8 CHAPTER

Aldehydes, Ketones & Carboxylic Acids

Level - 1

CORE SUBJECTIVE QUESTIONS MULTIPLE CHOICE QUESTIONS (MCQs)

(1 Mark)

1. Option (B) is correct

Explanation: Benzoic acid and ethanoic acid $H_2O + C_6H_5COOCOCH_3 \longrightarrow C_6H_5COOH + CH_3COOH$

It is a hydrolysis reaction involving breaking of ester bond by addition of water molecule.

2. Option (A) is correct

Explanation: Aldehyde and ketones give nucleophilic addition reactions. Other carbonyl compounds do not give nucleophilic addition reactions. The carbonyl group (C=O) in acetone is attacked by the nucleophilic nitrogen of hydroxylamine, forming a C=N-OH bond of oxime.

3. Option (A) is correct

Explanation: It is an example of cannizzaro reaction. Cannizaro reaction is a disproportionation reaction of an aldehyde which lacks alpha hydrogens, in the presence of a strong base.

4. Option (C) is correct

Explanation: $CH_3COOH + PCl_5 \rightarrow CH_3COCl + HCl$ acetic acid Acetyl chloride $+ POCl_3$

5. Option (A) is correct

Explanation: Rosenmund's reaction

6. Option (A) is correct

Explanation:

$$\begin{array}{ccc} R & & HO & CN \\ C = O + HCN & & Base & R - C - N \\ H & & Hydrogen & Cyanohydrin \\ Aldeliyde & cyanide & \end{array}$$

7. Option (D) is correct

Explanation: Benzaldehyde does not contain α -Hydrogen atom Hence, it does not undergo aldol condensation.

8. Option (B) is correct

Explanation: Crossed aldol condensation is a reaction where two different carbonyl compounds (aldehydes or ketones) react in the presence of a base to form a β -hydroxy aldehyde or ketone, also known as an aldol product. It is referred to as "crossed" because the reactants are not identical, unlike a regular aldol condensation.

9. Option (A) is correct

Explanation: Alcoholic KOH causes dehydrohalogenation and leads to formation of alkene. It is a type of elimination reaction.

$$CH_2$$
— CH_3 + $KOH(alc.)$ CI 1-phenyl-2-chloropropane CH = CH — CH_3

10. Option (A) is correct

Explanation: Presence of alkyl group decreases the reactivity of carbonyl atom making it less electron deficient due to inductive effect thus making the compoud less reactive towards the nucleophilic addition reactions.

11. Option (B) is correct

Explanation:

12. Option (B) is correct

Explanation: Presence of alkyl group decreases the reactivity of carbonyl group due to inductive effect.

13. Option (D) is correct

Explanation: Electron with drawing group such a NO₂, CN increases the acidity whereas electron donating group decreases acidity of a compound. pKa value

decreases with increasing. A lower pKa indicates a stronger acid. The strength of an acid is determined by the stability of its conjugate base. Electron withdrawing groups like the nitro group (–NO₂), CN– in withdraw electron density from the carboxylate group (—COO–), making it stable and easy to lose a proton. On the other hand, electron donating groups like alkyl gp decreases the acidity of a compoud.

14. Option (D) is correct

Explanation: Pentan-2-one give positive iodoform test because only methyl ketone group give a positive iodoform test.

15. Option (C) is correct

Explanation:

$$\begin{array}{c}
H \\
C = O + CH_3MgI \longrightarrow H \\
C \longrightarrow OMgI
\end{array}$$

Formaldehyde

ASSERTION-REASON QUESTIONS

(1 Mark)

1. Option (D) is correct

Explanation: Cl being electron with drawing group stablises the ClCH₂COO⁻ anion and therefore chloroacetic acid has lower pka value than acetic acid.

2. Option (A) is correct

Explanation: The carboxylic group in aromatic carboxylic acid is an electron withdrawing group that deactivates the benzene ring.

3. Option (B) is correct

Explanation: Acetic acid is halogenated in presence of of red P and Cl_2 but formic acid is not because formic acid does not have an α -hydrogen atom. Presence of methyl group which is an electron donating group increases the electron density on the carboxylate ion in acetic acid, making it weaker acid in comparison to formic acid.

VERY SHORT ANSWER TYPE QUESTIONS

(2 Marks)

1. (i) Clemmenson reduction

$$CH_{3}COCH_{2}CH_{3} + 4[H] \xrightarrow{Zn(Hg)} CH_{3}CH_{2}CH_{2}CH_{3} \\ + H_{2}O$$

$$CHO COONa CH_{3}OH$$

$$Conc. NaOH + COONa CH_{3}OH$$

$$Sodium Benzyl Benzyl$$

2. The mechanism occur in two steps

Step I:

$$\bigcup_{H}^{N} C = O + Nu \longrightarrow C$$

Step II:

$$C \xrightarrow{Nu} \xrightarrow{H^+} C \xrightarrow{Nu} OH$$

3. (i) Toluene to benzoic acid

(ii) Ethanol to 3-Hydroxybutanal

$$\begin{array}{ccc} \text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{\text{oxidation}} & \text{CH}_3\text{CHO} \\ \text{Ethanol} & & \text{Ethanal} \\ \\ \text{2CH}_3\text{CHO} & \xrightarrow{\text{Aldol}} & \text{CH}_3\text{--CH}\text{--CH}_2\text{--} \\ \text{CHO} & & \text{(dil NaOH)} & & | \\ & & & \text{OH} \\ \end{array}$$

