Class - 12 Chemistry (Aldehydes, Ketones and Carboxylic Acids)

- 1. Which of the following acids does not exhibit optical isomerism?
 - a. Maleic acid
 - b. Tartaric acid
 - c. α amino acids
 - d. Lactic acid
- 2. The correct sequence of steps involved in the mechanism of Cannizzaro's reaction is
 - a. electrophilic attack by OH⁻, transfer of H⁺ and transfer of H⁻
 - b. transfer of H^+ , nucleophilic attack and transfer of H^-
 - c. electrophilic attack by OH⁻, transfer of H⁺ and transfer of H⁻
 - d. nucleophilic attack, transfer of H⁻ and transfer of H⁺
- 3. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
 - a. benzyl alcohol and methyl alcohol
 - b. benzyl alcohol and sodium formate
 - c. sodium benzoate and methyl alcohol
 - d. sodium benzoate and sodium formate
- 4. How to do the following conversion:

 $RCOOCl + ? \rightarrow RCHO$

- a. Using H₂-Pd,BaSO₄
- b. Using DIBAL-H
- c. Using H_2 Pd
- d. Using NaBH₄
- 5. CH₃CHO and C₆H₅CH₂CHO can be distinguished chemically by:
 - a. Iodoform test
 - b. Benedict test
 - c. 2,4 DNP test
 - d. Tollen's reagent test

6. Write the IUPAC name of the following ketones and aldehyde. If possible, give also common name.

 $CH_3(CH_2)_5CHO$

- 7. Name two important uses of formalin.
- 8. Write the chemical name and structure of Rochelle salt.
- 9. Write the steps for the conversion of Acetaldehyde to Acetone.
- 10. Fluoroacetic acid is a stronger acid than acetic acid. Explain.
- 11. Write IUPAC name of CH
- 12. Show conversion of Ethyl alcohol to acetone.
- 13. Why is that alkene undergo electrophilic addition while aldehyde/ketone undergo nucleophilic addition reaction?
- 14. Give chemical tests to distinguish between the following pairs of compounds.
 - 1. Propanoyl chloride and propanoic acid
 - 2. Benzaldehyde and Acetophenone
- 15. An organic compound 'A' with molecular formula C_8H_8O gives positive DNP test and iodoform test. It does not reduce Tollen's or Fehling's reagent and does not decolourise bromine water. On oxidation with chromic acid (H_2CrO_4) it gives a carboxylic acid (B) with molecular formula $C_7H_6O_2$. Deduce the structures of A and B.

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1. (a) Maleic acid

Explanation: Maleic Acid shows Geometrical Isomerism due restricted bond roation along C=C bond but does not give optical isomerism as it has horizontal plane of symmetry, as C=C bond is planar and thus do not form a non superimposable mirror image and is optically inactive.

2. (d) nucleophilic attack, transfer of H⁻ and transfer of H⁺

Explanation: In Cannizzaro reaction 1st nucleophile OH⁻ attacks on carbonyl carbon. Then hydride shifting takes place. Followed by proton transfer as shown below (in, RCHO, R group has no alpha hydrogen):

Cannizaro is a kind of disproportionation reaction where aldehyde or ketones having no alpha hydrogen get oxidised to acid and reduced to alcohol.

3. (b) benzyl alcohol and sodium formate

Explanation: They will undergo cannizaro reaction as neither benzaldehyde nor formaldehyde has alpha hydrogen.

HCHO will be more reactive towards cannizaro compared to benzaldehyde because of less steric hinderance.

So, OH⁻ nucleophile will attck on HCHO first and then hydride shift from HCHO to benzaldehyde will occur. and thus HCHO will oxidise to HCOO⁻ ion and benzaldehyde will reduce to benzylalcohol.

4. (a) Using H_2 -Pd, $BaSO_4$

Explanation: Catalytic hydrogenation of acid chloride using H_2 -Pd, $BaSO_4$ converts acid chloride selectively to aldehydes. This is known as Rosenmud Reduction.

