

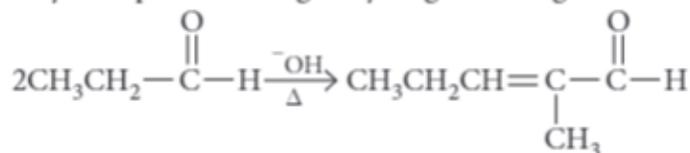
Aldehydes, Ketones and Carboxylic Acids

CASE STUDY / PASSAGE BASED QUESTIONS

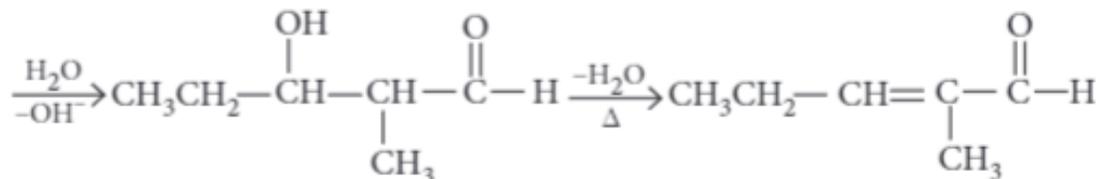
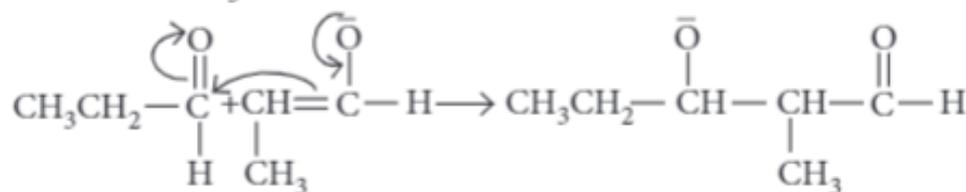
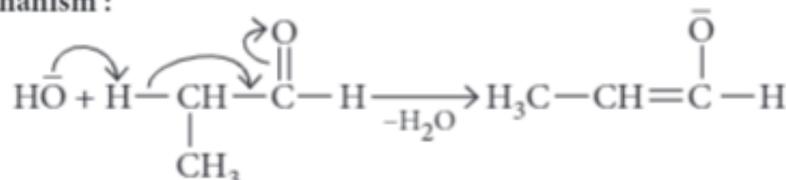
1

Read the passage given below and answer the following questions :

The addition reaction of enol or enolate to the carbonyl functional group of aldehyde or ketone is known as aldol addition. The β -hydroxyaldehyde or β -hydroxyketone so obtained undergo dehydration in second step to produce a conjugated enone. The first part of reaction is an addition reaction and the second part is an elimination reaction. Carbonyl compound having α -hydrogen undergoes aldol condensation reaction.



Mechanism :



The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) Condensation reaction is the reverse of which of the following reaction?
- (a) Lock and key hypothesis (b) Oxidation
(c) Hydrolysis (d) Glycogen formation
- (ii) Which of the following compounds would be the main product of an aldol condensation of acetaldehyde and acetone?
- (a) $\text{CH}_3\text{CH}=\text{CHCHO}$ (b) $\text{CH}_3\text{CH}=\text{CHCOCH}_3$
(c) $(\text{CH}_3)_2\text{C}=\text{CHCHO}$ (d) $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$

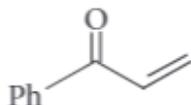
Syllabus

Aldehydes and Ketones : Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses.

Carboxylic Acids : Nomenclature, acidic nature, methods of preparation, physical and chemical properties, uses.

Carboxylic Acids : Nomenclature, acidic nature, methods of preparation, physical and chemical properties, uses.

(iii) Which combination of carbonyl compounds gives phenyl vinyl ketone by an aldol condensation?



- (a) Acetophenone and Formaldehyde (b) Acetophenone and acetaldehyde
(c) Benzaldehyde and acetaldehyde (d) Benzaldehyde and acetone

(iv) Which of the following will undergo aldol condensation?

- (a) HCHO (b) $\text{CH}_3\text{CH}_2\text{OH}$ (c) $\text{C}_6\text{H}_5\text{CHO}$ (d) $\text{CH}_3\text{CH}_2\text{CHO}$

OR

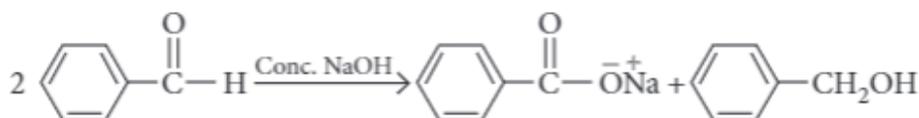
Which of the following does not undergo aldol condensation ?

- (a) CH_3CHO (b) $\text{CH}_3\text{CH}_2\text{CHO}$ (c) CH_3COCH_3 (d) $\text{C}_6\text{H}_5\text{CHO}$

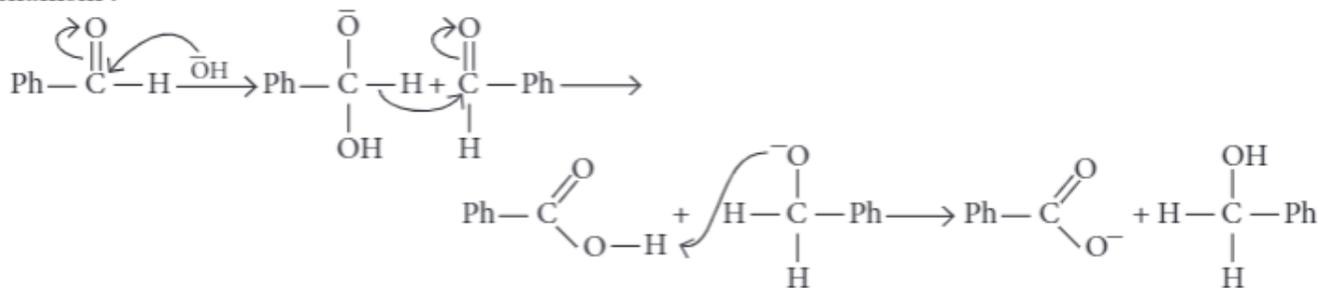
2

Read the passage given below and answer the following questions :

When an aldehyde with no α -hydrogen reacts with concentrated aqueous NaOH, half the aldehyde is converted to carboxylic acid salt and other half is converted to an alcohol. In other words, half of the reactant is oxidized and other half is reduced. This reaction is known as Cannizzaro reaction.