- i. (i) It is because the methyl group in CH₃CHO has a smaller +I effect than the two methyl groups in CH₃COCH₃. Hence, acetaldehyde has less steric hindrance and therefore it is more reactive acetone for nucleophilic reaction with CN⁻.
- (ii) Intermolecular hydrogen bonding between hydrogen of -OH group of one molecule with Oxygen of C=O in other molecule of carboxylic acids increases the boiling point of carboxylic acids. However, as aldehydes and ketones lack such bonding, their b.p are comparatively lower.

5. (i) Tollen's test

Propanal is an aldehyde. Thus it reduces Tollen's reagent. But propanone being a Ketone does not redue Tollon's reagent

CH₃CH₂CHO +
$$2[Ag(NH_3)_2]^+$$
 + $3OH^-$
Tollen's reagent
 \rightarrow CH₃CH₂COO⁻ + $Ag \downarrow$ + $4NH_3$ + $2H_2O$

(ii) Sodium bicarbonate (NaHCO₃) test:

Benzoic acid on reaction with NaHCO₃ give sodium salt of benzoic acid and release carbondioxide gas whereas benzaldehyde does not respond to this test.

6. (i) C₆H₅CH₂OH and C₆H₅COONa

Benzaldehyde Benzyl alcohol Sodium benzoate

NNHCONH2

- 8. (i) It is because of reasonance. The lone pairs on oxygen atom in the COOH group of carboxylic acids are involved in resonance which reduces the positive charge on the carboxyl carbon. This makes the carbon atom less and less electrophilic.
 - (ii) It is because propanone is sterically hindred by alkyl group on both sides of carboxyl carbon. So the reactivity of carbonyl carbon decreases by +I effect of alkyl group for nucleophilic addition of HCN.

9. (i) Reimer Tiemann reaction.

(ii) Acelytation of salicylic acid.

10. (i)
$$CH_3CN + CH_3MgCl \longrightarrow CH_3 - C = NMgCl \xrightarrow{+2H_2O}_{H^+}$$

(ii)
$$+ Na \xrightarrow{-\frac{1}{2}H_2} - \frac{NaOH}{CaO} + Na_2CO_3$$

- **11.** (i) It is because the chlorine atom in chloro acetic acid is electronegative and withdraws electron which stabilises the conjugate base.
 - (ii) Hell volhard Zelinsky reaction

$$CH_3 - CH_2 - COOH \xrightarrow{Br_2/red P} CH_3 - CH$$

$$\mid Br$$

$$- COOH + HBr$$

SHORT ANSWER TYPE QUESTIONS

(3 Marks)

1. (i) ETARD reaction

$$O_2N$$
 CH_3
 CrO_2Cl_2/H_3O^+
 NO_2

p-nitro toluene p-nitrobenzaldehyde

- (ii) Benzoic acid undergoes extensive intermolecular hydrogen bonding, leading to the formation of dimer in the presence of a protic solvent.
- (iii) Benzoic acid does not undergo reaction with CH₃Cl i.e Friedel Craft reaction because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.
- Compound 'X' = Benzaldehyde , Compound Y = Acetophenone

> (Major) Cross. Aldol product

(iii) Chemical test to distinguish between X and Y is the Tollen test.

Benzaldehyde undergoes Silver mirror test with Tollen's reagent and forms silver mirror. However, acetophenone does not react with Tollen's reagent.

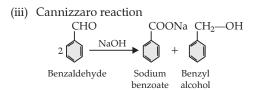
3. (i) Wolff-Kishner reduction

$$\begin{array}{c} \text{O} & \text{N--NH}_2 \\ \parallel & \parallel \\ \text{CH}_3\text{--C--CH}_3 \xrightarrow{\text{NH}_2\text{NH}_2} \text{CH}_3\text{--C--CH}_3 \end{array}$$

$$\xrightarrow{\text{KOH/heat}}$$
 CH₃—CH₂—CH₃ + N₂

(ii) Decarboxylation reaction

$$CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$$



- 4. Working backwards on the statements, given
 - Compound F monobasic acid (mol weight = 60)
 So its molecular formula is RCOOH.
 - Weight of "R' group = 60 45 = 15
 This implies compound F is ethanoic acid CH₃COOH (mol weight = 60)
 - Compound D- on oxidation gives F which implies Dmust be an aldehyde with formula-CH₃CHO (ethanal)
 - Compound B- on oxidation with PCC gives D which implies Bmust be an alcohol with formula C₂H₅OH (Ethanol)
 - Compound E-obtained by heating D (CH₃CHO) with dil NaOH and heating.
 Since acetaldehyde undergoes Aldol condensation with dil NaOH.

