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# NCERT Exemplar Problems Class 12 Chemistry Chapter 12 Aldehydes, Ketones and Carboxylic Acids

**Multiple Choice Questions** 

Single Correct Answer Type

Question 1. Addition of water to alkynes occurs in acidic medium and in the presence of Hg<sup>2+</sup> ions as a catalyst. Which one of the following product will be formed on addition of water to but-l-yne under these conditions?

(a)  $CH_3 - CH_2 - CH_2 - \overset{\parallel}{C} - H$ 

(b) 
$$CH_3 - CH_2 - \overset{\parallel}{C} - CH_3$$

(c) 
$$CH_3 - CH_2 - C - OH + CH_2$$
  
O O  
(d)  $CH_2 - C - OH + H - C - H$ 

Solution: (b)

$$CH_{3}CH_{2}C \equiv CH + H_{2}O \xrightarrow{H^{-}.Hg^{2+}} CH_{3}CH_{2}C = CH_{2} \xrightarrow{CH_{3}}CH_{3}CH_{2}C - CH_{3}$$

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



**Solution:** (a) CH<sub>3</sub>CHO is most reactive towards nucleophilic addition reactions. Carbonyl compounds are polar with positive charge on carbon atom which is attacked by nucleophiles. Two electron releasing alkyl groups in ketones make carbon less electron deficient than

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aldehydes. Benzene ring exhibits + R-effect which thereby decreases the ease of nucleophilic addition reaction in benzaldehyde and acetophenone. Hence the reactivity order

Question 3. The correct order of increasing acidic strength is

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

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

(c) Ethanol < Phenol Acetic acid < Eihloroacetic acid

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

**Solution:** (c) Phenol is more stable than alcohol due to formation of more stable conjugate base after removal of H<sup>+</sup> from phenol.

Whereas carboxylic acid is more acidic than phenol due to formation of more stable conjugate base after removal of H<sup>+</sup> as compared to phenol.



Chloroacetic acid is more acidic than acetic acid due to the presence of electron withdrawing chlorine group attached to  $\alpha$ -carbon of carboxylic acid.



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#### Question 4.

Compound Ph - O - C - Ph can be prepared by the reaction of

(a) phenol and benzoic acid in the presence of NaOH

0

- (b) phenol and benzoyl chloride in the presence of pyridine
- (c) phenol and benzoyl chloride in the presence of ZnCl<sub>2</sub>
- (d) phenol and benzaldehyde in the presence of palladium

**Solution:** (b)  $C_6H_5OCOC_6H_5$  can be prepared by the reaction of phenol and benzoyl chloride in the presence of pyridine.



#### Question 5. The reagent which does not react with both acetone and benzaldehyde is

#### (a) sodium hydrogen sulphite

#### (c) Fehling's solution

**Solution:** (c) Fehling's solution oxidises aliphatic aldehydes very easily but does not react with acetone and benzaldehyde.

# Question 6. Cannizzaro's reaction is not given by (a) CHO (b) (b)



**Solution:** (d) CH<sub>3</sub>CHO will not give Cannizzaro's reaction because it contains a-hydrogen while other three compounds have no a-hydrogen. Hence, they will give Cannizzaro's reaction.

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#### Question 7.

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



**Solution:** (b) Benzaldehyde is having no a hydrogen. So, on reaction with aqueous KOH solution, it undergoes Cannizzaro's reaction. One molecule of aldehyde is reduced and other is

Potassium benzoate

COOK

CH<sub>2</sub>OH

Banzyl alcohol



Benzaldehyde

#### **Question 8.**

$$CH_{3} - C \equiv CH \xrightarrow{40\%H_{2}SO_{4}} A \xrightarrow{Isomerisation} CH_{3} - C - CH_{3} \parallel O_{(Acetone)}$$

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

- (a) prop-1-en-2-ol, metamerism
- (b) prop-1-en-1-ol, tautomerism
- (c) prop-2-en-2-ol, geometrical isomerism
- (d) prop-1-en-2-ol, tautomerism