5. (a) Iodoform test

Explanation: CH_3CHO will give iodoform test and $C_6H_5CH_2CHO$ will not give iodoform test. Methyl aldehydes or ketones give iodoform test. In carbonyls like RCOR' one of R or R' should be a CH_3 group to give positive iodoform test.

$$CH_3CHO + NaOI \rightarrow CHI_3 + HCOO^-Na^+$$

CHI₃ formed is known as iodoform and is yellow precipitate.

$$C_6H_5CH_2CHO + NaOI \rightarrow no reaction$$

- 6. **IUPAC Name:** Heptanal; **Common name:** Oenanthaldehyde, Heptylaldehyde, Enanthole
- 7. The important uses of Formalin are:
 - i. to preserve biological specimens.
 - ii. as an antiseptic and disinfectant.
- 8. Rochelle salt is a double salt of tartaric acid, chemically known as potassium sodium tartrate tetrahydrate.

9.
$$\text{CH}_3\text{CHO} \xrightarrow{(O)} \text{CH}_3\text{COOH} \xrightarrow{slaked\ lime,\ Ca(OH)_2} \text{(CH}_3\text{COO)}_2\text{Ca} \xrightarrow{Heat} CH_3 - C - CH_3$$

10. $F-CH_2-C-OH$ Fluroacetic acid and CH_3-C-OH acetic acid In fluoroacetic acid, Fluorine is an electron withdrawing group. It stabilizes the conjugate base through de-localization of the negative charge by decreasing the electron density on carbonyl carbon atom. On the other hand, acetic acid has methyl group which is electron donating group, increases the electron density on carbonyl carbon atom which destabilizes the conjugate base.

Therefore, fluoroacetic acid is a stronger acid than acetic acid.

- 11. The IUPAC name is 2-Methylcyclohexanone
- 12. $\begin{array}{c} \operatorname{CH_3COOH} \xrightarrow{(i) \ LiAlH_4/ether} \operatorname{CH_3CH_2OH} \xrightarrow{red \ P/I_2} \operatorname{CH_3CH_2I} \xrightarrow{KCN} \operatorname{CH_3CHCN} \xrightarrow{H^+} \\ (ii) \ H_3O^+ \\ \operatorname{CH_3CH_2COOH} \end{array}$
- 13. In alkenes, the C=C bond is non-polar and contain π electron cloud present above and below the plane. This π bond of C = C is an electron source and is a nucleophilic site. Therefore, it is easier for an electrophile to attack.

In aldehydes/ketones, the carbonyl group is polar due to the electronegative difference. The carbonyl carbon (> C = O) is an electrophilic site and is attacked by a nucleophile; undergoes addition reaction.

$$\sum_{Nu} C \stackrel{f}{=} O \xrightarrow{r.d.s} Nu - C - O \xrightarrow{\epsilon^+} Nu - C - O \epsilon$$

14. i. On adding NaHCO $_3$ solution to each of them, propanoyl chloride will not react whereas propanoic acid will give brisk effervescence due to CO $_2$.

$$CH_{3}-CH_{2}-\overset{O}{C}-Cl + NaHCO_{3}
ightarrow No \ reaction \ CH_{3}-CH_{2}-\overset{O}{C}-OH+NaHCO_{3} \
ightarrow CH_{3}-CH_{2}-\overset{O}{C}-ON^{+}_{a}+H_{2}O+CO_{2}$$

ii. On adding I_2 and NaOH, Acetophenone will give yellow ppt of iodoform whereas benzaldehyde will not react.

Benzaldehyde + I_2 + NaOH \rightarrow No reaction

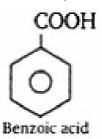
$$C_6H_5COCH_3 + 3NaOH_{Sodium\ hypoiodite} \
ightarrow C_6H_5COONa + CHI_3 + 2NaOH_{Sodium\ benzoate} + Iodoform(yellow\ ppt)$$

15. As 'A' does not give Fehling's or Tollen's test so it does not have - CHO group but it gives positive iodo form test and DNP test so it has $CH_3-C\!-\!$ group.