CH₃CHO + CH₃CHO — dil NaOH⁻ \longrightarrow CH₃CH(OH)CH₂CHO — heat \longrightarrow CH₃CH=CHCHO

D- H_2 OE- α , β-unsaturated carbonyl compound

- Compound E on reduction gives C
 CH₃CH = CHCHO catalytic hydrogenation
 E —→ CH₃CH₂CH₂CH₂OH
- Compound B (C₂H₅OH) and compound C (CH₃CH₂CH₂CH₂OH) are obtained from reduction of A (C₆H₁₂O₂) by LiAlH₄
- Compound A must be an ester which yields 2 alcohols on reduction.

$$C_6H_{12}O_2 \xrightarrow{LiAlH_4} CH_3CH_2 - CH_2 - CH_2 - OH + C_2H_5OH$$
(A) (C) (B)

$$C_2H_5OH \xrightarrow{PCC} CH_3CHO \xrightarrow{[O]} CH_3COOH$$
(B) (D) (F)

 $CH_3CHO \stackrel{NaOH}{\longleftarrow} CH_3CH \stackrel{CH}{\longleftarrow} CHO$

$$CH_3CH_2CH_2$$
— CH_2 — OH
 Pd/H_2
 CH_3 — CH — CH — CH — CH
 (C)
 (E)

5. (i)
$$2[Ag(NH_3)_2]^+OH^-$$
 2 Ag + $4NH_3 + 2H_2C$

CHO

CH₃

(ii)
$$CH_3$$
 CH_3 CH

+ CHI₃ Iodoform

(iv)

Br

$$CH_3$$
 $+ Mg$
 $Br + C = O$
 H_3O^+
 OH

1-Phenylethanol

- 7. (i) (1) When sodium bicarbonate (NaHCO₃) is added to benzoic acid, carbon dioxide is produced and the solution shows effervescence. Phenol does not show this test.
 - (2) Propanal give positive result with Tollen's reagent while propanone does not give this test.

CH₃ — CH₂CHO + 2 [Ag(NH₃)₂]⁺ +
$$3\overline{O}$$
H \downarrow
CH₃CH₂COO⁻ + 2Ag + 4NH₃ + 2H₂O

- (ii) Electron withdrawing group F increases acidity through—I effect and strength of—I effect decreases with increasing the distance from carboxyl group, so acidity of 3-fluoro butanoic acid is higher as compare to 4-fluoro butanoic acid.
- 8. (i) In benzoic acid the carboxylic group is meta directing because it is electron withdrawing group with -R effect There is positive charge on ortho and para position So electrophillic substitution takes place at meta position.
 - (ii) Sodium bisulphite is used for the purification because it can react selectively with carbonyl group of aldehyde and ketones.
 - (iii) Carboxylic acids do not give characteristic reactions of carbonyl group. It is because the carbonyl group in caroxylic acids is involved in resonance.

LONG ANSWER TYPE QUESTIONS

(5 Marks)

(ii)

m-nitroacetophenone

2. Acetic acid will give HVZ reaction.

Carboxylic acids having an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of a small amount of red phosphorus to give α -halo carboxylic acids.

2,4- dinitrophenylhydrazone

(ii) Electronegative oxygen in the carbonyl group makes the carbon atom electron deficient (electrophilic), facilitating nucleophilic attack. On the other hand, in esters- the alkoxy group, due to its electron-donating effect (inductive effect), reduces the electron deficiency of the carbonyl carbon making it comparatively less susceptible to nucleophilic attack. The steric hindrance due to larger alkyl groups further reduces it.

$$(CH_3)_3 C$$
— $COCH_3 < CH_3COCH_3 < CH_3CHO$

(iii)
$$\bigcirc$$
 MgBr + O = C = O $\stackrel{Dry \text{ ether}}{\longrightarrow}$ Phenyl magnesium bromide \bigcirc C = OMgBr \bigcirc H₂O H⁺ OH \bigcirc Benzoic acid \bigcirc Br

(iv) Ethanal react with NaOI (I₂/NaOH) to form yellow precipitate of iodoform while benzaldehyde does not give this test

CH₃CHO +
$$3I_2$$
 + 3 NaOH \rightarrow HCOONa + CHI₃ \downarrow
3 NaI + 3 H₂O

Ethyl (2-hydroxybutanoate)

- (i) (1) Oxidation of aldehyde is easier as compared to ketones because aldehyde have a hydrogen atom attached to the carbon oxygen double bond while ketone do not have an alpha hydrogen. Ketone is more tindered as compare to aldehyde and less electrophilic due to high - I effect of alley groups.
 - (2) The α-hydrogen atom in aldehydes is acidic because the carbonyl group strongly withdraws electron and conjugate base is resonance stabilised.

