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12

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S. No.	Chapter	Passage based/ MCQs/A & R (1 mark)	SA-I (2 marks)	SA-II (3 marks)	LA (5 marks)	Total
1.	The Solid State	1(1)	1(2)	1(3)	–	**11(24)**
2.	Solutions	2(2)	1(2)	–	–	
3.	Electrochemistry	1(1)	–	–	1(5)	
4.	Chemical Kinetics	–	2(4)	–	–	
5.	Surface Chemistry	1(4)	–	–	–	
6.	The *p*-Block Elements	1(1)	1(2)	1(3)	1(5)	**9(19)**
7.	The *d*- and *f*-Block Elements	2(2)	–	1(3)	–	
8.	Coordination Compounds	1(1)	1(2)	–	–	
9.	Haloalkanes and Haloarenes	1(1)	2(4)	–	–	**13(27)**
10.	Alcohols, Phenols and Ethers	2(5)	1(2)	–	–	
11.	Aldehydes, Ketones and Carboxylic Acids	1(1)	–	–	1(5)	
12.	Amines	1(1)	–	1(3)	–	
13.	Biomolecules	2(2)	–	1(3)	–	
	Total	**16(22)**	**9(18)**	**5(15)**	**3(15)**	**33(70)**

1. The Solid State....1
2. Solutions....12
3. Electrochemistry....25
4. Chemical Kinetics....35
5. Surface Chemistry....48
6. General Principles and Processes of Isolation of Elements⋆
7. The *p*-Block Elements....56
8. The *d*- and *f*-Block Elements....65
9. Coordination Compounds....72
10. Haloalkanes and Haloarenes....84
11. Alcohols, Phenols and Ethers....98
12. Aldehydes, Ketones and Carboxylic Acids....111
13. Amines....126
14. Biomolecules....137
15. Polymers⋆
16. Chemistry in Everyday Life⋆

⋆ *This chapter is not a part of the Board Examination 2020-21 syllabus*

[#] *For latest information please refer to www.cbse.nic.in*

CHAPTER

12

Aldehydes, Ketones and Carboxylic Acids

Syllabus

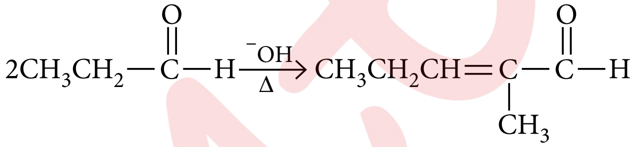
Aldehydes and Ketones : Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses. Carboxylic Acids : Nomenclature, acidic nature, methods of preparation, physical and chemical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

CASE STUDY / PASSAGE BASED QUESTIONS

1

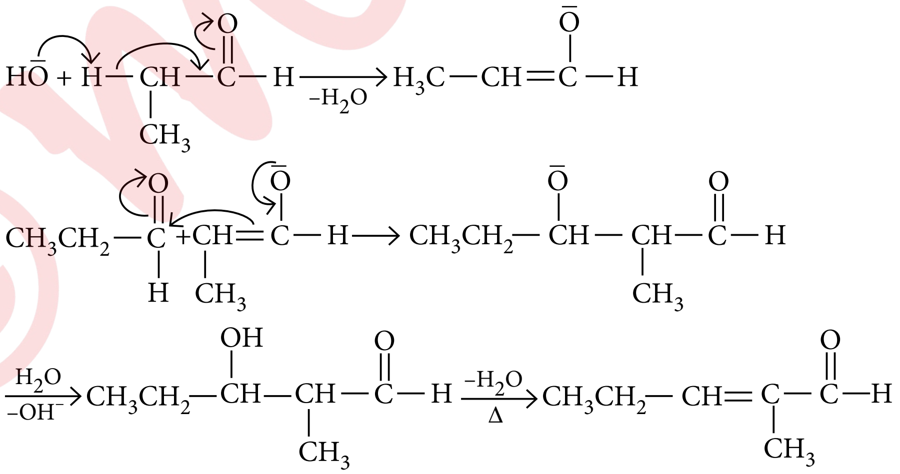
Read the passage given below and answer the following questions :

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.



$$2CH_3CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{^-OH} CH_3CH_2CH=\underset{CH_3}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

Mechanism :



$$H\bar{O} + H-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow[-H_2O]{} H_3C-CH=\overset{\bar{O}}{\overset{|}{C}}-H$$

$$CH_3CH_2-\underset{H}{\underset{|}{\overset{O}{\overset{\|}{C}}}} + \underset{CH_3}{\underset{|}{CH}}=\overset{\bar{O}}{\overset{|}{C}}-H \longrightarrow CH_3CH_2-\overset{\bar{O}}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H$$

$$\xrightarrow[-OH^-]{H_2O} CH_3CH_2-\overset{OH}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{-H_2O} CH_3CH_2-CH=\underset{CH_3}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

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

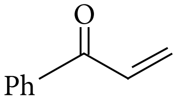
(i) Condensation reaction is the reverse of which of the following reaction?

(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) $CH_3CH=CHCHO$
(b) $CH_3CH=CHCOCH_3$
(c) $(CH_3)_2C=CHCHO$
(d) $(CH_3)_2C=CHCOCH_3$

(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) CH_3CH_2OH (c) C_6H_5CHO (d) CH_3CH_2CHO

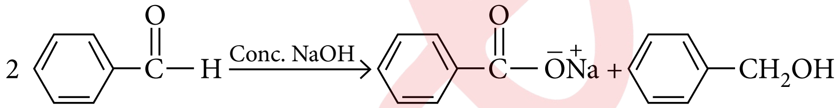
OR

Which of the following does not undergo aldol condensation ?
(a) CH_3CHO (b) CH_3CH_2CHO (c) CH_3COCH_3 (d) C_6H_5CHO

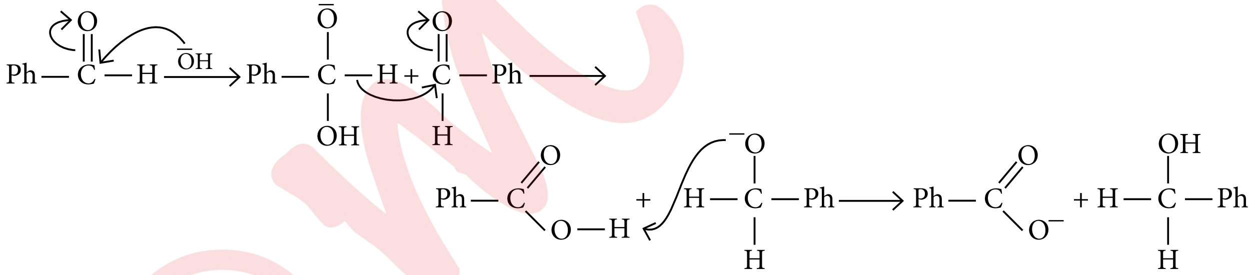
2

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) C_6H_5CHO (d) $C_6H_5CH_2CHO$

(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 compounds is
(a) 2, 2, 2-trichloroethanol (b) trichloromethanol
(c) 2, 2, 2-trichloropropanol (d) chloroform.

OR

In Cannizzaro reaction given below :

$2PhCHO \xrightarrow{\bar{O}H} PhCH_2OH + PhCO_2^-$ the slowest step is

4

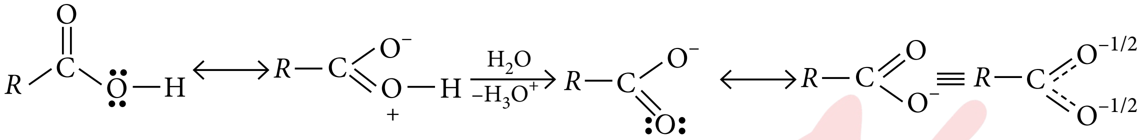
Read the passage given below and answer the following questions :

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

$$RCOOH + H_2O \longrightarrow RCOO^- + H_3O^+$$

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.

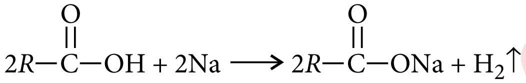
e.g.,

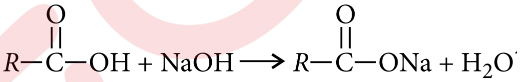


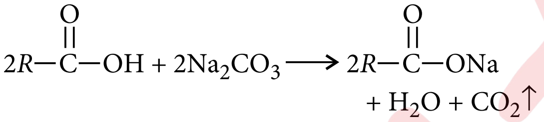
Carboxylic acids are stronger acids than phenols. Electron withdrawing groups (EWG) increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of negative charge by inductive and/or resonance effects. Electron donating group (EDG) decrease the acidity by destabilising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

(a) 
$2R-\overset{O}{\overset{\|}{C}}-OH + 2Na \longrightarrow 2R-\overset{O}{\overset{\|}{C}}-ONa + H_2\uparrow$

(b) 
$R-\overset{O}{\overset{\|}{C}}-OH + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + H_2O$

(c) 
$2R-\overset{O}{\overset{\|}{C}}-OH + 2Na_2CO_3 \longrightarrow 2R-\overset{O}{\overset{\|}{C}}-ONa + H_2O + CO_2\uparrow$

(d) All of these.

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

(a) $CF_3COOH > CHCl_2COOH > HCOOH > C_6H_5CH_2COOH > CH_3COOH$

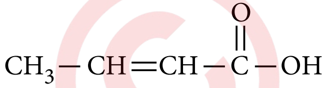
(b) $CH_3COOH > HCOOH > CF_3COOH > CHCl_2COOH > C_6H_5CH_2COOH$

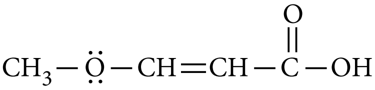
(c) $HCOOH > C_6H_5CH_2COOH > CF_3COOH > CHCl_2COOH > CH_3COOH$

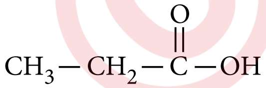
(d) $CF_3COOH > CH_3COOH > HCOOH > CHCl_2COOH > C_6H_5CH_2COOH$

OR

The acidic strength of the given compounds follows the order :

I. 
$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-OH$

II. 
$CH_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-CH=CH-\overset{O}{\overset{\|}{C}}-OH$

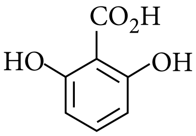
III. 
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$

(a) II > III > I (b) III > II > I (c) II > I > III (d) I > II > III

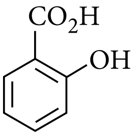
(iii) Which of the following acids has the smallest dissociation constant?

(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH (c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

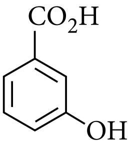
(iv) The correct order of acidity for the following compounds is



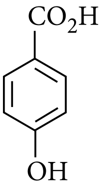
I



II



III



IV

(a) I > II > III > IV (b) III > I > II > IV (c) III > IV > II > I (d) I > III > IV> II

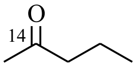
(ii) The carbonyl compound producing an optically active product by reaction with $LiAlH_4$ is

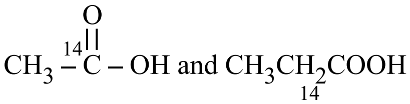
(a) propanone (b) butanone (c) 3-pentanone (d) benzophenone.

(iii) A substance $C_4H_{10}O(X)$ yields on oxidation a compound C_4H_8O 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

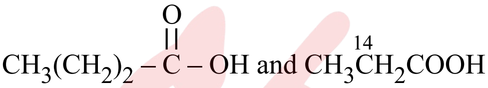
(a) $CH_3CH_2CH_2CH_2OH$ (b) $CH_3CH(OH)CH_2CH_3$

(c) $(CH_3)_3COH$ (d) $CH_3CH_2-O-CH_2CH_3$

(iv) In the oxidation of  by acidified $K_2Cr_2O_7$, the products are

(a) 

$CH_3-\overset{\overset{\large O}{\|}}{\overset{14}{C}}-OH$ and CH_3CH_2COOH

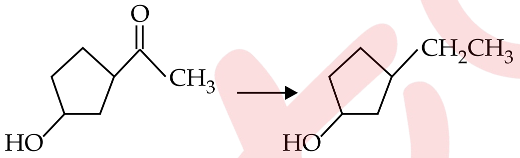
(b) 

$CH_3(CH_2)_2-\overset{\overset{\large O}{\|}}{C}-OH$ and $CH_3CH_2\overset{14}{C}OOH$

(c) $CH_3CH_2CH_2COOH + H\overset{14}{C}OOH$ (d) none of these.

OR

The appropriate reagent for the following transformation is

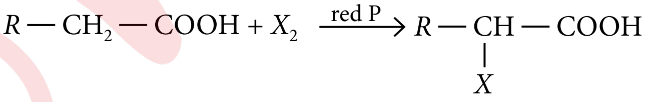


(a) $NH_2NH_2, {}^{-}OH$ (b) $NaBH_4$ (c) H_2/Ni (d) $AlCl_3$

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.



$$R-CH_2-COOH + X_2 \xrightarrow{\text{red P}} R-\underset{\underset{X}{|}}{CH}-COOH$$

$(X = Cl, Br)$

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

$$\underset{\text{Carboxylic acid}}{R-COOH} \xrightarrow{NaOH} \underset{\text{Sod. carboxylate}}{R-COONa} \xrightarrow[\Delta]{NaOH + CaO} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

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 :** $(CH_3)_3CCOOH$ does not give H.V.Z reaction.
Reason : $(CH_3)_3CCOOH$ does not have α-hydrogen atom.

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.

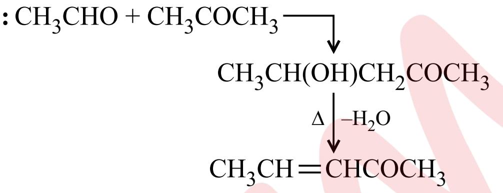
29. **Assertion :** *o*-Substituted benzoic acids are generally stronger acids than benzoic acids.
Reason : Increased strength is due to *ortho*-effect.

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.

(ii) (b) : $CH_3CHO + CH_3COCH_3$



$$CH_3CHO + CH_3COCH_3 \longrightarrow CH_3CH(OH)CH_2COCH_3 \xrightarrow[-H_2O]{\Delta} CH_3CH{=}CHCOCH_3$$

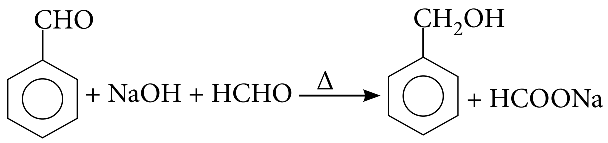
(iii) (a)

(iv) (d)

OR

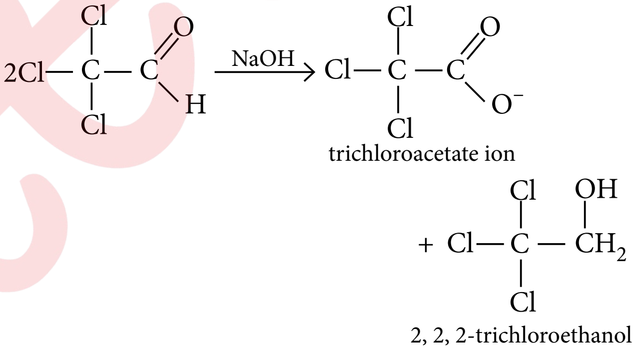
(d) : Benzaldehyde(C_6H_5CHO) with no α-hydrogen cannot undergo aldol condensation.

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).



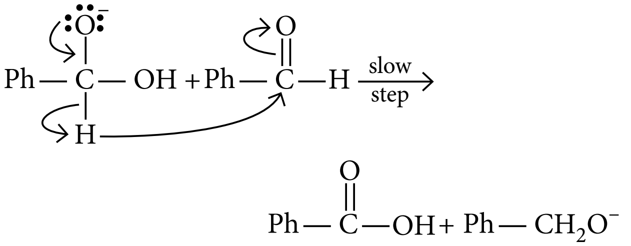
(ii) (c)

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



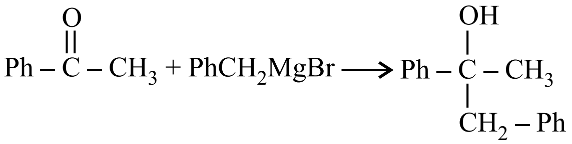
OR

(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) :



$$Ph-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + PhCH_2MgBr \longrightarrow Ph-\underset{\underset{\displaystyle CH_2-Ph}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3$$

(*H*)

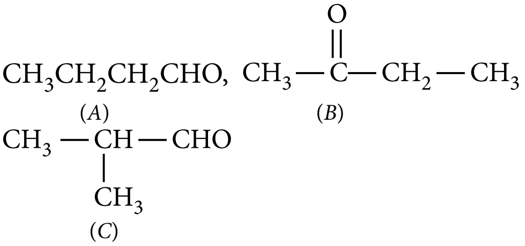
(iv) (c): Since compound $A(C_3H_6O)$ undergoes iodoform test, it must be CH_3COCH_3 (propanone). Further, the compound '*B*' obtained from '*A*' has three times more the number of carbon atoms as in '*A*' (propanone), '*B*' must be phorone, *i.e.*, 2, 6-dimethyl-2, 5-heptadien-4-one.

$$\underset{A\text{, propanone (3 molecules)}}{(CH_3)_2C{=}O + H_3CCOCH_3 + O{=}C(CH_3)_2}$$

$$\xrightarrow{HCl} \underset{\text{2,6-dimethyl-2,5-heptadien-4-one}}{(CH_3)_2C{=}CHCOCH{=}C(CH_3)_2}$$

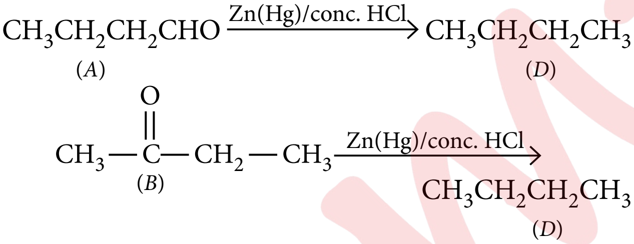
6. **(i) (b):** As (*A*) and (*C*) gives positive Tollens' test thus these two should be aldehydes while (*B*) should be a ketone (does not give Tollen's test) with $-\underset{\underset{O}{\|}}{C}-CH_3$ group (as it gives positive iodoform test).

Three isomers are,



$$\underset{(A)}{CH_3CH_2CH_2CHO},\ \underset{(B)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3}$$

$$\underset{(C)}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CHO}$$



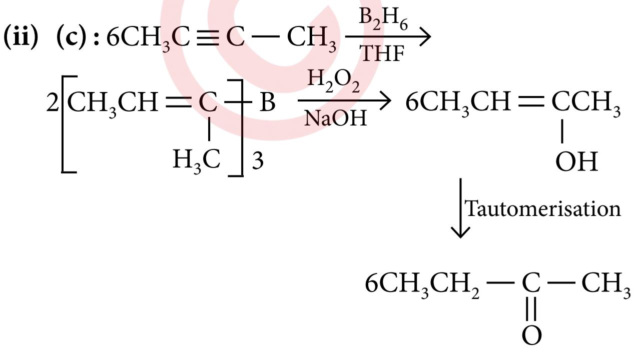
$$\underset{(A)}{CH_3CH_2CH_2CHO} \xrightarrow{Zn(Hg)/conc.\ HCl} \underset{(D)}{CH_3CH_2CH_2CH_3}$$

$$\underset{(B)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3} \xrightarrow{Zn(Hg)/conc.\ HCl} \underset{(D)}{CH_3CH_2CH_2CH_3}$$

OR

(d)

(ii) (c):

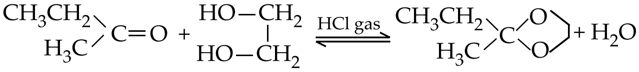


$$6CH_3C{\equiv}C-CH_3 \xrightarrow[THF]{B_2H_6} 2\left[CH_3CH{=}\underset{\underset{H_3C}{|}}{C}\right]_3B \xrightarrow[NaOH]{H_2O_2} 6CH_3CH{=}\underset{\underset{OH}{|}}{C}CH_3$$

$$\xrightarrow{\text{Tautomerisation}} 6CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

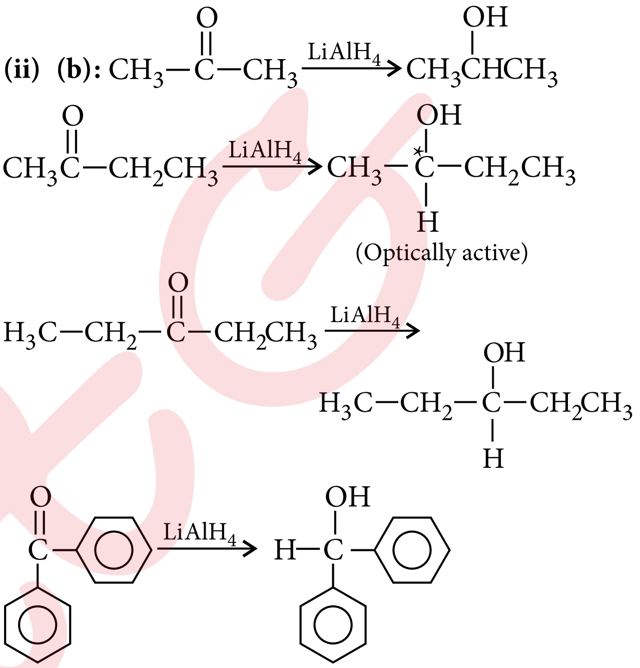
(iii) (b): (*B*) is least reactive among the three isomers towards addition of HCN. Aldehydes are more reactive than ketones towards nucleophilic addition reactions.

(iv) (a): When butanone reacts with ethylene glycol in presence of HCl, it forms a ketal.



7. **(i) (d):** 2-Methyl-2-propanol is $CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$. It cannot be obtained by reduction of an aldehyde or ketone with $NaBH_4$.

(ii) (b):



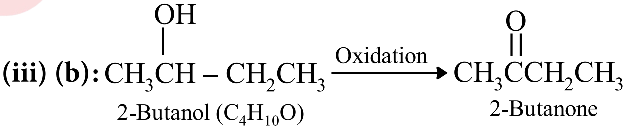
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} CH_3\overset{\overset{OH}{|}}{C}HCH_3$$

$$CH_3\overset{\overset{O}{\|}}{C}-CH_2CH_3 \xrightarrow{LiAlH_4} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{\overset{*}{C}}}-CH_2CH_3$$

(Optically active)

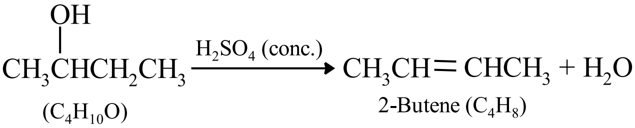
$$H_3C-CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3 \xrightarrow{LiAlH_4} H_3C-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CH_3$$

(iii) (b):



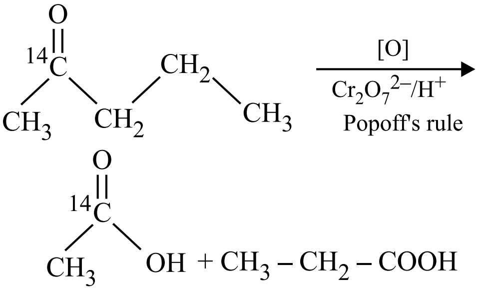
$$\underset{\text{2-Butanol }(C_4H_{10}O)}{CH_3\overset{\overset{OH}{|}}{C}H-CH_2CH_3} \xrightarrow{\text{Oxidation}} \underset{\text{2-Butanone}}{CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3}$$

2-Butanone forms oxime on reaction with hydroxylamine (NH_2OH) and also gives positive iodoform test.



$$\underset{(C_4H_{10}O)}{CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_3} \xrightarrow{H_2SO_4\ (conc.)} \underset{\text{2-Butene }(C_4H_8)}{CH_3CH{=}CHCH_3} + H_2O$$

(iv) (a):



OR

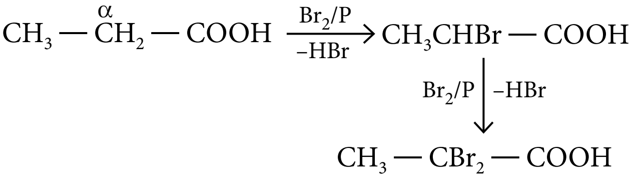
(a) : This reaction is Wolff-Kishner reduction. The reagents used for this reduction are NH_2NH_2/KOH.

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.

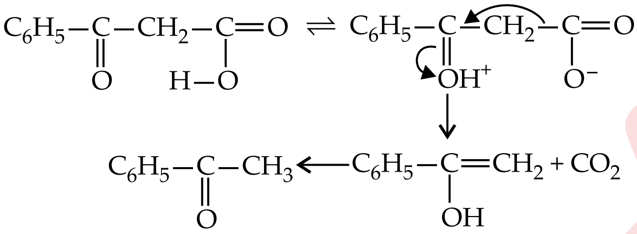
OR

(d) : Bromination occurs at α-positions.

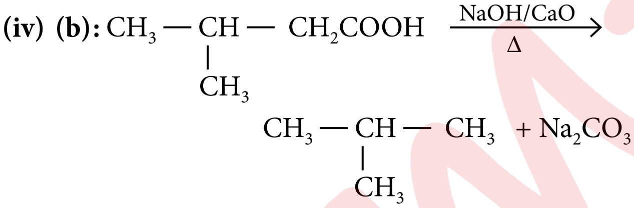


$$CH_3-\overset{\alpha}{C}H_2-COOH \xrightarrow[-HBr]{Br_2/P} CH_3CHBr-COOH \xrightarrow[-HBr]{Br_2/P} CH_3-CBr_2-COOH$$

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



(iv) (b):



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_2COOH \xrightarrow[\Delta]{NaOH/CaO} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3 + Na_2CO_3$$

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 $C_6H_5CH_2CHO$ both are aliphatic aldehydes, hence cannot be distinguished by Fehling's solution. CH_3CHO contains CH_3CO- group whereas $C_6H_5CH_2CHO$ does not contain any CH_3CO- group. Thus, CH_3CHO will give yellow ppt. with I_2 and NaOH but $C_6H_5CH_2CHO$ 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.

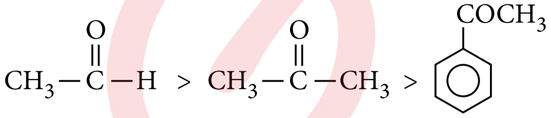
$$HCHO + 2Cu^{2+} + 5OH^- \longrightarrow HCOO^- + \underset{\text{Reddish brown ppt.}}{Cu_2O} + 3H_2O$$

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.

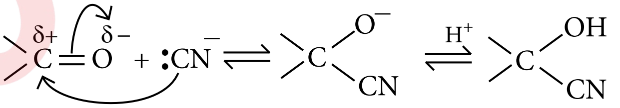
Therefore, the ease of nucleophilic addition will follow the order :



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 nuclephile and readily adds to carbonyl compound.

$$\overset{-}{O}H + HCN \rightleftharpoons :\overset{-}{C}N + H_2O$$

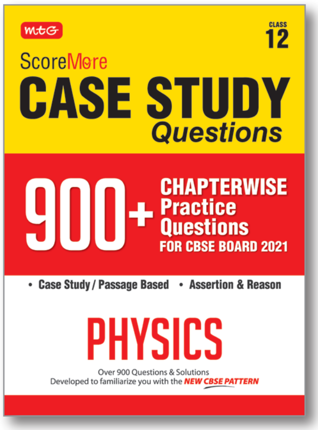


(iv) (b): Electron withdrawing group ($-NO_2$) increases the reactivity towards nucleophilic addition reactions, whereas electron donating group ($-CH_3$) decreases the reactivity towards nucleophilic addition reactions.

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, –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.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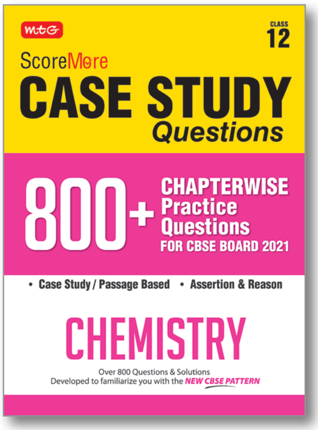
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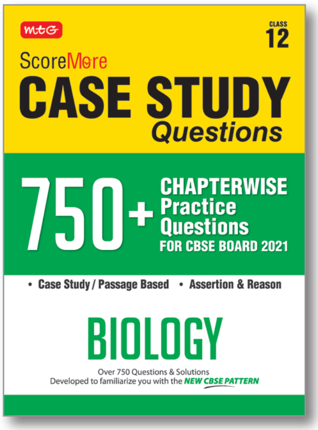
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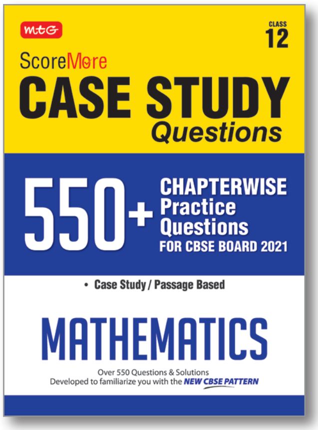
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