Mechanism :

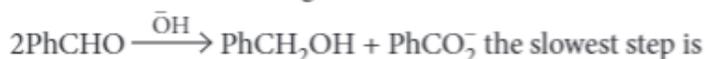


The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
(a) benzyl alcohol and sodium formate (b) sodium benzoate and methyl alcohol
(c) sodium benzoate and sodium formate (d) benzyl alcohol and methyl alcohol.
- (ii) Which of the following compounds will undergo Cannizzaro reaction?
(a) CH_3CHO (b) CH_3COCH_3
(c) $\text{C}_6\text{H}_5\text{CHO}$ (d) $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$
- (iii) Trichloroacetaldehyde is subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is
(a) 2, 2, 2-trichloroethanol (b) trichloromethanol
(c) 2, 2, 2-trichloropropanol (d) chloroform.

OR

In Cannizzaro reaction given below :



- (a) the attack OH^- at the carboxyl group
- (b) the transfer of hydride to the carbonyl group
- (c) the abstraction of proton from the carboxylic group
- (d) the deprotonation of PhCH_2OH .

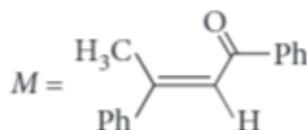
(iv) Which of the following reaction will not result in the formation of carbon-carbon bonds?

- (a) Cannizzaro reaction
- (b) Wurtz reaction
- (c) Reimer-Tiemann reaction
- (d) Friedel-Crafts' acylation

3

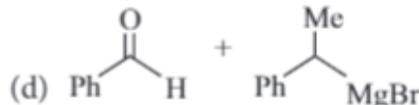
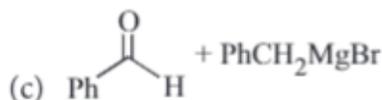
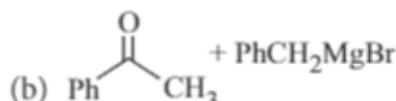
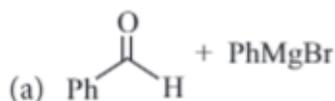
Read the passage given below and answer the following questions :

A tertiary alcohol *H* upon acid catalysed dehydration gives a product *I*. Ozonolysis of *I* leads to compounds *J* and *K*. Compound *J* upon reaction with KOH gives benzyl alcohol and a compound *L*, whereas *K* on reaction with KOH gives only *M*.



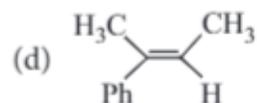
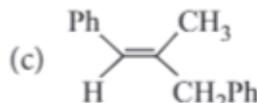
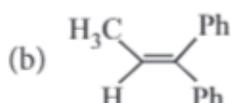
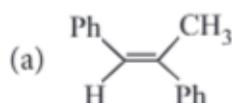
The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Compound *H* is formed by the reaction of



OR

The structure of compound *I* is



(ii) The structures of compound *J*, *K* and *L*, respectively, are



(iii) When (*J*) is treated with acetic anhydride, in the presence of corresponding salt of an acid, the product obtained is

- (a) cinnamic acid
- (b) crotonic acid
- (c) maleic acid
- (d) benzylic acid.

(iv) Which of the following statements is correct for compound (*K*)?

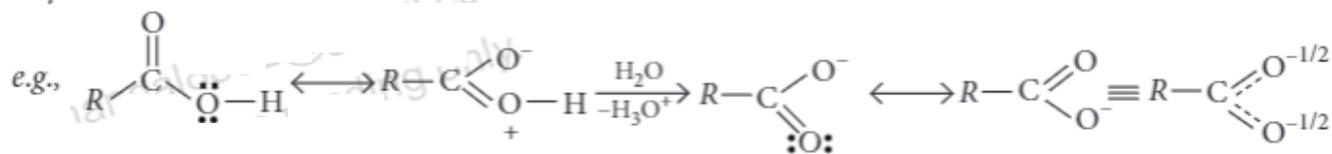
- (a) It reacts with alkaline KMnO_4 followed by acidic hydrolysis and forms benzoic acid.
- (b) It reacts with iodine and NaOH to form triiodomethane.
- (c) It is prepared by the reaction of benzene with benzoyl chloride in presence of anhydrous aluminium chloride.
- (d) It reacts with freshly prepared ammoniacal silver nitrate solution.

Read the passage given below and answer the following questions :

Carboxylic acids dissociate in water to give carboxylate ion and hydronium ion.



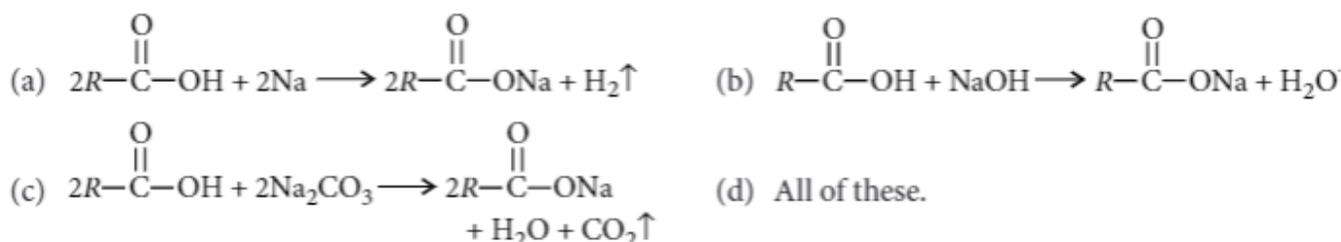
The acidity of carboxyl group is due to the presence of positive charge on oxygen which liberates proton. The carboxylate ion formed is resonance stabilised.



