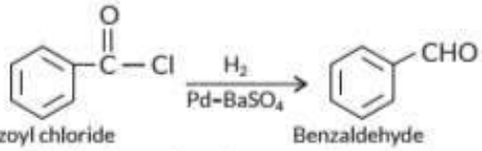
$$R-\underset{\underset{O^-}{|}}{C}=O \longleftrightarrow R-\underset{\underset{O}{||}}{C}-O^-$$

(d) (i) The acidity of α-hydrogens of aldehydes and ketones is due to the $-I$ effect of the carbonyl group which weakens the C_α-H bond and due to the resonance stabilisation of the resulting enolate anion.

(ii) $2C_6H_5CHO + \text{conc. } NaOH \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$

OR

(i) 

(ii) 

116. (a) Aldehydes having α-H undergo aldol condensation. Thus, HCHO and C_6H_5CHO will not undergo aldol condensation, only CH_3CHO will undergoes aldol condensation.

(b) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} CH_3CH_2COO^- + 2Ag\downarrow$$

Silver mirror

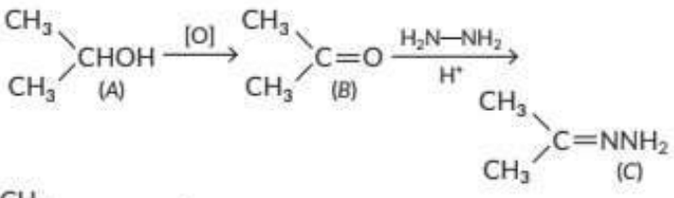
$$\underset{\text{Propan-2-one}}{CH_3COCH_3} + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} \text{No reaction}$$

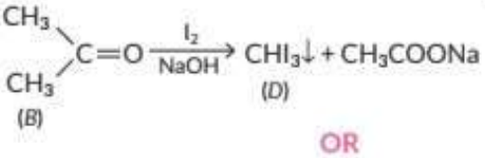
(c) $CH_2=CH-CH_2OH \xrightarrow[273-295K]{CrO_3-H_2SO_4,\ (CH_3)_2CO-H_2O} CH_2=CH-CHO$

Jones reagent is a solution of CrO_3 in H_2SO_4 in aqueous acetone. It is used to oxidise allylic and benzylic 1° and 2° alcohols to corresponding aldehyde.

(d) (i) As '*B*' gives negative Tollens' test, hence it is a ketone. '*B*' reacts with NaOH and I_2, so it is a methyl ketone.

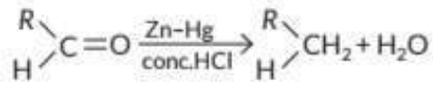
Hence '*A*' is a 2° alcohol.





OR

(ii) (I) **Clemmensen reduction :**

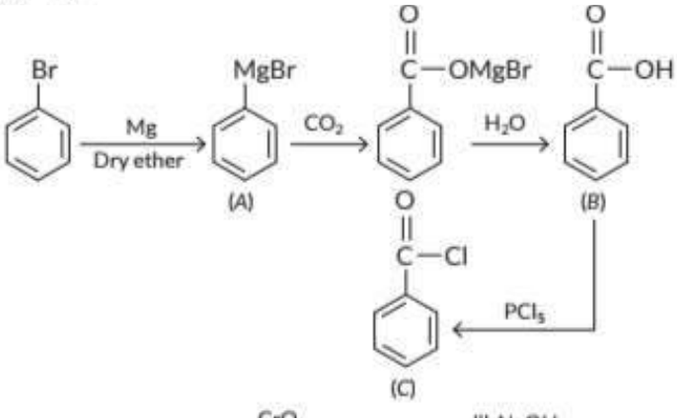


(II) **HVZ reaction :**

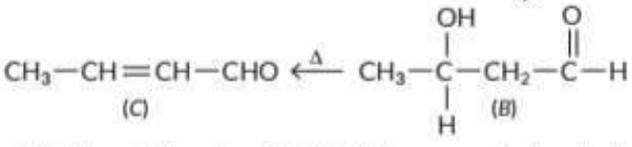
$$RCH_2-COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\text{Red P}} R-CHX-COOH \quad (X = Cl \text{ or } Br)$$

117.