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Question 9. Compounds A and C in the following reactions are  $CH_{3}CHO \xrightarrow{(i) CH_{3}MgBr}_{(ii) H_{2}O} (A) \xrightarrow{H_{2}SO_{4}, \Delta} (B) \xrightarrow{\text{oxidation}} (C)$ (a) identical (b) positional isomers (c) functional isomers (d) optical isomers Solution: (b)  $CH_{3}CHO \xrightarrow{(i) CH_{3}MgBr}_{(ii) H_{2}O} CH_{3} \xrightarrow{-} CH \xrightarrow{-} OH \xrightarrow{H_{2}SO_{4}, \Delta}_{Dehydration} CH_{3} \xrightarrow{-} C = CH_{2}$ Ethanal  $CH_{3} \xrightarrow{-} CH_{2} \xrightarrow{-} CH_{2}OH \xrightarrow{(i) BH_{3}}_{H_{2}O_{2}/OH^{\circ}}$ (i) BH\_{3} (B)  $CH_{3} \xrightarrow{-} CH_{2} \xrightarrow{-} CH_{2}OH \xrightarrow{(i) BH_{3}}_{(ii) H_{2}O_{2}/OH^{\circ}}$ (i) BH\_{3} (CH\_{3} \xrightarrow{-} CH\_{2} \xrightarrow{-} CH\_{2}OH \xrightarrow{(i) BH\_{3}}\_{H\_{2}O\_{2}/OH^{\circ}}
Thus,  $CH_{3}CH \xrightarrow{-} OH$  and  $CH_{3} \xrightarrow{-} CH_{2} \xrightarrow{-} CH_{2}OH$  are positional isomers.  $CH_{3} \xrightarrow{-} CH_{2} \xrightarrow{-} CH_{2}OH$ 



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Solution: (c)  $CH_3CH=CH-CH_2 \xrightarrow{H_2} CH_3 \xrightarrow{I_2 + NaOH} CH_3CH=CHCH_2 \xrightarrow{O} CH_2 ONA + CHI_3$   $\downarrow H_2O$  $CH_3CH=CHCH_2 \xrightarrow{H_2} OH$ 

Question 11. Which of the following compounds will give butanone on oxidation with alkaline KMnO<sub>4</sub>solution?

(a) Butan-I-ol (b) Butan-2-ol

(c) Both (a) and (b) (d) None of these Solution:

(b)  $CH_3CH_2CHCH_3 \xrightarrow{alk} CH_3CH_2COCH_3$  $\downarrow \\ OH \\ Butan-2-ol$ 

Question 12. In Clemmensen reduction carbonyl compound is treated with

(a) zinc amalgam + HCI (b) sodium amalgam + HCI

(c) zinc amalgam + nitric acid (d) sodium amalgam + HNO<sub>3</sub>

**Solution:** (a) Clemmensen reduction is used to convert carbonyl group to CH<sub>2</sub> group as follows

$$C=O \xrightarrow{Zn (Hg) + HCl} CH_2$$

Zinc amalgam and HCl act as reagent in this reaction.

#### More than One Correct Answer Type

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



#### Solution: (b, d)

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In these compounds, a-hydrogen is absent. So, aldol condensation does not take place in these compounds.

Question 14.



Ph-ONa

Sodium phenoxide

Question 15. Which of the following conversions can be carried out

by Clemmensen reduction?

(a) Benzaldehyde into benzyl alcohol

(b) Cyclohexanone into cyclohexane

(c) Benzoyl chloride into benzaldehyde

(d) Benzophenone into diphenylmethane

Solution: (b, d)

Clemmensen reduction is used to convert cyclohexanone into cyclohexane and

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benzophenone into diphenyl methane.



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

(a) Grignard reaction (b) Cannizzaro's reaction

#### (c) Aldol condensation (d) HVZ reaction

Solution: (a, c) Grignard reagent is used to add number of carbon atom in chain.

$$RCHO + R'MgX \xrightarrow{H_2O} R - CH - OH$$

Aldol condensation involves condensation of aldehydes and ketones with  $\alpha$ -hydrogen.