Carboxylic acids are stronger acids than phenols. Electron withdrawing groups (EWG) increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of negative charge by inductive and/or resonance effects. Electron donating group (EDG) decrease the acidity by destabilising the conjugate base.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following reactions is showing the acidic property of carboxylic acid?

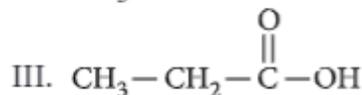


(ii) Which one of the following is the correct order of acidic strength?

- (a) $\text{CF}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{HCOOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{CH}_3\text{COOH}$
 (b) $\text{CH}_3\text{COOH} > \text{HCOOH} > \text{CF}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$
 (c) $\text{HCOOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{CF}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{CH}_3\text{COOH}$
 (d) $\text{CF}_3\text{COOH} > \text{CH}_3\text{COOH} > \text{HCOOH} > \text{CHCl}_2\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$

OR

The acidic strength of the given compounds follows the order :

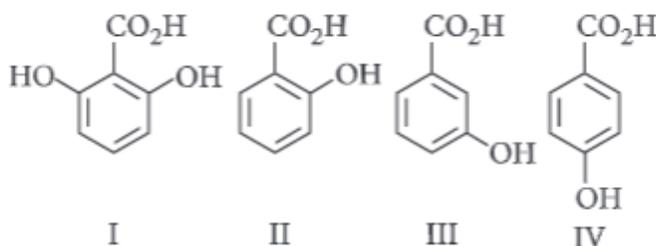


- (a) $\text{II} > \text{III} > \text{I}$ (b) $\text{III} > \text{II} > \text{I}$ (c) $\text{II} > \text{I} > \text{III}$ (d) $\text{I} > \text{II} > \text{III}$

(iii) Which of the following acids has the smallest dissociation constant?

- (a) $\text{CH}_3\text{CHFCOOH}$ (b) $\text{FCH}_2\text{CH}_2\text{COOH}$ (c) $\text{BrCH}_2\text{CH}_2\text{COOH}$ (d) $\text{CH}_3\text{CHBrCOOH}$

(iv) The correct order of acidity for the following compounds is



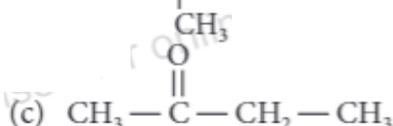
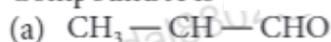
- (a) $\text{I} > \text{II} > \text{III} > \text{IV}$ (b) $\text{III} > \text{I} > \text{II} > \text{IV}$ (c) $\text{III} > \text{IV} > \text{II} > \text{I}$ (d) $\text{I} > \text{III} > \text{IV} > \text{II}$

Read the passage given below and answer the following questions :

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

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Compound A is

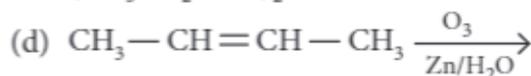
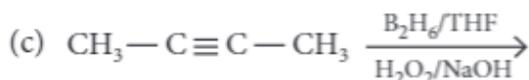
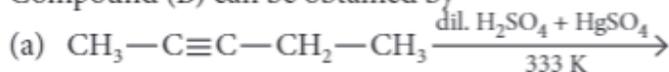


OR

Compound (C) is



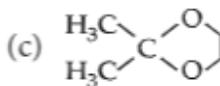
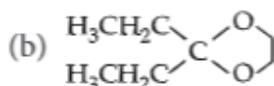
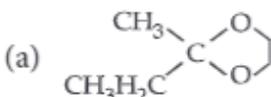
(ii) Compound (B) can be obtained by



(iii) Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN?

- (a) A (b) B
(c) C (d) All are equally reactive

(iv) What will be the product when (B) reacts with ethylene glycol in presence of HCl gas?



(d) None of these.

Read the passage given below and answer the following questions :

Aldehydes and ketones are reduced to primary and secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$ as well as catalytic hydrogenation. The carbonyl group of aldehydes and ketones is reduced to $>CH_2$ group on treatment with $Zn-Hg$ and conc. HCl (Clemmensen reduction) or with hydrazine followed by $NaOH$ or KOH in highly boiling solvent such as ethylene glycol (Wolff-Kishner reduction).

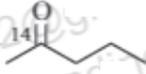
Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with HNO_3 , $KMnO_4$, $K_2Cr_2O_7$ etc. Even mild oxidising agents mainly Tollen's reagent and Fehling's solution also oxidise aldehydes. Ketones are generally oxidised under vigorous conditions *i.e.*, strong oxidising agents and at elevated temperatures, to give mixture of carboxylic acids having lesser number of C-atoms than the parent ketone.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following cannot be made by reduction of ketone or aldehyde with $NaBH_4$ in methanol?