(i) (I)



(II) $CH_3-CH_2OH \xrightarrow{CrO_3} \underset{(A)}{CH_3CHO} \xrightarrow{\text{dil. NaOH}}$

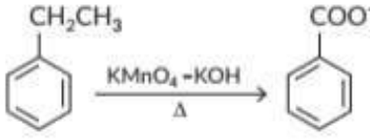


(ii) (I) Ethanol (having CH_3CHOH- group) give iodo form test while benzaldehyde will not.

$$CH_3CH_2OH \xrightarrow[\Delta]{I_2/NaOH} CHI_3\downarrow + HCOONa$$

(II) Acetic acid reacts with $NaHCO_3$ to give effervescence while ethanol acid do not

$$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + H_2O + CO_2\uparrow$$

118. (i) (I) 

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(II) $CH_2=CH-CHO \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_2=CH-CH_2-OH$

(ii) $CH_3-CH_2-\underset{\underset{N-OH}{\|}}{C}-H$

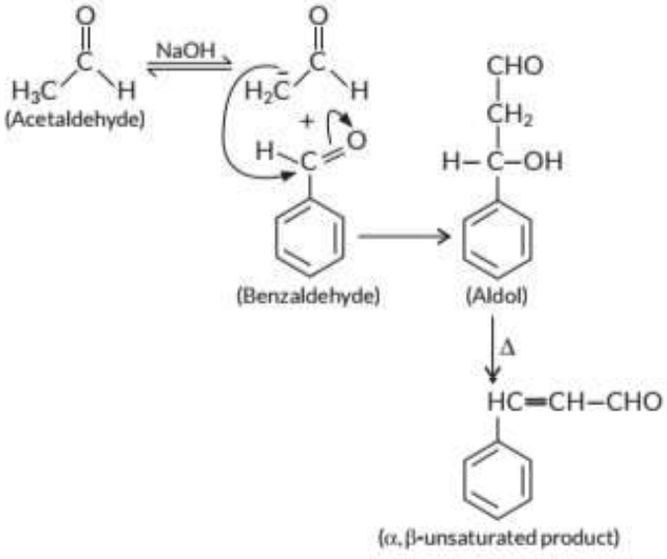
(iii) The carbonyl group in $-COOH$ is inert and does not show nucleophilic addition reaction like carbonyl compounds. It is due to resonance stabilisation of carboxylate ion :

$$R-\underset{\underset{O^-}{|}}{C}=O \longleftrightarrow R-\underset{\underset{O}{\|}}{C}-O^-$$

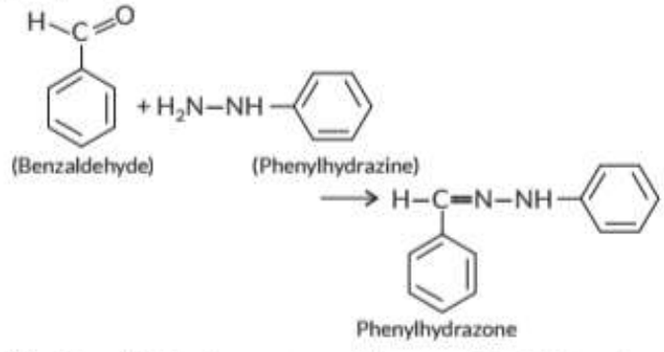
(iv) $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

The reactivity towards nucleophilic addition reactions decreases as the steric hindrance and $+I$ effect of the alkyl groups increases. Due to $+R$ effect of the benzene ring, the aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones.

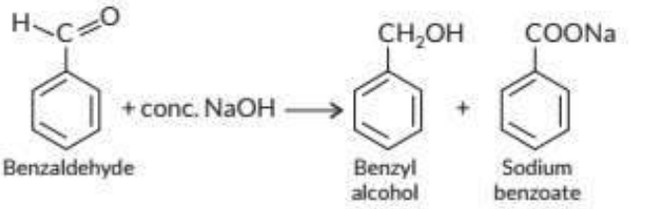
119. (a) (i) When benzaldehyde reacts with CH_3CHO in presence of dilute NaOH, aldol condensation reaction occurs in which α, β-unsaturated product is formed.



