Unit

12

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

I. Multiple Choice Questions (Type-I)

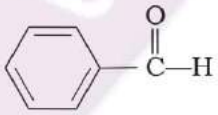
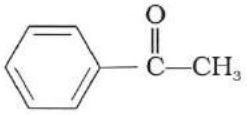
1. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these conditions.

(i) $CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—H$ (ii) $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$

(iii) $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—OH + CO_2$ (iv) $CH_3—\overset{\overset{O}{\|}}{C}—OH + H—\overset{\overset{O}{\|}}{C}—H$

2. Which of the following compounds is most reactive towards nucleophilic addition reactions?

(i) $CH_3—\overset{\overset{O}{\|}}{C}—H$ (ii) $CH_3—\overset{\overset{O}{\|}}{C}—CH_3$

(iii)  (iv) 

3. The correct order of increasing acidic strength is _____.

(i) Phenol < Ethanol < Chloroacetic acid < Acetic acid

(ii) Ethanol < Phenol < Chloroacetic acid < Acetic acid

(iii) Ethanol < Phenol < Acetic acid < Chloroacetic acid

(iv) Chloroacetic acid < Acetic acid < Phenol < Ethanol

4. Compound  can be prepared by the reaction of _____.

(i) Phenol and benzoic acid in the presence of NaOH

(ii) Phenol and benzoyl chloride in the presence of pyridine

(iii) Phenol and benzoyl chloride in the presence of $ZnCl_2$

(iv) Phenol and benzaldehyde in the presence of palladium

5. The reagent which does not react with both, acetone and benzaldehyde.

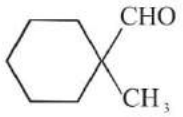
(i) Sodium hydrogensulphite

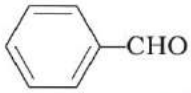
(ii) Phenyl hydrazine

(iii) Fehling's solution

(iv) Grignard reagent

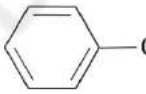
6. Cannizaro's reaction is **not** given by _____.

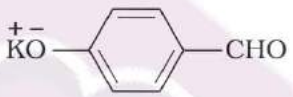
(i) 

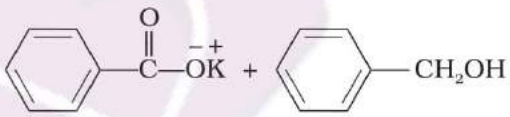
(ii) 

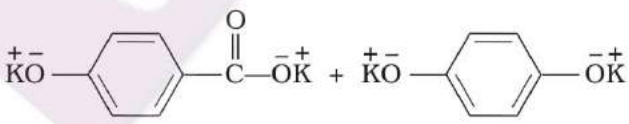
(iii) H CHO

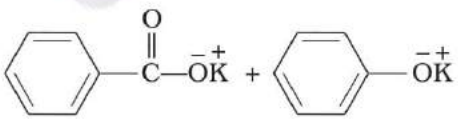
(iv) CH_3CHO

7. Which product is formed when the compound  is treated with concentrated aqueous KOH solution?

(i) 

(ii) 

(iii) 

(iv) 

8. $CH_3—C\equiv CH \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} A \xrightarrow{\text{Isomerisation}} CH_3—\underset{\underset{O}{\|}}{C}—CH_3$

Structure of 'A' and type of isomerism in the above reaction are respectively.

(i) Prop–1–en–2–ol, metamerism

(ii) Prop-1-en-1-ol, tautomerism

(iii) Prop-2-en-2-ol, geometrical isomerism

(iv) Prop-1-en-2-ol, tautomerism

9. Compounds A and C in the following reaction are _____.

$$CH_3CHO \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} (A) \xrightarrow{H_2SO_4,\ \Delta} (B) \xrightarrow[\text{oxidation}]{\text{Hydroboration}} (C)$$

(i) identical

(ii) positional isomers

(iii) functional isomers

(iv) optical isomers

10. Which is the most suitable reagent for the following conversion?

$$CH_3—CH=CH—CH_2—\overset{\overset{O}{\|}}{C}—CH_3 \longrightarrow CH_3—CH=CH—CH_2—\overset{\overset{O}{\|}}{C}—OH$$

(i) Tollen's reagent

(ii) Benzoyl peroxide

(iii) I_2 and NaOH solution

(iv) Sn and NaOH solution

11. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution?