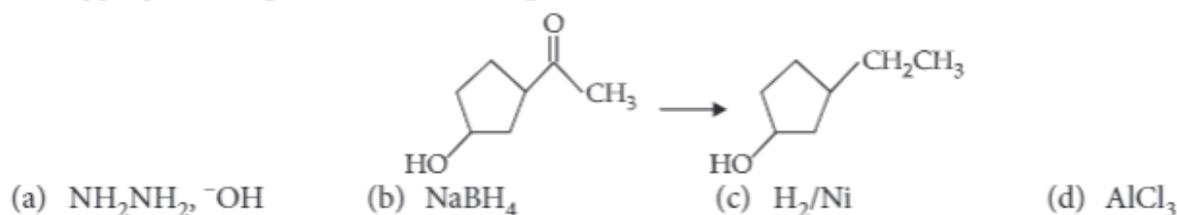
- (a) 1-Butanol (b) 2-Butanol
(c) 2-Methyl-1-propanol (d) 2-Methyl-2-propanol

- (ii) The carbonyl compound producing an optically active product by reaction with LiAlH_4 is
 (a) propanone (b) butanone (c) 3-pentanone (d) benzophenone.
- (iii) A substance $\text{C}_4\text{H}_{10}\text{O}(X)$ yields on oxidation a compound $\text{C}_4\text{H}_8\text{O}$ which gives an oxime and a positive iodoform test. The substance X on treatment with conc. H_2SO_4 gives C_4H_8 . The structure of the compound (X) is
 (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
 (c) $(\text{CH}_3)_3\text{COH}$ (d) $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$

- (iv) In the oxidation of  by acidified $\text{K}_2\text{Cr}_2\text{O}_7$, the products are
 (a) $\text{CH}_3^{14}\text{C}-\text{OH}$ and $\text{CH}_3\text{CH}_2\text{COOH}$ (b) $\text{CH}_3(\text{CH}_2)_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ and $\text{CH}_3^{14}\text{CH}_2\text{COOH}$
 (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{HCOOH}$ (d) none of these.

OR

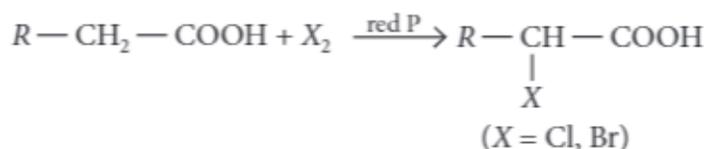
The appropriate reagent for the following transformation is



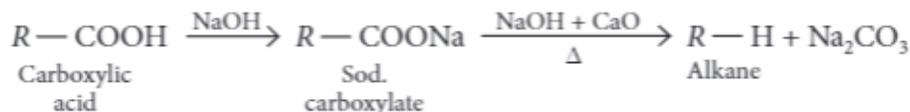
8

Read the passage given below and answer the following questions :

Carboxylic acids having an α -hydrogen atom when treated with chlorine or bromine in the presence of small amount of red phosphorus gives α -halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.



When sodium salt of carboxylic acid is heated with soda lime it loses carbon dioxide and gives hydrocarbon with less number of C-atoms.



In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 (c) Assertion is correct statement but reason is wrong statement.
 (d) Assertion is wrong statement but reason is correct statement.
- (i) **Assertion :** $(\text{CH}_3)_3\text{CCOOH}$ does not give H.V.Z reaction.
Reason : $(\text{CH}_3)_3\text{CCOOH}$ does not have α -hydrogen atom.

(ii) **Assertion** : H.V.Z. reaction involves the treatment of carboxylic acids having α -hydrogens with Cl_2 or Br_2 in presence of small amount of red phosphorus.

Reason : Phosphorus reacts with halogens to form phosphorus trihalides.

OR

Assertion : Propionic acid with Br_2/P yields $\text{CH}_3\text{Br} + \text{CHBr} - \text{COOH}$.

Reason : Propionic acid has two α -hydrogen atoms.

(iii) **Assertion** : $\text{C}_6\text{H}_5\text{COCH}_2\text{COOH}$ undergoes decarboxylation easily than $\text{C}_6\text{H}_5\text{COCOCH}_3$.

Reason : $\text{C}_6\text{H}_5\text{COCH}_2\text{COOH}$ is a β -keto acid.

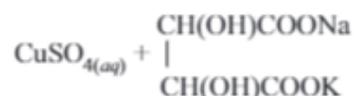
(iv) **Assertion** : On heating 3-methylbutanoic acid with soda lime, isobutane is obtained.

Reason : Soda lime is a mixture of $\text{NaOH} + \text{CaO}$ in the ratio 3 : 1.

9

Read the passage given below and answer the following questions :

Fehling's reagent : Fehling's reagent is a mixture of two solutions. Fehling's solution A is aqueous copper sulphate solution. Fehling's solution B is alkaline sodium potassium tartarate (Rochelle salt).



It is a mild oxidising agent. It is weaker than Tollens' reagent. It oxidises only aliphatic aldehydes to carboxylate ions and itself gets reduced to reddish brown precipitate of cuprous oxide.

Aromatic aldehydes do not respond to Fehling's test. This reaction is used for the test of aliphatic aldehydes known as Fehling's reagent test.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion** : Fehling's solution can be used to distinguish between acetaldehyde and acetone.

Reason : Fehling's reagent is a mixture of two solutions.

(ii) **Assertion** : Aromatic aldehydes can be distinguished from aliphatic aldehydes by Fehling's solution.

Reason : Aromatic aldehydes reduce Fehling's solution, but aliphatic aldehydes do not.

OR

Assertion : Fehling's solution oxidises acetaldehyde to acetic acid but not benzaldehyde to benzoic acid.

Reason : The C — H bond of — CHO group in benzaldehyde is stronger than in acetaldehyde.

(iii) **Assertion** : CH_3CHO and $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ cannot be distinguished chemically by Fehling's solution.

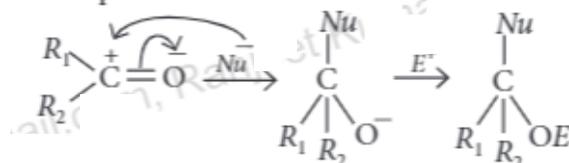
Reason : CH_3CHO and $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ can be distinguished by iodoform test.