(ii) Benzaldehyde reacts with phenylhydrazine to form phenyl hydrazone.



(iii) Benzaldehyde reacts with conc. NaOH to form benzyl alcohol and sodium benzoate.



(b) (i) $CH_3CH=CHCOCH_3$ and $CH_3CH_2COCH=CH_2$ can be distinguished by iodoform test.

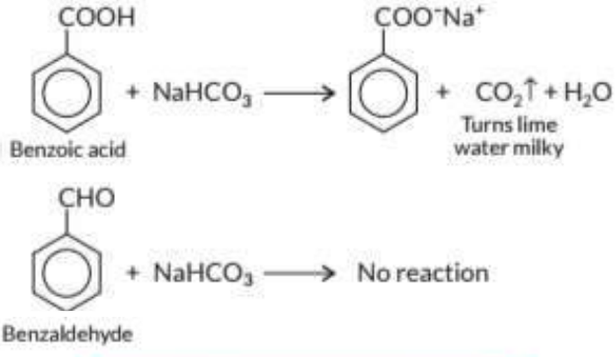
$$CH_3-CH=CH-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[NaOH]{I_2} CH_3-CH=CH-\overset{\overset{O}{\|}}{C}-O^-Na^+ + CHI_3$$

(Methyl ketone) (Iodoform yellow ppt.)

$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH=CH_2 \xrightarrow{I_2/NaOH} \text{No yellow ppt.}$$

Pent-3-en-2-one will give yellow precipitate of iodoform on reaction with I_2 and NaOH due to presence of $(CH_3-\overset{\overset{O}{\|}}{C}-)$ group.

(ii) Benzoic acid and benzaldehyde can be distinguished by $NaHCO_3$ (sodium bicarbonate). Benzoic acid turns lime water milky due to release of CO_2 while benzaldehyde does not undergo such reaction.



CBSE Sample Questions

1. (a) **(1)**

2. (c) : 2,4-DNP test is given by both aldehydes and ketones.
Fehling's, Tollens' and Cannizzaro reaction is shown by aldehydes only. **(1)**

3. $(CH_3)_2CHCHO$ (2-Methyl propanal) + C_2H_5MgBr (Ethyl magnesium bromide) → dry ether → $(CH_3)_2CH\underset{\underset{OMgBr}{|}}{C}H-CH_2CH_3$ $\xrightarrow{H^+/H_2O}$ $(CH_3)_2CHCH(C_2H_5)(OH)$ (2-Methylpentan-3-ol)

(2)

4. (a) The alpha hydrogen atoms are acidic in nature due to presence of electron withdrawing carbonyl group which makes the anion resonance stabilised. In

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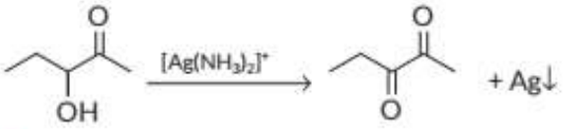
aldol condensation, alkali reacts with α-hydrogen of aldehyde or ketone to form β-hydroxyaldehyde (aldol) or β-hydroxyketones (ketol), respectively. **(1)**

(b) Tollens' reagent is a weak oxidising agent not capable of breaking the C–C bond in ketones . Thus, ketones cannot be oxidised by using Tollens' reagent except α-hydroxyketones.



(1)

5. Compound *A* is an alkene, on ozonolysis it will give carbonyl compounds. As both *B* and *C* have >C=O group, *B* gives positive Fehling's test so it is an aldehyde and it gives iodoform test so it has $H_3C-\overset{O}{\overset{\|}{C}}-$ group. This means the aldehyde is acetaldehyde. *C* does not give Fehling's test, so it is a ketone. It gives positive iodoform test showing that it is a methyl ketone means it has $H_3C-\overset{O}{\overset{\|}{C}}-$ group.

Compound *A* (C_5H_{10}) on ozonolysis gives *B* (CH_3CHO) and *C*(CH_3COR). So '*C*' is CH_3COCH_3.

$$CH_3CH{=}C(CH_3)_2 \xrightarrow[(ii)\ Zn/H_3O^+]{(i)\ O_3} CH_3CHO + CH_3COCH_3$$ **(1/2)**

$$CH_3CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3COO^- + \underset{\text{(red ppt.)}}{Cu_2O} + 3H_2O$$

$CH_3COCH_3 + 2Cu^{2+} + 5OH^- \longrightarrow$ No reaction **(1/2)**

$CH_3CHO + 3I_2 + 3NaOH \longrightarrow \underset{\text{(Yellow ppt.)}}{CHI_3} + 3HI + HCOONa$ **(1/2)**

$$CH_3COCH_3 + 3I_2 + 3NaOH \rightarrow \underset{\text{(Yellow ppt.)}}{CHI_3} + CH_3COONa + 3HI$$

$A = CH_3CH{=}C(CH_3)_2$ **(1/2)**

$B = CH_3CHO$ **(1/2)**

$C = CH_3COCH_3$ **(1/2)**

6. *A* is an alkene while '*B*' gives Silver mirror test so, *B* is an aldehyde with $-CH_3$ group.

As '*C*' gives yellow precipitate so, *C* is a methyl ketone.

(a) *A* : $CH(CH_3){=}C(CH_3)_2$; *B* : CH_3CHO; *C* : $O{=}C(CH_3)_2$ **(1)**

(b) $\underset{(B)}{CH_3CHO} + [Ag(NH_3)_2]^+ + OH^- \longrightarrow CH_3COO^- + Ag + NH_3 + H_2O$ **(1)**

(c) $CH_3COCH_3 + NaOH + I_2 \longrightarrow CHI_3 + CH_3COONa$ **(1)**

(d) $\underset{(C)}{CH_3COCH_3} + \underset{(B)}{CH_3CHO}$

$\downarrow Ba(OH)_2$

$(CH_3)_2C(OH)CH_2COCH_3 + CH_3CH(OH)CH_2CHO +$
$(CH_3)_2C(OH)CH_2CHO + CH_3CH(OH)CH_2COCH_3$

$\downarrow$ heat

$(CH_3)_2C{=}CHCOCH_3 + CH_3CH{=}CHCHO +$
$(CH_3)_2C{=}CHCHO + CH_3CH{=}CHCOCH_3$ **(2)**

OR

(a) *A* : CCl_3COOH *B* : CH_3COOH **(1)**

(b) $\underset{(B)}{CH_3COOH} \xrightarrow[(ii)\ H_2O]{(i)\ Red\ P/Cl_2} \underset{(A)}{CCl_3COOH},$ **(1)**

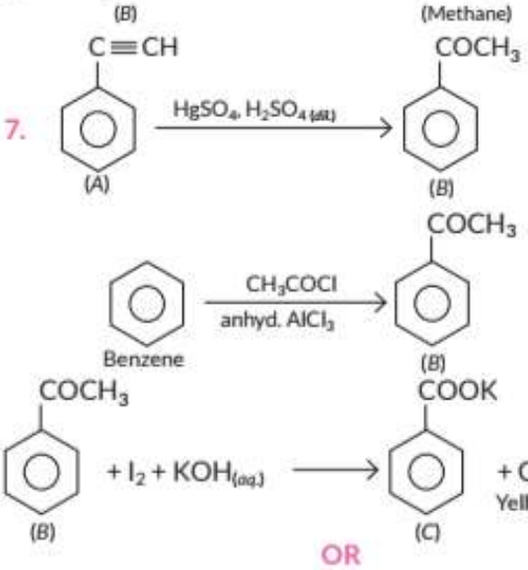
It is known as Hell Volhard Zelinsky reaction.

(c) $CH_3COCl \xrightarrow{H_2O} CH_3COOH$ **(1)**

(d) *A* will be more acidic due to presence of 3 Cl groups (electron withdrawing groups) which increase acidity of carboxylic acid.