(i) Butan-1-ol

(ii) Butan-2-ol

(iii) Both of these

(iv) None of these

12. In Clemmensen Reduction carbonyl compound is treated with _____.

(i) Zinc amalgam + HCl

(ii) Sodium amalgam + HCl

(iii) Zinc amalgam + nitric acid

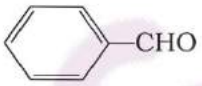
(iv) Sodium amalgam + HNO_3

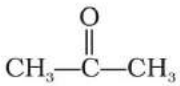
II. Multiple Choice Questions (Type-II)

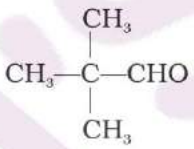
Note : In the following questions two or more options may be correct.

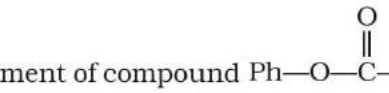
13. Which of the following compounds do not undergo aldol condensation?

(i) $CH_3—CHO$

(ii) 

(iii) 

(iv) 

14. Treatment of compound  with NaOH solution yields

(i) Phenol

(ii) Sodium phenoxide

(iii) Sodium benzoate

(iv) Benzophenone

15. Which of the following conversions can be carried out by Clemmensen Reduction?

(i) Benzaldehyde into benzyl alcohol

(ii) Cyclohexanone into cyclohexane

(iii) Benzoyl chloride into benzaldehyde

(iv) Benzophenone into diphenyl methane

16. Through which of the following reactions number of carbon atoms can be increased in the chain?

(i) Grignard reaction

(ii) Cannizaro's reaction

(iii) Aldol condensation

(iv) HVZ reaction

17. Benzophenone can be obtained by _____.

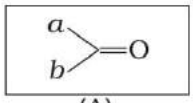
(i) Benzoyl chloride + Benzene + $AlCl_3$

(ii) Benzoyl chloride + Diphenyl cadmium

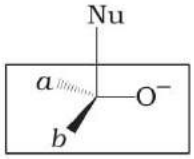
(iii) Benzoyl chloride + Phenyl magnesium chloride

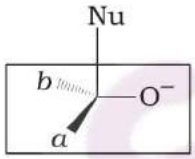
(iv) Benzene + Carbon monoxide + $ZnCl_2$

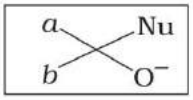
18. Which of the following is the correct representation for intermediate of nucleophilic addition reaction to the given carbonyl compound (A) :

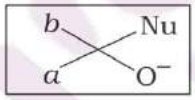


(A)

(i) 

(ii) 

(iii) 

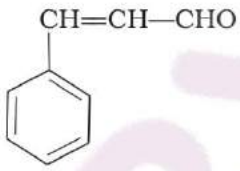
(iv) 

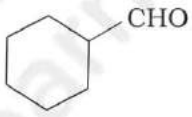
III. Short Answer Type

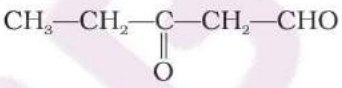
19. Why is there a large difference in the boiling points of butanal and butan-1-ol?

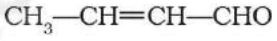
20. Write a test to differentiate between pentan-2-one and pentan-3-one.