(iv) **Assertion** : Formaldehyde, when heated with Fehling's reagent produces a reddish brown ppt. of Cu.

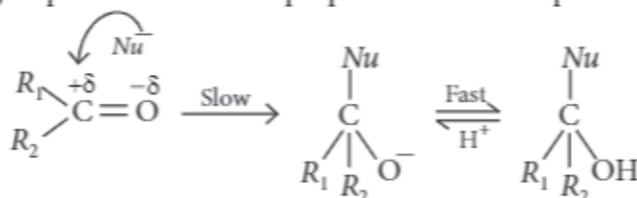
Reason : Fehling's reagent oxidises formaldehyde to formate ion.

Read the passage given below and answer the following questions :

Aldehydes and ketones undergo nucleophilic addition reactions.



Carbonyl carbon is electron deficient hence acts as an electrophile. Nucleophile attacks on the electrophilic carbon atom of the carbonyl group from a direction perpendicular to the plane of the molecule.



In this process, hybridisation of carbon atom changes from sp^2 to sp^3 and a tetrahedral alkoxide ion is formed as intermediate. This intermediate captures proton from the reaction medium to give the neutral product. Aldehydes are generally more reactive than ketones in nucleophilic addition reactions.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

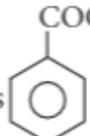
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 (d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Benzaldehyde is more reactive than ethanal towards nucleophilic attack.

Reason : The overall effect of $-I$ and $+R$ effect of phenyl group decreases the electron density on the carbon atom of $>C=O$ group in benzaldehyde.

(ii) **Assertion :** $(CH_3)_3CCOC(CH_3)_3$ and acetone can be distinguished by the reaction with $NaHSO_3$.

Reason : HSO_3^- is the nucleophile in bisulphite addition.

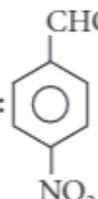
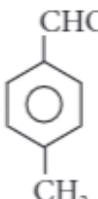
(iii) **Assertion :** Ease of nucleophilic addition of the compounds  (I), CH_3CHO (II) and CH_3COCH_3 (III) is $I > II > III$.

Reason : Aldehydes and ketones undergo nucleophilic addition reactions.

OR

Assertion : The formation of cyanohydrin from an aldehyde or ketone occurs very slowly with pure HCN. This reaction is catalysed by a base.

Reason : Base generates CN^- ion which is a stronger nucleophile.

(iv) **Assertion :**  is more reactive towards nucleophilic addition reaction than .

Reason : Reactivity of carbonyl group is due to electrophilic nature of carbonyl carbon.

ASSERTION & REASON

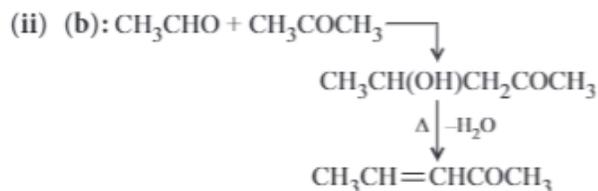
In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 - (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 - (c) Assertion is correct statement but reason is wrong statement.
 - (d) Assertion is wrong statement but reason is correct statement.
11. **Assertion :** Hydrogen bonding in carboxylic acids is stronger than alcohols.
Reason : Highly branched carboxylic acids are more acidic than unbranched acids.
 12. **Assertion :** Cross aldol condensation of ethanal and propanal gives a mixture of four products.
Reason : Ethanal and propanal, both contain α -hydrogen atom.
 13. **Assertion :** Boiling point of aldehydes lie in between parent alkanes and corresponding alcohols.
Reason : Aldehydes cannot form intermolecular hydrogen bonds like alcohols.
 14. **Assertion :** NaHSO_3 is used for the purification of carbonyl compounds.
Reason : They are used in the blending of perfumes and flavouring agents.
 15. **Assertion :** *m*-Chlorobenzoic acid is a stronger acid than *p*-chlorobenzoic acid.
Reason : In *m*-chlorobenzoic acid both $-I$ -effect and $+R$ -effect of Cl operate but in *p*-chlorobenzoic acid only $+R$ -effect of Cl operates.
 16. **Assertion :** Presence of acids and bases activates carbonyl compounds for reaction.
Reason : Carbonyl compounds possess positive and negative centres and provide a seat for electrophilic and nucleophilic attack.
 17. **Assertion :** Formic acid is a stronger acid than benzoic acid.
Reason : $\text{p}K_a$ of formic acid is lower than that of benzoic acid.
 18. **Assertion :** Aldol condensation can be catalysed both by acids and bases.
Reason : β -Hydroxy aldehydes or ketones readily undergo acid catalysed dehydration.
 19. **Assertion :** Carboxylic acids have higher boiling points than alkanes.
Reason : Carboxylic acids are resonance hybrids.
 20. **Assertion :** Lower aldehydes and ketones are soluble in water but the solubility decreases as the molecular mass increases.
Reason : Distinction between aldehydes and ketones can be done by Tollens' test.
 21. **Assertion :** Fluoroacetic acid is stronger than chloroacetic acid.
Reason : Carboxylic acids are weak acids and turn blue litmus red.
 22. **Assertion :** Ketones can be converted into acids by haloform reaction.
Reason : Addition of Grignard reagents to dry ice followed by hydrolysis gives ketones.
 23. **Assertion :** Benzaldehyde undergoes aldol condensation.
Reason : Aldehydes having α -hydrogen atom undergo aldol condensation.
 24. **Assertion :** Acetic acid in vapour state shows a molecular mass of 120.
Reason : It undergoes intermolecular hydrogen bonding.
 25. **Assertion :** Nitration of benzoic acid gives *m*-nitrobenzoic acid.
Reason : Carboxyl group increases the electron density at the *meta*-position.