So 'A' is



B is carboxylic acid obtained by the oxidation of 'A' with ${
m H_2CrO_4}$. So 'B' is



Class - 12 Chemistry (Aldehydes, Ketones and Carboxylic Acids)

- 1. The aldehydes and ketones undergo one of the following reactions:
 - a. None of these
 - b. electrophilic addition reaction
 - c. substitution reaction
 - d. nucleophilic addition reactions
- 2. A strong base can abstract an α hydrogen from
 - a. Alkene
 - b. Amine
 - c. Alkane
 - d. Ketone
- 3. Aldehydes are prepared by reducing nitriles to corresponding imines with stannous chloride in the presence of hydrochloric acid. This reaction is called
 - a. Gatterman Koch reaction
 - b. Etard reaction
 - c. Stephens reaction
 - d. Friedel Crafts reaction
- 4. In Hell Volhard Zelinsky reaction, halogen reacts with
 - a. aldehydes
 - b. ketones
 - c. carboxylic acids
 - d. ethers
- 5. The product formed in Aldol condensation is
 - a. a beta hydroxy aldehyde or a beta hydroxy ketone.
 - b. an alpha hydroxy aldehyde or ketone.
 - c. a beta hydroxy acid
 - d. an alpha, beta unsaturated ester
- 6. Write a chemical test to distinguish between aldehyde and ketone.
- 7. What IUPAC name would you give to the following compound?

8. Write the IUPAC name of the following aldehyde. If possible, give also common name.

9. Write IUPAC names of:

- 10. How is acetone obtained from ethanol?
- 11. Write the IUPAC names for the following:

i.
$$CH_3CH_2$$
 - CH - $COOH$

- 12. Give reasons for the following:
 - a. Carboxylic acids do not give characteristic reactions of carbonyl group.
 - b. Treatment of benzaldehyde with HCN gives a mixture of two isomers which cannot be separated even by careful fractional distillation.
 - c. Sodium bisulphite is used for the purification of aldehydes and ketones.
- 13. Write the structures of products of the following reactions:

- 14. a. Explain the mechanism of a nucleophilic attack on the carbonyl group of an aldehyde or a ketone.
 - b. Identify A, B and C in the following sequence of reactions:

$$CH_3CHO \xrightarrow{C_2H_5MgCl} A \xrightarrow{Conc. \ H_2SO_4} B \xrightarrow{HBr+Peroxide} C$$

- c. Predict the structure of the product formed when benzaldehyde is treated with
 - i. Conc. NaOH
 - ii. HNO₃,H₂SO₄ (at 23-383 K)
- 15. An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

Class - 12 Chemistry (Aldehydes, Ketones and Carboxylic Acids) Solutions

1. (d) nucleophilic addition reactions

Explanation: Aldehydes and Ketones undergoes the characteristic nucleophilic addition reaction. this is because of presence of polar>C=O bond in aldehydes and ketones. due to electronegativity difference between C and O, O bears a small (delta) negative charge while C bears a small (delta) positive charge. now because of delta positive charge on C nucleophile can add to >C=O bond giving nucleophilic addition reaction

2. (d) Ketone

Explanation: Conjugate base of ketone which is formed is stable due to electron with drawing nature of adjacent CO group and resonance.

3. (c) Stephens reaction

Explanation: Reaction for preparation of aldehydes by reducing RCN in presence of SnCl₂ is Stephen's Reaction.

The mechanism of the reaction is as shown below.

$$SnCl_2 + 2HCl \longrightarrow SnCl_2 + 2[H]$$

$$R - C \equiv N + 2[H] + HCl \longrightarrow R - CH = NH.HCl \xrightarrow{\text{Boiling H}_2O} 0 + NH_4Cl$$

4. (c) carboxylic acids

Explanation: Alpha Hydrogen containing carboxylic acids undergo HVZ reaction.