21. Give the IUPAC names of the following compounds

(i) 

(ii) 

(iii) 

(iv) 

22. Give the structure of the following compounds.

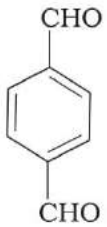
(i) 4-Nitropropiophenone

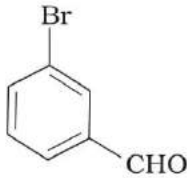
(ii) 2-Hydroxycyclopentanecarbaldehyde

(iii) Phenyl acetaldehyde

23. Write IUPAC names of the following structures.

(i) 

(ii) 

(iii) 

24. Benzaldehyde can be obtained from benzal chloride. Write reactions for obtaining benzalchloride and then benzaldehyde from it.

25. Name the electrophile produced in the reaction of benzene with benzoyl chloride in the presence of anhydrous $AlCl_3$. Name the reaction also.

26. Oxidation of ketones involves carbon-carbon bond cleavage. Name the products formed on oxidation of 2, 5-dimethylhexan-3-one.

27. Arrange the following in decreasing order of their acidic strength and give reason for your answer.

CH_3CH_2OH, CH_3COOH, $ClCH_2COOH$, FCH_2COOH, $C_6H_5CH_2COOH$

28. What product will be formed on reaction of propanal with 2-methylpropanal in the presence of NaOH? What products will be formed? Write the name of the reaction also.

29. Compound 'A' was prepared by oxidation of compound 'B' with alkaline $KMnO_4$. Compound 'A' on reduction with lithium aluminium hydride gets converted back to compound 'B'. When compound 'A' is heated with compound B in the presence of H_2SO_4 it produces fruity smell of compound C to which family the compounds 'A', 'B' and 'C' belong to?

30. Arrange the following in decreasing order of their acidic strength. Give explanation for the arrangement.

C_6H_5COOH, FCH_2COOH, NO_2CH_2COOH

31. Alkenes ($\rangle C{=}C \langle$) and carbonyl compounds ($\rangle C{=}O$), both contain a π bond but alkenes show electrophilic addition reactions whereas carbonyl compounds show nucleophilic addition reactions. Explain.

32. Carboxylic acids contain carbonyl group but do not show the nucleophilic addition reaction like aldehydes or ketones. Why?

33. Identify the compounds A, B and C in the following reaction.

$$CH_3{-}Br \xrightarrow{Mg/ether} (A) \xrightarrow[(ii)\ Water]{(i)\ CO_2} (B) \xrightarrow[\Delta]{CH_3OH/H^+} (C)$$

34. Why are carboxylic acids more acidic than alcohols or phenols although all of them have hydrogen atom attached to a oxygen atom (—O—H)?

35. Complete the following reaction sequence.

$$CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} (A) \xrightarrow[Ether]{Na\ metal} (B) \xrightarrow{CH_3{-}Br} (C)$$

36. Ethylbenzene is generally prepared by acetylation of benzene followed by reduction and not by direct alkylation. Think of a possible reason.

37. Can Gatterman-Koch reaction be considered similar to Friedel Craft's acylation? Discuss.

IV. Matching Type

Note : Match the items of Column I and Column II in the following questions.

38. Match the common names given in Column I with the IUPAC names given in Column II.

Column I (Common names)	**Column II (IUPAC names)**
(i) Cinnamaldehyde	(a) Pentanal
(ii) Acetophenone	(b) Prop-2-enal
(iii) Valeraldehyde	(c) 4-Methylpent-3-en-2-one
(iv) Acrolein	(d) 3-Phenylprop-2-enal
(v) Mesityl oxide	(e) 1-Phenylethanone

39. Match the acids given in Column I with their correct IUPAC names given in Column II.

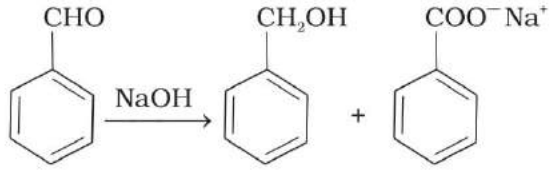
Column I (Acids)	**Column II (IUPAC names)**
(i) Phthalic acid	(a) Hexane-1,6-dioic acid
(ii) Oxalic acid	(b) Benzene-1,2-dicarboxylic acid
(iii) Succinic acid	(c) Pentane-1,5-dioic acid
(iv) Adipic acid	(d) Butane-1,4-dioic acid
(v) Glutaric acid	(e) Ethane-1,2-dioic acid