26. **Assertion :** Carboxylic acids are stabilised by resonance.
Reason : Chloroacetic acid is weaker than acetic acid.
27. **Assertion :** α -Hydrogen atoms in aldehydes and ketones are acidic.
Reason : The anion left after the removal of α -hydrogen is stabilised by inductive effect.
28. **Assertion :** During reaction of carboxylic acids with NaHCO_3 , the CO_2 evolved comes from carboxylic acid and not from NaHCO_3 .
Reason : Carbonic acid is a weaker acid than carboxylic acid.
29. **Assertion :** *o*-Substituted benzoic acids are generally stronger acids than benzoic acids.
Reason : Increased strength is due to *ortho*-effect.
30. **Assertion :** Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.
Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

HINTS & EXPLANATIONS

1. (i) (c): Condensation reaction is the reverse of hydrolysis, which splits a chemical entity into two parts through the action of the polar water molecule.



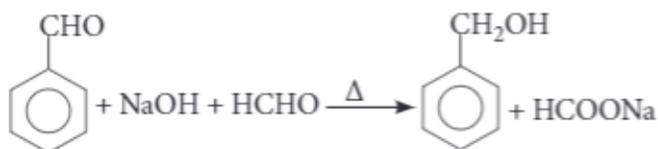
(iii) (a)

(iv) (d)

OR

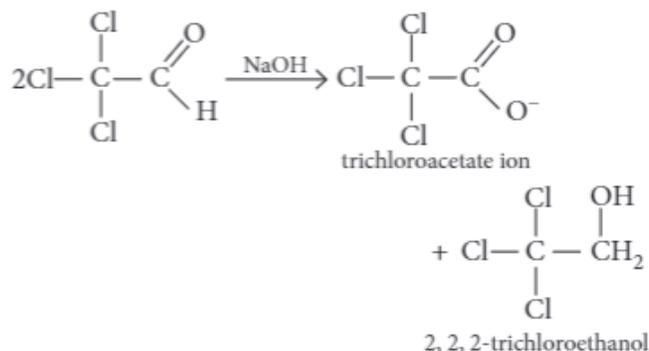
(d) : Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) with no α -hydrogen cannot undergo aldol condensation.

2. (i) (a): It is an example of cross Cannizzaro reaction where aromatic aldehyde gets reduced to alcohol and aliphatic aldehyde gets oxidised to its sodium salt (both aldehydes must not contain any α -hydrogen).



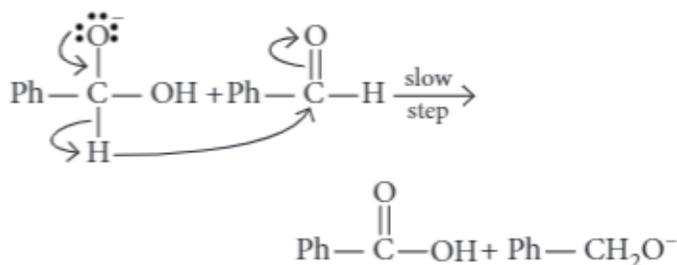
(ii) (c)

(iii) (a): The Cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.



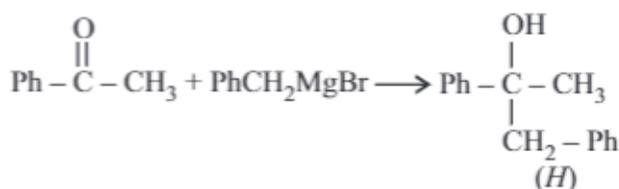
OR

(b) : Hydride transfer is the slowest step.

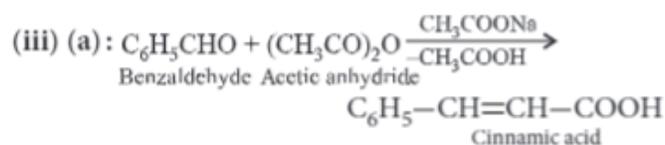
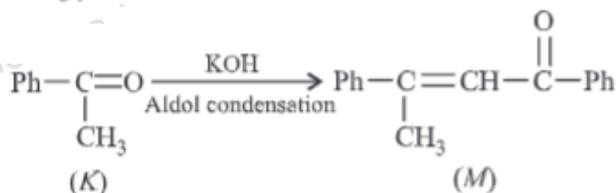
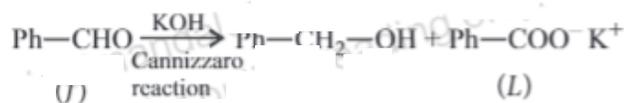
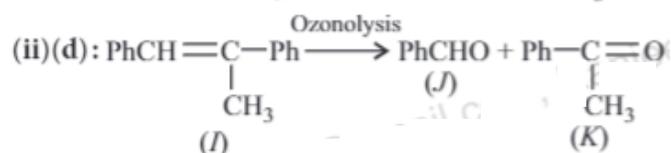
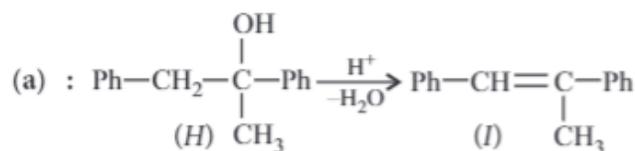


(iv) (a): C—C bond is not formed in Cannizzaro reaction while other reactions result in the formation of C—C bond.

3. (i) (b) :



OR



(iv) (b)

4. (i) (d): All the reactions are showing the acidic properties of carboxylic acid. Carboxylic acid forms the sodium salts with all *i.e.*, alkali metals, NaOH and Na_2CO_3 etc. and removes the acidic proton from the carboxylic acid.

(ii) (a): In general, greater the $+I$ effect of the group attached to the carboxyl group, lesser will be the acidic strength and greater the $-I$ effect of the group, greater will be acidic strength. As number of halogen atoms and electronegativity of halogen atom increases, acidic strength increases.

Thus, correct order of acidic strength is



OR

(d)

(iii) (c): Stronger $-I$ group attached closer to $-\text{COOH}$ makes the acid stronger, *i.e.*, acid has the larger dissociation constant. $-\text{Br}$ shows poor ($-I$) effect and also far away from $-\text{COOH}$ group *i.e.*, option (c) has smallest dissociation constant.

(iv) (a): Due to *ortho*-effect, (I) and (II) are stronger acids than (III) and (IV). Due to two *ortho*-hydroxyl groups in (I), it is stronger acid than (II). (III) is a

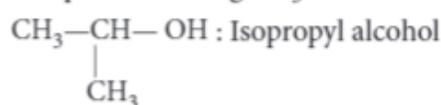
stronger acid than (IV) because at *m*-position, $-\text{OH}$ group cannot exert its $+R$ effect but can only exert its $-I$ effect while at *p*-position, $-\text{OH}$ group exerts its strong $+R$ effect.

Thus, the correct order of acidity is:



5. (i) (a): Iodoform test is given by the organic

compounds having $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$ or $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-$ group.



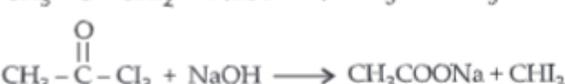
$\text{CH}_3\text{CH}_2\text{CHO}$: Propionaldehyde



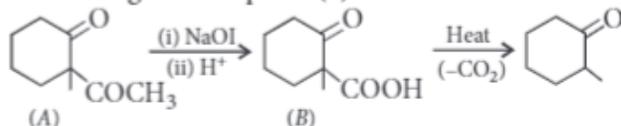
$\text{C}_6\text{H}_5-\text{CH}_2-\text{OH}$: Benzyl alcohol

Therefore, isopropyl alcohol will give positive iodoform test.

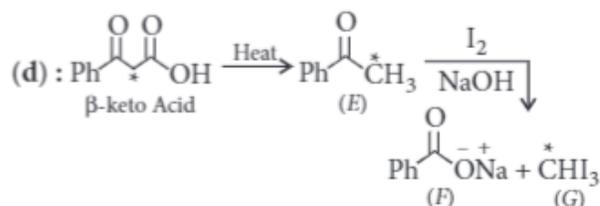
(ii) (b): Iodoform reaction of acetone occurs in following steps:



(iii) (c): Given reagents indicate the presence of $-\text{COCH}_3$ group in the starting compound A. Further, since the $-\text{COOH}$ group introduced in B due to iodoform reaction is absent in the final product, B should be a β -keto acid. Hence, A should have structure given in option (c).



OR

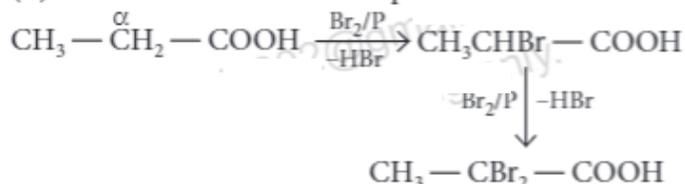


8. (i) (a)

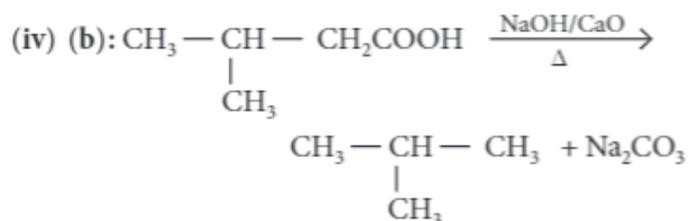
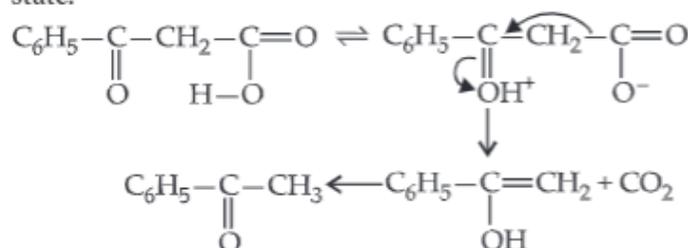
(ii) (c): Phosphorus converts a little of the acid into acid chloride which is more reactive than the parent carboxylic acid. Thus, it is the acid chloride, not the acid itself, that undergoes chlorination at the α -carbon.

OR

(d): Bromination occurs at α -positions.



(iii) (a): β -ketoacids are unstable acids. They readily undergo decarboxylation through a cyclic transition state.



9. (i) (b): All aliphatic aldehydes give red ppt. with Fehling's solution, but ketones do not reduce Fehling's solution.

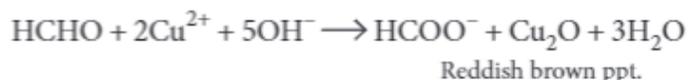
(ii) (c): Aliphatic aldehydes reduce Fehling's solution, but aromatic aldehydes do not.

OR

(a): Fehling's solution is a mild oxidising agent. It cannot oxidise aromatic aldehydes to corresponding carboxylate ion.

(iii) (b): CH_3CHO and $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ both are aliphatic aldehydes, hence cannot be distinguished by Fehling's solution. CH_3CHO contains CH_3CO -group whereas $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ does not contain any CH_3CO -group. Thus, CH_3CHO will give yellow ppt. with I_2 and NaOH but $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ will not.

(iv) (d): Formaldehyde when heated with Fehling's reagent, undergo oxidation to give formate ion and produce reddish brown ppt. of Cu_2O .

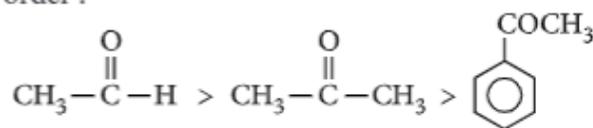


10. (i) (a)

(ii) (b): HSO_3^- is a bulky nucleophile, hence, cannot attack on sterically hindered ketones.

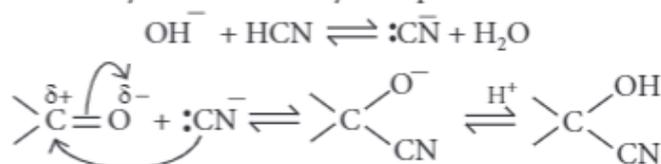
(iii) (d): Aromatic aldehydes and ketones are less reactive than the corresponding aliphatic analogues towards nucleophilic addition reactions due to the +R effect of benzene ring. Further, aldehydes are more reactive than ketones due to +I effect and steric effect of alkyl group.

Therefore, the ease of nucleophilic addition will follow the order :



OR

(a): Formation of cyanohydrin from an aldehyde or ketone occurs very slowly with pure HCN because it is feebly ionised. This reaction is catalysed by a base. Base generates CN^- ion which is a stronger nucleophile and readily adds to carbonyl compound.



(iv) (b): Electron withdrawing group ($-\text{NO}_2$) increases the reactivity towards nucleophilic addition reactions, whereas electron donating group ($-\text{CH}_3$) decreases the reactivity towards nucleophilic addition reactions.

11. (c): Highly branched carboxylic acids are less acidic than unbranched acids. The +I effect of alkyl groups in branched acid increases the magnitude of negative charge. Thus, $-\text{COOH}$ group is shielded from solvent molecules and cannot be stabilized by solvation as effectively as in unbranched carboxylic acids.

12. (a)

13. (b): Aldehydes have higher molecular weight than parent alkanes as well as polarity in aldehydes shows higher boiling point than parent alkanes. Aldehydes do not have any hydrogen atom attached directly to the oxygen so they cannot form hydrogen bond with each other.

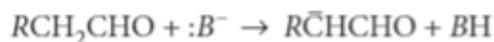
14. (b): Carbonyl compounds form solid additive products with NaHSO_3 which are separated out. The solid bisulphites of carbonyl compounds on hydrolysis with dilute acid regenerate original carbonyl compounds and thus, this property is used for the purification of carbonyl compounds as well as for their separation.

15. (c): In *p*-chlorobenzoic acid, both $+R$ and $-I$ effect operate together but in *m*-chlorobenzoic acid only $-I$ effect operates. Therefore, *m*-chlorobenzoic acid is a stronger acid than *p*-chlorobenzoic acid.

16. (b): Presence of acid intensifies the partial positive charge on carbonyl carbon and hence, activates the group.



Presence of base activates α -methylene component of the carbonyl compounds by converting them in carbanions.



17. (b): Due to overall electron-donating effect of the phenyl group, benzoate ion is less stable than formate ion.

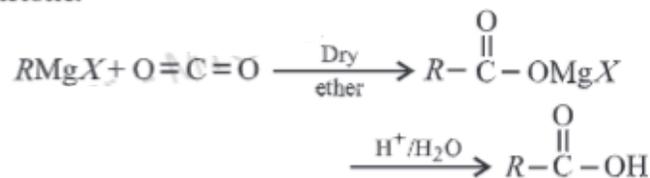
18. (b): Both carbanions (formed in presence of base) and enol form (formed in presence of an acid) act as nucleophiles and hence add on the carbonyl group of aldehydes and ketones to give aldols.

19. (b): Boiling points of carboxylic acids are higher due to their tendency to associate and form dimers to a greater extent by hydrogen bonding.

20. (b): Lower aldehydes and ketones are soluble in water due to polar effect of $\text{>C}=\text{O}$ group which makes hydrogen bonds with water molecules. As the size of the aldehydes and ketones increases the hydrophobic part *i.e.*, alkyl chain increases which weakens the H-bond formations with H_2O molecules and decreases the solubility.

21. (b): The $-I$ effect of F is greater than inductive effect of Cl and thus fluoroacetate ion is more stabilized to show more tendency to lose proton by its acid.

22. (c): Addition of Grignard reagents to dry ice followed by hydrolysis gives carboxylic acid not ketone.



23. (d): Aldehydes having a methyl or methylene group in the α -position or more correctly having at least one hydrogen atom in the α -position undergo dimerisation in presence of a base at low temperature to form β -hydroxy aldehydes called aldols. As benzaldehyde does not have any α -hydrogen hence it does not undergoes aldol condensation.

24. (a)

25. (c): Carboxyl group only marginally decreases the electron density at *m*-position relative to *o*- and *p*-positions.

26. (c): Chlorine atom has $-I$ effect which increases the ionisation of chloroacetic acid and stabilizes the chloroacetate ion by dispersal of negative charge. In acetic acid, methyl group due to $+I$ effect destabilizes the acetate ion by intensification of negative charge. Hence, chloroacetic acid dissociates to a greater extent than acetic acid.

27. (c): The anion left after the removal of α -hydrogen is stabilized by resonance effect.

28. (d): During reaction of carboxylic acids with NaHCO_3 , CO_2 evolved comes from NaHCO_3 . Carboxylic acid is a stronger acid than carbonic acid.

29. (a): *o*-Substituted benzoic acids are generally stronger acids than benzoic acid. This is regardless of the nature ($+I$ or $-I$) of the substituent. This is called *ortho*-effect and is probably due to a combination of steric and electronic factors.

30. (c): Aromatic aldehydes and formaldehyde do not contain α -hydrogen and thus undergo Cannizzaro reaction. Formaldehyde is more reactive than aromatic aldehydes.