(e) $\underset{(B)}{CH_3COOH} \xrightarrow{(i)\ NaOH,\ CaO\ (ii)\ heat} \underset{(Methane)}{CH_4} + Na_2CO_3$ **(1)**

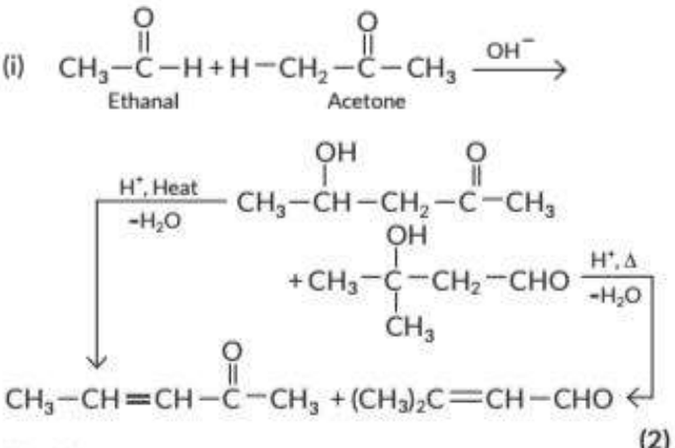
7.



(5)

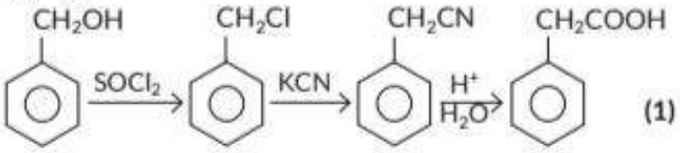
OR

(i)



(2)

(ii) (a)

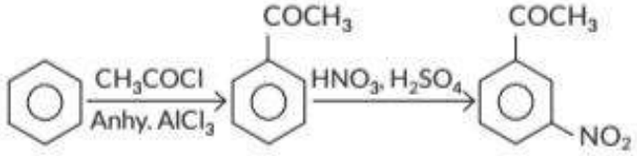


(1)

(b) $CH_3COCH_3 \xrightarrow{H_2/Pd} CH_3CH(OH)CH_3$

$\xrightarrow{H_2SO_4} CH_3CH{=}CH_2$ **(1)**

(c)



(1)

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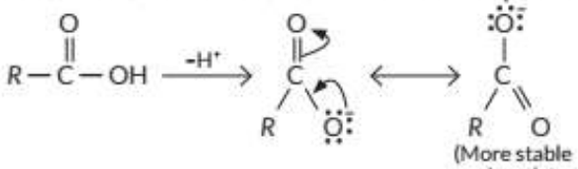
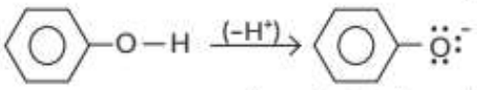
8. (b) : Carboxylic acids are more acidic than phenols. This can be explained on the basis of stability of conjugate base obtained after removal of H^+ from acid or phenol.





(Less stable phenoxide ion)

The conjugate base of carboxylic acid is stablized by two equivalent structures in which negative charge delocalises on more electronegative oxygen atom whereas in case of phenol, the negative charge delocalises on one oxygen atom and less electronegative carbon atom making less stable. Therefore, carboxylic acids are more acidic than phenol.

The (—OH) group present on phenol makes it *ortho* and *para*-directing as the carbocation formed is comparatively more stable at *o*- and *p*-position rather than *meta*-postion. **(1)**

9. (a) Picric acid < Salicylic acid < Benzoic acid < Phenol. Higher is the pK_a value lesser is the K_a value, then lesser is the acidic character. **(1)**

(b) Methyl *tert* - butyl ketone < Acetone < Acetaldehyde (Reaction with NH_2OH is a nucleophilic addition reaction). **(1)**

(c) Ethanol < ethanoic acid < benzoic acid

Boiling point of carboxylic acids is higher than alcohols due to extensive hydrogen bonding. Further, among carboxylic acids, boiling point increases with increase in molar mass. **(1)**

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