formed

$$COCI$$
 $COCH_3$ $+ (CH_3)_2Cd$ $+ CdCI_3$

- (iii) Sodium bicarbonate test: Add a small amount of sodium bicarbonate (NaHCO₃) to both ethanoic acid and ethanol separately. Ethanoic acid will produce effervescence while ethanal will not respond to this test.
- 5. (i) (1) In semicarbazide, only one - NH2 group is involved in the formation of semicarbazone with aldehydes and ketones as the other -NH2 group directly connected to the carbonyl carbon donates its lone pair to carbon and becomes resonance stablised, thus making it unavailable for nucleophilic attack and does not participate in semicarbazone formation.
 - Acetaldehyde is more reactive than acetone towards the addition of HCN because it has lower stearic hindrance around its carbonyl carbon.
 - (ii) $(1) O_2N$ — CH_2 — $COOH > HCOOH > CH_3COOH$ (2) Diisobutylauminum hydride (DIBAL—H)
 - (iii) Hell-volhard-Zelinsky Reaction $CH_3COOH + Cl_2 \xrightarrow{Red P} CH_2 - COOH$ C1
- 6. (i) (1) Benzoic acid is formed

Benzalacetone is formed

(3) (i) m-Bromobenzoic acid is formed

(ii) (1) also known as acetophenone

give a positive iodoform test and a yellow COCH₂CH₃ precipitate of iodoform while

Benzalacetone

does not respond to this test.

(2) Pentanal give silver mirror on reaction with Tollon's reagent while pentan-3-one will not respond to this test. $C_4H_9CHO + 2[Ag(NH_3)_2]^+$ $+ 3OH^- \rightarrow C_4H_9COO^- + 2Ag \downarrow + 2H_2O +$ (Silver mirror) 4NH₃

- (2) Acetophenone and cadmium chloride is 7. (i) (1) This is because of the strong electron withdrawing nature of the carbonyl groups and resonance stabilisation of the conjugate base.
 - (2) Oxidation of aldehyde is easier than Ketones because aldehyde have a hydrogen atom attached to the carbon oxygen double bond while ketone do not.
 - (ii) (1) propanal > acetone > benzaldehyde
 - (2) propane < dimethylether < propanal < ethanol
 - (iii) Tollen's test.

Benzaldehyde react with Tollen's reagent to produce a shiny silver mirror on the inner wall of the test tube. Benzoic acid does not reduce the silver ions and instead forms a white precipitate of silver benzoate.

- CompoundAforms2,4-DNPderivative-which 8. (i) indicates presence of carbonyl group (>C = O) (The 2, 4-Dinitrophenylhydrazine (2, 4-DNP) test is used to detect the presence of carbonyl groups in aldehydes and ketones).
 - Compound A with the molecular formula C₉H₁₀O reduces Tollen's solution- which means it is an aldehyde(-CHO).
 - Compound A undergoes Cannizzaro reaction- which means it is an aldehyde without alpha hydrogen.
 - Compound A on vigorous oxidation, gives 1, 2-benzene dicarboxylic acid or Phthalic acidwhich indicates the presence of a benzene ring with two adjacent carbon atoms oxidized to carboxyl groups (-COOH)
 - As compound A has a molecular formula as C₉H₁₀O - it has to be a derivative of Benzaldehyde- C₆H₅CHO So the remaining group has to be C_2H_5 – so the substituent is ethyl group CH₂CH₃
 - Compound A is 2-ethyl benzaldehyde

2-Ethylbenzaldehyde

(ii) (1)
$$CHO$$
 CHO
 CH_2CH_3
 CH_2CH_3
 CH_2CH_3
 CH_2CH_3

Ethanal

2-Ethylbenzaldehyde

$$CH = NNH - NO_2 + H_2O$$

$$CH_2CH_3$$

(2)
$$CHO$$
 $Ag(NH_3)_2$ OHO $Ag(NH_3)_2$ OHO $Ag(NH_3)_2$ OHO OHO $Ag(NH_3)_2$ OHO OH

$$+2Ag\downarrow + 2H_2O + 4NH_3$$

CH₂CH₃

(iii)
$$C-H$$
 C_2H_5
 C_2H_5
 $C-H$
 $C-ONa$
 C_2H_5

Cannizaro reaction

9. (i) CH₃CHO
$$\stackrel{[O]}{\longrightarrow}$$
 CH₃COOH $\stackrel{PCl_5}{\longrightarrow}$ CH₃COCI (B)

$$2\text{CH}_3\text{COCl} + (\text{CH}_3)_2\text{Cd} \rightarrow 2\text{CH}_3\text{COCH}_3 + \text{CdCl}_2$$
 (B) (C)

$$CH_3COCH_3 \xrightarrow{\quad Zn\text{-Hg} \quad } CH_3 \quad -CH_2 -CH_3 \quad + \\ H_2O$$

(D)

 $A = CH_3COOH$ (Ethanoic acid)