CH<sub>3</sub>CHO 
$$\xrightarrow{\text{dil NaOH}}$$
 CH<sub>3</sub>CHCH<sub>2</sub>CHO  $\xrightarrow{\Delta}$  CH<sub>3</sub>CH=CHCHO  
OH  
Aldol

Question 17. Benzophenone can be obtained by

(a) benzoyl chloride + benzene + AICI<sub>3</sub>

(b) benzoyl chloride + diphenylcadmium

(c) benzoyl chloride + phenylmagnesium chloride

(d) benzene + carbon monoxide + ZnCl<sub>2</sub>

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



**Solution:** (a, b) Since, carbonyl compound is a planar molecule hence two orientation of molecule regarding attack of nucleophile is possible as follows



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Since, the product contains a chiral carbon, therefore, attack of nucleophile can occur either from front side attack or rear side attack giving enantiomeric products.

#### **Short Answer Type Questions**

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

**Solution:** Butan-1 -ol has higher boiling point (391 K) than butanal due to intermolecular hydrogen bonding between -OH groups of alcohols.

# Question 20. Write a test to differentiate between pentan-2-one and pentan-3-one. Solution:

Pentan-2-one having a  $-C-CH_3$  group forms a yellow ppt. of iodoform with an alkaline solution of iodine (i.e., iodoform test) while pentan-3-one does not.



Question 21. Give the IUPAC names of the following compounds:



Solution: (a) 3-Phcnylprop-2-en-1 -al

(b) Cyclohexanecarbaldehyde

(c) 3-Oxopentan-I-al

(d) But-2-en-I-al

#### Question 22. Give the structure of the following compounds:

#### (a) 4-Nitropropiophenone

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#### (b) 2-Hydroxycyclopentane + carbaldehyde

(c) Phenyl acetaldehyde

Solution: (a)  $O_2N \longrightarrow C - CH_2CH_3$  (4-Nitropropiophenone)

(b) -CHO (2-Hydroxycyclopentane carbaldehyde) (c)  $-CH_2CHO$  (Phenyl acetaldehyde)

#### Question 23. Write IUPAC names of the following structures:



Solution: (a) Ethane-1,2-dial

(b) Benzene-1, 4-dicarbaldehyde

(c) 3-Bromobenzaldehyde

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



Question 25. Name the electrophile produced in the reaction of benzene with benzoyl chloride in the presence of anhydrous AICI<sub>3</sub>. Name of the reaction also.

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Solution:

 $\begin{array}{ccc} & & O \\ & & & \\ & & \\ C_6H_5C - Cl + AlCl_3 \longrightarrow C_6H_5C - Cl - AlCl_3 \longrightarrow C_6H_5CO^+ + AlCl_4 \end{array}$ 

Friedel-Crafts acylation reaction.

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



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

Solution:  $CH_3CH_2OH$ ,  $CH_3COOH$ ,  $CICH_2COOH$ ,  $FCH_2COOH$ ,  $C_6H_5CH_2COOH$  $FCH_2COOH > CICH_2COOH > C_6H_5CH_2COOH > CH_3COOH > CH3CH_2OH$ 

[This is due to -I effect and acidic strength increases proportionately with the increase in electronegativity.

(i.e.,  $F > CI > C_6H_5 > H$ ).

Further CH<sub>3</sub>COOH is much stronger acid than CH<sub>3</sub>CH<sub>2</sub>OH because CH<sub>3</sub>COO<sup>-</sup> ion that has left after the loss of proton is stabilised by resonance but CH<sub>3</sub>CH<sub>2</sub>O<sup>-</sup> does not.]

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

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Solution:



Question 29. Compound 'A' was prepared by oxidation of compound 'B' with alkaline KMnO<sub>4</sub>. 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<sub>2</sub>SO<sub>4</sub> it produces fruity smell of compound 'C' to which family the compounds 'A', 'B' and 'C' belong to?

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#### Solution:

'A' is carboxylic acid (R – COOH), 'B' is an alcohol (R –  $CH_2OH$ ) and 'C' is an ester (RCH<sub>2</sub> – COOR)



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

#### $C_6H_5COOH, FCH_2COOH, NO_2CH_2COOH$

**Solution:** NO<sub>2</sub>CH<sub>2</sub>COOH > FCH<sub>2</sub>COOH > C<sub>6</sub>H<sub>5</sub>COOH

 $-NO_2$  and -F groups are electron withdrawing groups. Out of the two  $-NO_2$  has greater electron withdrawing effect.  $C_6H_5$ -group has electron denoting effect.

Question 31. Alkenes (>C = C<) and carbonyl compounds (>C = O), both contain a rcbond but alkenes show electrophilic addition reactions whereas carbonyl compounds show nucleophilic addition reactions. Explain.

**Solution:** Carbonyl group is polar in nature. Due to larger electronegativity of oxygen as compared to carbon, carbon acquires partial positive charge while O acquires partial negative charge.



Because of slight positive charge on C atom, it is attacked by nucleophiles and, therefore, undergoes nucleophilic addition reaction.

Ethylenic double bond is a non-polar bond and is a source of electrons. Therefore, it is attacked by electrophiles and undergoes electrophilic addition reactions.

Question 32. Carboxylic acids contain carbonyl group but do not show the nucleophilic addition reaction like aldehydes or ketones. Why? Solution: It is due to resonance as shown below. The partial positive charge on the carbonyl

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carbon atom is reduced

$$\begin{array}{c} C \\ R \\ R \\ -C \\ - \\ C \\ - \\ C$$

Similarly, a carbonyl group of aldehydes and ketones may be regarded as the resonance hybrid of the following structures.



The carbonyl carbon of carboxylic group is less electrophilic than carbonyl carbon in aldehydes and ketones and hence nucleophilic addition reactions of aldehydes and ketones do not takes place with carboxylic acids.

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



0

$$CH_{3}-C-OCH_{3} \leftarrow CH_{3}OH/H^{+}, \Delta$$
(Esterification)
Methyl ethanoate
(ester) (C)

Question 34. Why are carboxylic acids more acidic than alcohols or phenols although all of them have hydrogen atom attached to an oxygen atom (-O-H)? Solution: The aliphatic carboxylic acids are stronger acids than alcohols and phenols. The

difference in the relative acidic strengths can be understood if we compare the resonance hybrids of carboxylate ion and ethoxide phenoxide ion.

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Carboxylate ion Phenoxide ion (No resonance)

The electron charge on the carboxylate ion is more dispersed in comparison to the phenate ion since there are two electronegative oxygen atoms in carboxylate ion as compared to only one oxygen atom in phenoxide ion. In other words, the carboxylate ion is

relatively more stable as compared to phenate ion. Thus, the release of H<sup>+</sup> ion from carboxylic acid is comparatively easier or it behaves as a stronger acid than phenol.

#### Question 35. Complete the following reaction sequence.

 $CH_{3} \xrightarrow{\text{CH}} CH_{5} \xrightarrow{\text{(i) CH}_{3}\text{MgBr}} (A) \xrightarrow{\text{Na metal}} (B) \xrightarrow{\text{CH}_{3} \xrightarrow{\text{Br}}} (C)$ 

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Question 36. What happen when benzene diazonium chloride is heated with water? Solution:



In (ii) reaction, it readily undergoes further alkylation to produce polysubs- tituted derivative.

# Question 37. Can Gattermann-Koch reaction be considered similar to Friedel-Crafts acylation? Discuss.

**Solution:** Gattermann-Koch reaction is formylation (introduction of-CHO group) to the benzene nucleus.

Friedel-Crafts acylation reaction is introduction of RCO— group in the benzene ring.

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In Friedel-Crafts acylation reactions, the benzene is treated with an acid chloride in presence of anhydrous AlCl<sub>3</sub>. So, Gattermann-Koch reaction can be considered similar to Friedel-Crafts acylation reaction.

#### **Matching Column Type Questions**

Question 38.	Match the	common nai	mes given in	Column I	with the I	UPAC na	ames
given in Colu	umn 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	

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Solution: (i —> d), (ii —» e), (iii —> a), (iv —> b), (v -> c)

(Common names)	Structure	(IUPAC names)
(i) Cinnamaldehyde	H_C=C< <sup>H</sup> CHO	3-Phenylprop-2-enal
(ii) Acetophenone	O C C C C C C H <sub>3</sub>	1-Phenylethanone
(iii) Valeraldehyde	5 4 2 1 H	Pentanal
(iv) Acrolein	3 O H	Prop-2-enal
(v) Mesityl oxide	5 4 3 2 1	4-Methylpent-3-en-2- one

Question 39. Match the acids given in Column 1 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		

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**Solution:** (i —> b), (ii —> e), (iii —> d), (iv -> a), (v -> c)

Acids	IUPAC names	Structure
(i) Phthalic acid	Benzene-1, 2 dicarboxylic acid	СООН
(ii) Oxalic acid	Ethane-1, 2-dioic acid	COOH   COOH
(iii) Succinic acid	Butane-1, 4-dioic acid	Соон
(iv) Adipic acid	Hexane-1, 6-dioic acid	Соон
(v) Glutaric acid	Pentane-1, 5-dioic acid	Соон

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

Column I (Reactions)		Column II (Reagents)	
(i)	Benzophenone $\rightarrow$ Diphenylmethane	(a)	LiAlH <sub>4</sub>
(ii)	Benzaldehyde $\rightarrow$ 1-Phenylethanol	(b)	DIBAL – H
(iii)	Cyclohexanone $\rightarrow$ Cyclohexanol	(c)	Zn(Hg)/Conc. HCl
(iv)	Phenyl benzoate $\rightarrow$ Benzaldehyde	(d)	CH <sub>3</sub> MgBr

Solution: (i —> c), (ii —> d), (iii —> a), (iv —» b)

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

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Column I (Examples)			Column II (Reaction)	
(i)	$CH_{3} \xrightarrow{H} C - Cl + H_{2} \xrightarrow{Pd-C/BaSO_{4}} CH_{3} \xrightarrow{O} H$	(a)	Friedel– Crafts acylation	
(ii)	$\begin{array}{c c} CHO & CH_2OH & COO^-Na^+ \\ \hline & & & & \\ \hline & & & & \\ \hline & & & & \\ \hline & & & &$	(b)	HVZ reaction	
(iii)	$O = C + CH_3 + CH_3 - C + CI - CI - CH_3$	(c)	Aldol condensation	
(iv)	$\begin{array}{c} R-CH_2-COOH \xrightarrow{Br_2/Red P} R-CH-COOH \\ & Br \end{array}$	(d)	Cannizzaro's reaction	
(v)	$CH_3 \longrightarrow CN \xrightarrow{(i) SnCl_2/HCl}{(ii) H_2O/H^{\bullet}} CH_3CHO$	(e)	Rosenmund's reduction	
(vi)	$2CH_{3}CHO \xrightarrow{\text{NaOH}} CH_{3} \longrightarrow CH = CHCHO$	(f)	Stephen's reaction	

Solution: (i —> e), (ii -» d), (iii -> a), (iv b), (v -> f), (vi —> d)

#### **Assertion and Reason Type Questions**

In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices:

(a) Assertion and Reason both are correct and Reason is the correct explanation of Assertion.

- (b) Assertion and Reason both are wrong.
- (c) Assertion is correct but Reason is wrong.
- (d) Assertion is wrong but Reason is correct.

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(e) Assertion and Reason both are correct statements but Reason is not the correct explanation of Assertion.

Question 42. Assertion (A): Formaldehyde is a planar molecule.

Reason (R): It contains sp<sup>2</sup> hybridised carbon atom.

**Solution:** (a) Formaldehyde is a planar molecule because it contains sp<sup>2</sup> hybridised carbon atom.

Question 43. Assertion (A): Compounds containing -CHO group are easily oxidized to corresponding carboxylic acids.

**Reason (R): Carboxylic acids can be reduced to alcohols by treatment with LiAlH**<sub>4</sub>**. Solution:** (e) Due to electron withdrawing nature of -C = O group, C — H bond in aldehydes is weak and thus can be easily oxidized to the corresponding carboxylic acids even with mild oxidizing agents like Fehling's solution and Tollens reagents.

Question 44. Assertion (A): The a-hydrogen atom in carbonyl compounds is less acidic. Reason (R): The anion formed after the loss of a-hydrogen atom in carbonyl compounds is more acidic.

**Solution:** (d) The a-hydrogen atom in carbonyl compounds is more acidic.

# Question 45. Assertion (A): Aromatic aldehydes and formaldehyde undergo Cannizzaro's reaction.

Reason (R): Aromatic aldehydes are almost as reactive as formaldehyde.

**Solution:** (c) Aromatic aldehydes and formaldehyde do not contain a-hydrogen and thus undergo Cannizzaro's reaction. Formaldehyde is more reactive than aromatic aldehydes.

Question 46. Assertion (A): Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.

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

**Solution:** (d) Both aldehyde and ketones have carbonyl group but only aldehydes react with Tollen's reagent to give silver mirror.

#### Long Answer Type Questions

Question 47. An alkene 'A' (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

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forms iodoform on treatment with I2 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 iodoformfrom B and C.

**Solution:** Compound B gives positive Fehling's test. It shows that it is an aldehyde and gives iodoform test which shows it has  $-COCH_3$  group. Compounds C is a ketone because it does not give Fehling's test but gives iodoform test which shows it also has  $-COCH_3$  groups. Hence compound A is  $CH_3CH=C--CH_3$ 

(i) 
$$CH_3 - CH = C - CH_3 \xrightarrow{(i) O_3} CH_3 - CHO + O = C - CH_3$$
  

$$\stackrel{1}{\underset{(H_3)}{}} CH_3 \xrightarrow{(ii) Zn/H_2O} CH_3 - CHO + O = C - CH_3$$
Acetaldehyde 1  
(Ethanal) CH\_3  
2-Methylbut-2-ene (B) (Acetone)  
(A) (C)  
Other isomer of (A) will not give products corresponding to the given test.  
(2NaOH + I\_2  $\rightarrow$  NaOI + NaI + H<sub>2</sub>O)  
(ii) CH\_3CHO + 3NaOI  $\longrightarrow$  CI\_3CHO + 3NaOH  
(B) Sodium Tri-iodo  
hypoiodite acetaldehyde  
CH\_3CHO + NaOH  $\xrightarrow{Hydrolysis} CHI_3 + HCOONa$   
Iodal

(iii) 
$$CH_3 - C - CH_3 + 3NaOI \longrightarrow CI_3 - C - CH_3 + 3NaOH$$
  
(C) Tri-iodoacetone  $O$   
 $CH_3 - C - CH_3 + 3NaOH - CH_3 + 3NaOH$ 

$$CH_3 - C - CH_3 + NaOH \xrightarrow{Hydrolysis} CHI_3 + CH_3COONa$$
  
Iodoform Sodium acetate

Question 48. An aromatic compound 'A' (Molecular formula CgHgO) 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 Tollens 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

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#### the above reaction. Identify A, B and C and write all reactions involved.

**Solution:** Molecular formula of compound is  $C_8$ HgO. As 'A' does not give Tollens' or Fehling's test. It must be a ketone. It gives positive test with 2, 4-DNP and iodoform test. It means it is methyl ketone.



Question 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?

**Solution:** C<sub>3</sub>H<sub>6</sub>O will have following isomer.

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 $\begin{array}{c}
O \\
\parallel \\
CH_3 - C - CH_3 \\
Propan-2-one (II)
\end{array}$ 

Compound I will react faster with HCN due to less steric hindrance and greater positive charge on carbon atom of carbonyl group. Two methyl groups increase electron density on carbonyl carbon in compounds II hence the rate of nucleophilic attack is less.

Mechanism of the reaction:



The reaction will not lead to completion since it is a reversible reaction, hence equilibrium is established.

If a strong acid is added to reaction mixture, the addition is inhibited because the formation of CN" ions form HCN is prevented.

Question 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 hydrogen sulphite. Liquid 'B' also forms a white crystalline solid with sodium hydrogen sulphite 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.

Solution: Liquid 'A' forms a bright silver mirror on treatment

with ammoniacal AgNO3 solution, therefore, liquid 'A' is an aldehyde.

Liquid B does not give test with ammoniacal AgNO3 solution, therefore, liquid 'B' must be a

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methyl ketone.

Chemical equations for these reactions are:



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