40. Match the reactions given in Column I with the suitable reagents given in Column II.

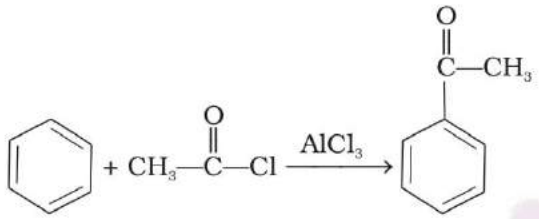
Column I (Reactions)	**Column II (Reagents)**
(i) Benzophenone → Diphenylmethane	(a) $LiAlH_4$
(ii) Benzaldehyde → 1-Phenylethanol	(b) DIBAL—H
(iii) Cyclohexanone → Cyclohexanol	(c) Zn(Hg)/Conc. HCl
(iv) Phenyl benzoate → Benzaldehyde	(d) CH_3MgBr

41. Match the example given in Column I with the name of the reaction in Column II.

Column I (Example)	**Column II (Reaction)**
(i) $CH_3-\overset{\overset{O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd\text{-}C/BaSO_4} CH_3-\overset{\overset{O}{\|}}{C}-H$	(a) Friedel Crafts acylation

(ii) 

(b) HVZ reaction

(iii) 

(c) Aldol condensation

(iv) $R—CH_2—COOH \xrightarrow{Br_2/Red\ P} R—\underset{\displaystyle Br}{\underset{|}{CH}}—COOH$ (d) Cannizaro's reaction

(v) $CH_3—CN \xrightarrow[(ii)\ H_2O/H^+]{(i)\ SnCl_2/HCl} CH_3CHO$ (e) Rosenmund's reduction

(vi) $2CH_3CHO \xrightarrow{NaOH} CH_3—CH=CHCHO$ (f) Stephen's reaction

V. Assertion and Reason Type

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(i) Assertion and reason both are correct and reason is correct explanation of assertion.

(ii) Assertion and reason both are wrong statements.

(iii) Assertion is correct statement but reason is wrong statement.

(iv) Assertion is wrong statement but reason is correct statement.

(v) Assertion and reason both are correct statements but reasson is not correct explanation of assertion.

42. Assertion : Formaldehyde is a planar molecule.

Reason : It contains sp^2 hybridised carbon atom.

43. Assertion : Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids.

Reason : Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.

44. **Assertion** : The α-hydrogen atom in carbonyl compounds is less acidic.

Reason : The anion formed after the loss of α-hydrogen atom is resonance stabilised.

45. ***Assertion*** : Aromatic aldehydes and formaldehyde undergo Cannizaro reaction.

Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

46. **Assertion** : Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.

Reason : Both, aldehydes and ketones contain a carbonyl group.

VI. Long Answer Type

47. 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 reaction for ozonolysis and formation of iodoform from B and C.

48. An aromatic compound 'A' (Molecular formula C_8H_8O) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide solution. Compound 'A' does not give Tollen's or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid 'C' (Molecular formula $C_7H_6O_2$), which is also formed along with the yellow compound in the above reaction. Identify A, B and C and write all the reactions involved.

49. Write down functional isomers of a carbonyl compound with molecular formula C_3H_6O. Which isomer will react faster with HCN and why? Explain the mechanism of the reaction also. Will the reaction lead to the completion with the conversion of whole reactant into product at reaction conditions? If a strong acid is added to the reaction mixture what will be the effect on concentration of the product and why?

50. When liquid 'A' is treated with a freshly prepared ammoniacal silver nitrate solution, it gives bright silver mirror. The liquid forms a white crystalline solid on treatment with sodium hydrogensulphite. Liquid 'B' also forms a white crystalline solid with sodium hydrogensulphite but it does not give test with ammoniacal silver nitrate. Which of the two liquids is aldehyde? Write the chemical equations of these reactions also.

ANSWERS

I. Multiple Choice Questions (Type-I)

1. (ii)	2. (i)	3. (iii)	4. (ii)	5. (iii)	6. (iv)
7. (ii)	8. (iv)	9. (ii)	10. (iii)	11. (ii)	12. (i)

II. Multiple Choice Questions (Type-II)

13. (ii), (iv); [**Hint :** in compounds (ii) and (iv) α-hydrogen is absent.]

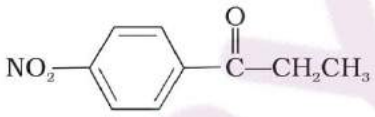
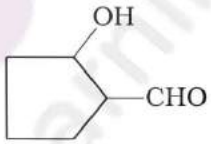
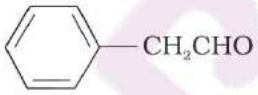
14. (ii), (iii) 15. (ii), (iv) 16. (i), (iii) 17. (i), (ii) 18. (i), (ii)

III. Short Answer Type

19. [**Hint :** Butan-1-ol has higher boiling point due to intermolecular hydrogen bonding.]

20. [**Hint :** Iodoform test]

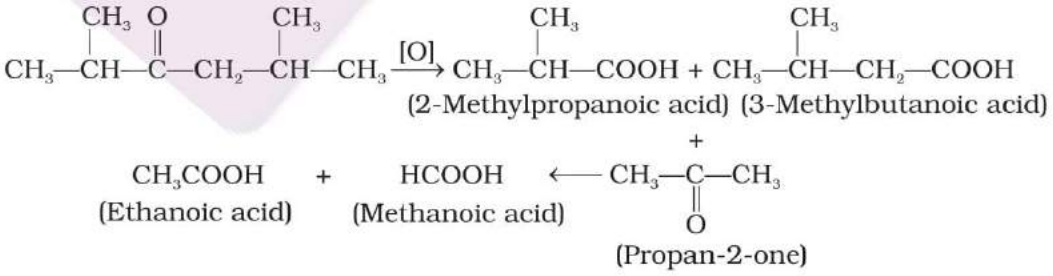
21. (i) 3-Phenylprop-2-enal (ii) Cyclohexanecarbaldehyde
(iii) 3-oxopentanal (iv) But -2-enal

22. (i) 
(ii) 
(iii) 

23. (i) Ethane-1, 2 – dial (ii) Benzene-1, 4-dicarbaldehyde
(iii) 3-Bromobenzaldehyde

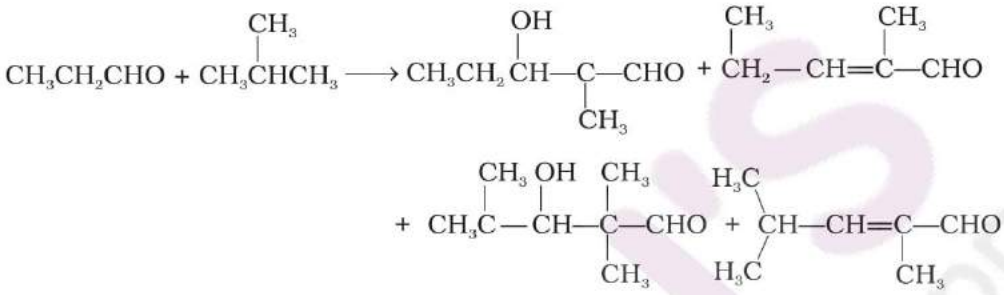
24. See NCERT textbook for Class XII

25. $C_6H_5\overset{\oplus}{C}O$ benzoyliumcation or $C_6H_5-\overset{O}{\overset{\|}{C}}\overset{\delta^+}{.....}Cl.....\overset{\delta^-}{AlCl_3}$. Friedel Craft's acylation reaction.

26. 

27. **Hint :** $FCH_2COOH > ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2OH$

28. It is cross Aldol condensation



29. 'A' is a carboxylic acid, 'B' is an alcohol and 'C' is an ester.

30. $NO_2CH_2COOH > FCH_2COOH > C_6H_5COOH$

[**Hint :** electron withdrawing effect.]

31. [**Hint :** Carbon atom in carbonyl compounds acquires slight positive charge and is attacked by nucleophile.]

32. [**Hint :** Due to resonance as shown below the partial positive charge on carbonyl carbon atom is reduced.]

33. $A = CH_3MgBr$ $B = CH_3COOH$ $C = CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3$

34. **Hint :** Compare the stability of anion formed after the loss of H^+ ion. More stable the anion formed, more easy will be the dissociation of O—H bond, stronger will be the acids.

35. **Hint :** $A = CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$ $B = CH_3-\overset{\overset{O^-Na^+}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$ $C = CH_3-\overset{\overset{O-CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

IV. Matching Type

38. (i) — (d), (ii) — (e), (iii) — (a), (iv) — (b), (v) — (c)

39. (i) — (b), (ii) — (e), (iii) — (d), (iv) — (a), (v) — (c)

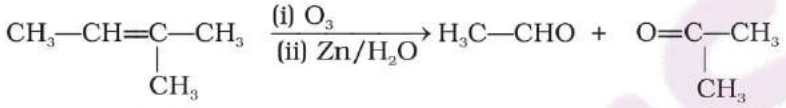
40. (i) — (c), (ii) — (d), (iii) — (a), (iv) — (b)

41. (i) — (e), (ii) — (d), (iii) — (a), (iv) — (b), (v) — (f), (vi) — (c)

V. Assertion and Reason Type

42. (i) 43. (v) 44. (iv) 45. (iii) 46. (iv)

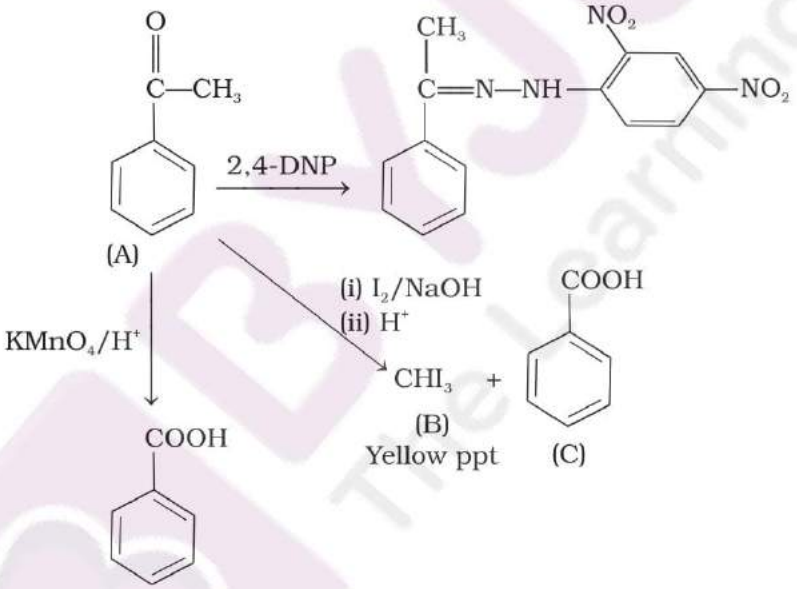
VI. Long Answer Type

47. 

2-Methylbut-2-ene
(A) (B) (C)

Other isomers of 'A' will not give products corresponding to the given test.

48. **Hint :**



49. CH_3CH_2CHO CH_3COCH_3
(I) (II)

- Compound I will react faster with HCN due to less steric hinderance and electronic reasons than II.
- No, It is a reversible reaction. Hence equilibrium is established.
- Addition of acid inhibits the reaction because the formation of ^-CN ions is prevented.

50. **Hint :** Liquid 'A'