 $B = CH_3COCl$ (Acetyl chloride)

 $C = CH_3COCH_3$ Acetone)

 $D = CH_3CH_2CH_3$ (Propane)

(ii) (1)
$$CH_3 - C - CH_3 \xrightarrow{\text{LiAlH}_4} CH_3 - CH - CH_3$$
Propanone Propan-2-ol

alc. KOH
$$\rightarrow$$
 CH $_3$ — CH — CH $_2$

Propane

(2)
$$\bigcirc$$
 SOCl₂ Pd/BaSO₄ \bigcirc Pd/BaSO₄

Benzoic acid

Benzaldehyde

(3)
$$CH_3CHO \xrightarrow{OH^-} CH_3 - CH - CH_2 - CHO$$

$$\xrightarrow{\Delta} CH_3CH - CH - CHO$$
Rut 2 and

semicarbazide

10. (i) (I)
$$CH_3 = O + H_2NNHCONH_2$$

Acetone

$$c = NNHCONH_2$$

Acetone semicarbazone

(II)
$$\bigcirc$$
 COONa \bigcirc CH $_2$ OH \bigcirc + \bigcirc

Two molecules of benzaldehyde undergo Cannizaro reaction and form sodium benzoate and benzyl alcohol.

(III)
$$CH_3$$
— CH_2 — CO — CH_3 $\xrightarrow{Zn-Hg}$ HCl HCl CH_3 — CH_2 — CH_2 — CH_3 $Butane$

The reaction of butan-2-one with Zn-Hg and conc. HCl is known as clemmensen reduction. In the reaction the carbonyl group in butan-2one is reduced to a methylene group forming

- (ii) (I) $CH_3CH_2CH_2COOH < Br CH_2CH_2CH_2COOH$ < CH₃CH Br CH₂COOH < CH₃CH₂CH Br
 - (II) 4-Methoxybenzoic acid < Benzoic acid 4-Nitrobenzoic acid < 3, 4 Dinitrobenzoic acid.
- **11.** (i) Sodium bicarbonate test: Add small amount of sodium bicarbonate to both ethanol and ethanoic acid. Ethanoic acid react with sodium bicarbonate to produce carbon dioxide which will be observed as effervescence. Ethanol will not react with sodium bicarbonate and no effervescence is observed.
 - The α-hydrogen atoms of aldehyde and ketones are acidic because of the carbonyl group's strong electron withdrawing nature and the resonance stabilisation of the conjugate base.
 - (iii) (1) $A = C_4H_8O_2$ ($CH_3COOC_2H_5$) Reaction involved are

$$\begin{array}{c} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{dil.H}_2\text{SO}_4} \rightarrow \text{CH}_3\text{COOH} \\ \text{(A)} & \text{(B)} \\ & + \text{CH}_3\text{CH}_2 - \text{OH} \\ \text{(C)} & \end{array}$$

$$CH_3CH_2OH \xrightarrow{KMnO_4H^+} CH_3COOH_3$$

$$CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$$

Sodium salt of B

 $A = CH_3COOC_2H_5$

 $B = CH_3COOH$

12. (i)

 $C = CH_3CH_2 - OH$

(2) B has higher boiling point than C. This is because of high tendency. So Carboxylic acid have higher boiling temperatures than alcohol.

(1)
$$\frac{\text{KMnO}_4}{\text{KOH}}$$
 $\frac{\text{H}_3\text{O}^+}{\text{Benzoic acid}}$

Acetophenone Benzoic acid

(2) $\frac{\text{KMnO}_4}{\text{KOH}}$ $\frac{\text{COOK}}{\text{KOH}}$ $\frac{\text{COOH}}{\text{Benzoic acid}}$

Benzoic acid

Br. MgBr. $\frac{\text{O}}{\text{Benzoic acid}}$

(3) Bromobenzene
$$MgBr$$
 $O = C = O$ O $OMgB$ $O = C = O$ $OMgB$ $OOMgB$ $OOMgB$

Benzoic acid

(ii) (1) F-CH₂—COOH < CN—CH₂COOH < O₂N—CH₂—COOH.

As fluorine is the most electronegative group it withdraws electrons from the carboxylic group. CN- also an electron withdrawing group but lesser than Nitro group which exerts both inductive effect as well as resonance with carboxylate ion making nitro group substituted carboxylic acid most acidic.

(2) Butanone < propanone < propanal < Ethanal

Reactivity of aldehydes and ketones in nucleophilic addition reactions is determined by steric hindrance and electronic effects. Aldehydes are more reactive as compared to ketones which have two alkyl groups.

13. (i) (1) 2CH₃CHO + NaOH $\xrightarrow{\text{Aldol Condeusation}}$

Ethanal

$$CH_3 - CH = CH - CHO + H_2O$$

 $But - 2 - en - 1 - al$

(2) $CH_3CH_2COOH + Cl_2 \xrightarrow{red P}$

Propanoic acid

2-chloropropionic acid

(ii) Structure of B

Structure of C

$$O = C - CH_3$$
 CH_3
Acetone

Therefore, Structure of A

2- Methyl-but-2-ene

$$CH_3 - C = C - CH_3 - O_3/Zn_1H_2O$$
 $H - CH_3$

$$CH_3 - C = O + O = C - CH_3$$
 H
 CH_3
Acetaldehyde
Acetone

Iodoform

 $CH_3CHO \xrightarrow{NaOH/I_2} CH_3COONa + CHI_3$

14. (i) NO₂ NO₂ NO₂ NH — N

2,4-Dinitrophenyl hydrazone of benzaldehyde

(ii) F_3C —COOH due to – I effect of F

(iii) Rosenmund reaction

$$R - C - C1 \xrightarrow{H_2} R - CHO + HC1$$

$$R - C - C1 \xrightarrow{Pd-BaSO_4} R - CHO + HC1$$

- (iv) The α -hydrogen atoms of aldehyde and ketones are acidic because of the carbonyl group's strong electron withdrawing nature and the resonance stabilisation of the conjugate base.
- (v) Sodium bicaronate (NaHCO₃) test:

Benzoic acid react with NaHCO₃ to give sodium salt of benzoic acid and effervescence of CO₂ gas Benzaldehyde does not give this test

OH + NaHCO₃

ONA + H₂O + CO₂
$$\uparrow$$

Sodium salt of benzoic acid

OH + NaHCO₃

No reaction

- **15.** (i) (1) Tollen's reagent test: Add ammoniacal solution of silver nitrate in both solution CH₃CH₂CH₂CHO (butanal) give silver mirror where as CH₃COCH₃CH₃ (butan-2-one) does not give this test.
 - (2) Sodium bicarbonate test: Add a small amount of sodium bicarbonate (NaHCO₃) to both ethanoic acid and ethanal separately. Ethanoic acid will produce effervescence while ethanal will not respond this test.
 - (ii) The structure of acetone oxime is (CH₃)₂CNOH

(iii)

CH₃COOH
$$\xrightarrow{\text{PCl}_5}$$
 CH₃COCI $\xrightarrow{\text{H}_2/\text{Pd-BaSO}_4}$ CH₃CHO

(A)

(B)

CH₃CH₂OH $\xleftarrow{\text{LiAlH}_4}$ CH₃ CHO

(D)

(i) CH₃MgBr

(ii) H₃O⁺

Ethanal

OH

CH₃-CH - CH₃

(C)

A ketone with methyl group attached to carbonyl carbon gives Iodoform test.

(2) (CH₃)₃CCHO

Cannizaro reaction is given by aldehydes lacking alpha hydrogen.

$$CH_3 O$$
 | || (3) $CH_3 - CH_2 - C - C - H$ | H

Tollen's reagent is reduced by an aldehyde. C-2 is the chiral centre of the molecule as it has 4 different groups attached.

(ii) (1) Wolff Kishner reduction

$$CH_{3}COCH_{3} \xrightarrow{\text{(i) } NH_{2}-NH_{2}} CH_{3}CH_{2}CH_{3}$$

Propanone

Propane

(2) Hell – Volhord – Zelinsky reaction

$$CH_3 - CH_2COOH \xrightarrow{\text{(i) } Cl_2/red P} CH_3 - CH - COOH$$

| Cl

- 17. Compound B does not give Fehling's test-which means it is either a ketone or an aldehyde lacking alpha hydrogen.
 - Compound Aundergoes Rosenmund's reductionwhich means A is an acyl chloride which yields an aldehyde on this reduction. This implies B is an aldehyde.
 - Compound Breacts with NaOH to give C and D- which means it is an aldehyde which lacks alpha hydrogen so it yields a mixture of alcohol and carboxylic acid (Cannizaro reaction), otherwise the reaction would result in aldol formation (condensation).

- As compound B has a molecular formula as C₇H₆O – it has to be Benzaldehyde-C₆H₅CHO.
- Hence, compound A is C₆H₅COCl- Benzoyl chloride.
- Compound C- Sodium benzoate
- Compound D- Benzyl alcohol

$$C_6H_5COC1 \xrightarrow{H_2(Pd\text{-BaSO}_4)} C_6H_5CHO$$
(A) (B)
$$2. C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$$
(B) (C) (D)

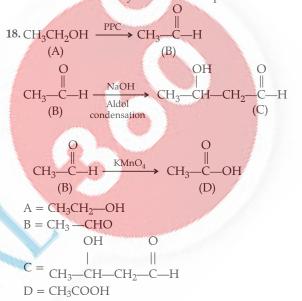
 $A = C_6H_5COC1$

 $B = C_6H_5CHO$

 $C = C_6H_5CH_2$ —OH

 $D = C_6H_5COONa$

Iodoform test: Propanone give positive iodoform test forming a yellow precipitate of iodoform (CHI₃) whereas Benzaldehyde does not respond to this test.



Level - 2 ADVANCED COMPETENCY FOCUSED QUESTIONS

MULTIPLE CHOICE QUESTIONS (MCQs)

1. Option (A) is correct

Explanation: Formalin is a 40% aqueous solution of formaldehyde, a simple aldehyde. It cross-links amino groups in proteins, effectively denaturing them and deactivating enzymes, which prevents microbial decay and preserves tissue structure. This is why it is widely used for preserving biological specimens.

2. Option (C) is correct

Explanation: Acetone is widely used as a nail polish remover because it is a powerful solvent that can dissolve the resins and polymers in nail polish, it evaporates quickly, leaving no sticky residue, and it does not react chemically with nails or oxidise the polish — it simply dissolves it effectively.

3. Option (C) is correct

Explanation: Ethanoic acid (acetic acid) is the main component of vinegar (typically 4–8% by volume). Its suitability comes from its sharp sour taste, which enhances flavour, its mild antimicrobial properties, which help in preserving food by inhibiting the growth of some bacteria and fungi, and it is not a strong oxidising agent, doesn't have antiseptic use like phenol, and does not polymerise in air.

(1 Mark)

4. Option (C) is correct

Explanation: 2,4-DNPtest(2,4-dinitrophenylhydrazine test) is a general test used to detect the presence of carbonyl groups in aldehydes and ketones. It forms a yellow/orange precipitate when it reacts with a ketone or an aldehyde. Tollen's test and Fehling's test are specific for aldehydes, not ketones. Iodoform test identifies methyl ketones (like acetone) specifically, not all ketones.

5. Option (C) is correct

Explanation: Benzoic acid is commonly used as a food preservative because it inhibits the growth of bacteria, yeast, and fungi, it is most effective in

acidic environments, where it lowers the pH, making conditions unsuitable for microbial growth, and it is found naturally in cranberries, prunes, and other acidic fruits.

ASSERTION-REASON QUESTIONS

(1 Mark)

1. Option (A) is correct

Explanation: Assertion is true. Acetone is widely used in cosmetics, especially in nail polish removers, because it can quickly dissolve many organic compounds found in nail polishes.

Reason is also true. The presence of the polar carbonyl group (C=O) makes acetone miscible with both polar and some non-polar substances. This enables it to dissolve a wide variety of organic compounds like resins, oils, and esters in nail polish.

2. Option (A) is correct

Explanation: Assertion is true. Vinegar is a dilute solution (usually $\sim 4-8\%$) of ethanoic acid in water. It is widely used in food preparation for its preservative and flavouring properties.

Reason is also true. Acetic acid inhibits the growth of many microorganisms, making it useful as a food preservative. Its sour taste also contributes to the flavour profile of vinegar.

3. Option (A) is correct

Explanation: Assertion is true. Formalin is a 37–40% aqueous solution of formaldehyde and is widely used to preserve biological specimens by preventing microbial decay and decomposition.

Reason is also true. Formaldehyde cross-links the amino groups in proteins, causing them to denature. This halts enzymatic activity and microbial decomposition, thereby preserving tissue structure.

4. Option (A) is correct

Explanation: Assertion is true. Tollen's reagent is a mild oxidising agent that reacts with aldehydes, not ketones, to produce a silver mirror. So ketones typically do not respond to this test.

Reason is also true. Aldehydes are readily oxidised to carboxylic acids, whereas ketones require strong oxidising agents for further oxidation, which is not provided by Tollen's reagent.

VERY SHORT ANSWER TYPE QUESTIONS

(2 Marks)

- Acetone has a polar carbonyl group (C=O) which allows it to dissolve a wide range of polar and nonpolar substances. Its small molecular size and low boiling point also enable it to evaporate quickly, making it ideal for cleaning and processing materials like plastics, synthetic fibres, and paints in industries.
- 2. Ethanoic acid (acetic acid) is a weak acid that lowers the pH of food, creating an acidic environment that is unfavourable for the growth of bacteria and fungi. Its antimicrobial property helps prevent spoilage and extends the shelf life of preserved food products like pickles and sauces.
- 3. Formaldehyde preserves tissues by cross-linking proteins through chemical reactions with their amino groups. This process denatures enzymes and prevents microbial growth, thereby halting tissue decay and

- maintaining the structure of the specimen during embalming or dissection.
- 4. Benzoic acid is effective as a preservative in beverages because it inhibits the growth of bacteria, yeasts, and fungi by lowering the internal pH of microbial cells, which disrupts their metabolism. Its antimicrobial action is most effective in acidic environments, like soft drinks and fruit juices, making it highly suitable for such applications.
- 5. Certain ketones like muscone are used in perfumes because they have a pleasant, long-lasting fragrance and are more chemically stable than aldehydes. Aldehydes tend to oxidise easily and may produce unpleasant odours over time, whereas ketones retain their scent longer, making them ideal for perfumery and cosmetic applications.

SHORT ANSWER TYPE QUESTIONS

(3 Marks)

- 1. (i) Ethanoic acid (acetic acid) lowers the pH of food, creating an acidic environment that inhibits the growth of bacteria, yeast, and moulds. This antimicrobial property helps in preserving food for a longer time.
 - (ii) Due to its acidic nature, ethanoic acid can dissolve mineral deposits, grease, and grime, especially limescale (calcium carbonate). It also acts as a natural disinfectant, helping to kill some harmful microbes on surfaces.
- **2.** (i) Acetone has a low molecular weight and a simple ketone structure with no hydrogen bonding between its own molecules. This results in weak

- intermolecular forces, making it highly volatile (i.e., it evaporates quickly at room temperature).
- (ii) Acetone contains a polar carbonyl group (C=O) which allows it to dissolve both polar and many non-polar substances. This makes it an excellent organic solvent, particularly useful in dissolving resins, plastics, and paints in industrial and cosmetic applications.
- 3. (i) Formaldehyde reacts with the amino groups of proteins, forming cross-links between protein molecules. This denatures the proteins, halting enzymatic and microbial activity, thereby preserving the tissue structure and preventing decomposition.

- (ii) Pure formaldehyde is a gas at room temperature, making it difficult and hazardous to handle. It is stored as formalin (a 37–40% aqueous solution) because it is safer, easier to store and use, and remains stable for longer periods in this form.
- **4. (i)** Benzoic acid inhibits the growth of bacteria, yeast, and fungi by interfering with their enzymatic activity and metabolic pathways, especially in the cell membrane. This helps prevent microbial spoilage and extends the shelf life of acidic foods and beverages.
 - (ii) Benzoic acid is more effective in acidic environments because in low pH, it remains mostly in its undissociated (protonated) form, which can

- easily penetrate microbial cell membranes and disrupt internal functions, making it a potent preservative under such conditions.
- 5. (i) Large cyclic ketones like muscone and civetone have low volatility and high molecular stability, which allows them to evaporate slowly, releasing fragrance over a longer period. This makes them ideal for creating long-lasting scents in perfumes.
 - (ii) Ketones are generally less reactive and more stable than aldehydes. They are less prone to oxidation, ensuring the perfume retains its original fragrance over time. Unlike aldehydes, which can sometimes develop unpleasant odours due to degradation, ketones maintain a consistent and pleasant scent.

CASE BASED QUESTIONS

(4 Mark)

1. (i) Acetal

CH₃CHO
$$C_2H_5$$
 C_2H_5OH CH_3 —CH OC_2H_5 C_2H_5OH OC_2H_5 CH_3 —CH OC_2H_5 OC_2H_5

- (ii) It is because the carboxylate ion is more stablised than the phenoxide ion by resonance.
- (iii) (a) (1)

Steric hindrance and the electron donating effect due to presence of alkyl groups in ketones make them less reactive with Grignard reagent compared to aldehydes.

(2) Propanal give positive result with Tollen's reagent while propanone does not give this test.

R—CHO + 2[Ag (NH₃)₂]
$$^{-}$$
OH $^{-}$ \rightarrow RCOOH
Aldehyde + 2Ag \downarrow + 4NH₃ + H₂OOR
OR O + Ag \downarrow + NH₃

Silver mirror

CHO
$$H_2$$
NCONHN H_2

CHO
 H_2 NCONHN H_2

CHO
 CH_3
 CH_3

This is called ETARD reaction.

- (ii) This is because polarity of the carbonyl group is reduced in benzaldehyde due to resonance. Hence, it is less reactive towards nucleophilic addition reaction.
- (iii) (a) Tollen's reagent acts as a mild oxidising agent and oxidises the aldehydes to corresponding carboxylic acids and itself gets reduced forming silver mirror. Thus, it show positive tests for aromatic aldehydes.

OR

(b)
$$CH_3CH_2CHCH_3 \xrightarrow{\text{alkaline KMnO}_4} \rightarrow CH_3CH_2COCH_3$$
 | OH

LONG ANSWER TYPE QUESTIONS

(5 Marks)

1. (i) In benzaldehyde the carbocation is less electrophillic than in formaldehyde due to resonance with the ring electrons.

The initial nucleophilic addition of hydroxide anion is therefore faster on formaldehyde than on benzaldehyde.

The aldehyde that undergoes nucleophilic attack by OH is converted to the sodium salt of the acid and the other aldehyde to the alcohol. (ii) Yes

It does not have an alpha hydrogen atom.

- 2. (i) O CH₃
 - (ii) Since it forms a 2, 4, –DNP derivative, it contains a carbonyl group and must be an aldehyde or a ketone.

- (iii) Since it does not reduce Tollen's reagent it cannot be an aldehyde and is therefore a ketone.
- (iv) Since it gives the iodoform reaction, it must have a methyl group linked to the carbonly carbon atom and is, therefore, a methyl ketone.

Since it gives 1, 2-benzenedicarboxylic acid on oxidation it is a 1,2 substituted benzene derivative. Using the molecular formula together with the points above, we arrive at the structure of the compound.