HVZ reaction is used for alpha halogenation of carboxylic acid.

- 5. (a) a beta hydroxy aldehyde or a beta hydroxy ketone.
 - **Explanation:** In aldol, we get beta hydroxyl aldehyde/Ketone which undergo further dehydration to give alpha beta unsaturated aldehyde / ketone.
- 6. Aldehydes and ketones are distinguished using Tollen's test. Aldehydes give a silver mirror on reacting with Tollen's reagent whereas ketones do not react. The reaction is $RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow RCOO^- + 2Ag$ (silver mirror) $+ 2H_2O + 4NH_3$
- 7. The IUPAC name for the compound is 4-Chloropentan-2-one.
- 8. IUPAC Name: 4-Bromo-2-methylhexanal; Common Name: γ -Bromo- α -methyl caproaldehyde
- 9. i. 5-Bromo-3-chloro-2-iodobenzoic acid
 - ii. 4-Formyl-2-methylpentanoic acid

- 11. i. 2-Phenylacetaldehyde
 - ii. 2-Bromobutanoic acid
- 12. a. This is due to the lone pairs on oxygen atom attached to the hydrogen atom in the COOH group, are involved in resonance and hence making the carbon atom less electrophilic. Hence, carboxylic acids do not give their action of carbonyl groups

$$\begin{array}{cccc}
O & O^{\ominus} \\
R - C - OH & \longleftrightarrow & R - C = OH
\end{array}$$

b. C_6H_5CHO reacts with HCN to form isomeric benzaldehyde cyanohydrins because an asymmetric carbon atom is introduced

$$C_6H_5C=O~+~HCN~ o~C_6H_5-C=OH$$
 (Asymmetric carbon atom)

These two isomers are enantiomers and therefore, cannot be separated by physical methods like fractional distillation.

c. Aldehydes and ketones form addition compounds with $NaHSO_3$ whereas impurities do not. On hydrolysis, we get pure aldehydes and ketones back.

$$CH_3-C-H + {\rm NaHSO}_3 \rightarrow {\rm CH_3-CH-SO_3Na} \xrightarrow{H_2O/H} CH_3-C-H + {\rm NaHSO}_3$$

iii.
$$H_3C$$
— $H + H_2O$ H_2SO_4 H_3C HO H_3C

14. a. $HCN \rightarrow H^+ + CN^-$

b.

Planar

$$CH_3CHO$$
 CH_3CHO
 C

c. In this part, first one is cannizzaro reaction and the other one is nitration of benzaldehyde.

i.
$$2C_6H_5CHO \xrightarrow{Conc.} C_6H_5-CH_2OH + C_6H_5COONa$$

CHO

CHO

 $\frac{CHO}{273 - 383 \text{ K}} + H_2O$

15. Percentage of carbon = 69.77 %, Percentage of hydrogen = 11.63 %, Percentage of oxygen = $\{100 - (69.77 + 11.63)\}\% = 18.6$ %

Thus, the ratio of the number of carbon, hydrogen, and oxygen atoms in the organic compound is given as: $C:H:O=\frac{69.77}{12}:\frac{11.63}{1}:\frac{18.6}{16}$ =5.81: 11.63: 1.16 =5:10:1 Therefore, the empirical formula of the compound is $C_5H_{10}O$. Now, the empirical formula mass of the compound can be given as: $5\times12+10\times1+1\times16$ = 86 Molecular mass of the compound = 86 Therefore, the molecular formula of the compound is given $C_5H_{10}O$. Since the given compound does not reduce Tollen's reagent, it is not an aldehyde. Again, the compound forms sodium hydrogen sulphate addition products and gives a positive iodoform test. Since the compound is not an aldehyde, it must be a methyl ketone. The given compound also gives a mixture of ethanoic acid and propanoic acid. Hence, the given compound is Pentan-2-one.

$$CH_3-CH_2-CH_2-CH_3$$
 Pentan - 2 - ol

The given reactions can be explained by the following equations: