CHAPTER

11 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.*

Chapter Analysis

List of Topics	2016		2017		2018
	D	OD	D	OD	D/OD
Name Reactions	–	–	1Q (2 marks)	1Q (5 marks)$	–
Writing the structure of products in reactions	1Q (5 marks)*	–	1Q (3 marks) ^ 1Q (5 marks)@	1Q (5 marks)$	–
Miscellaneous type	1Q (5 marks)*	1Q (5 marks)#	–	–	1Q (3 marks)
Conversion	–	–	1Q (3 marks) ^	1Q (5 marks)$	1Q (2 marks)&
Chemical test to distinguish between	–	–	1Q (5 marks)@	1Q (5 marks)$	–
Give reason	–	–	–	–	1Q (2 marks)$

- * One question of 5 marks with two choices was asked. First choice was on writing the structures of reactions. Second choice was Miscellaneous type.
- # One question of 5 marks with two choices of Miscellaneous type was asked.
- ^One question of 3 marks with two options. First choice was on writing the structure of compounds in the series of reactions. Second choice was on conversion.
- @One question of 5 marks with one question of 3 marks on writing the structure of products in reactions and another of 2 marks on chemical test to distinguish between pair of compounds.
- $ One question of 5 marks with two choices was asked. First choice has one question of 3 marks on writing the structure of products in reactions and another of 2 marks on chemical test to distinguish between pair of compounds. Second choice has one question of 2 marks on Name Reactions and one of 3 marks on Conversion.
- & One question of 2 marks with two choices was asked. First choice was on Conversion and second choice was to give reason for different conditions.

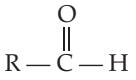
On the basis of above analysis, it can be said that from exam point of view, Name reactions, writing the structure of products in reactions, conversion and chemical test to distinguish between a pair of compounds are the most important types of questions from the chapter.

TOPIC-1
Aldehydes and Ketones

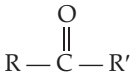
Revision Notes

TOPIC - 1
Aldehydes and Ketones .... **P. 245**
TOPIC - 2
Carboxylic Acids .... **P. 261**

- **Carbonyl group :** The functional group >C=O is called carbonyl group. Organic compounds containing carbonyl group are aldehydes, ketones. The general formulae of these compounds are

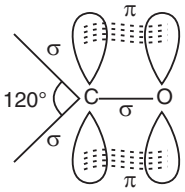


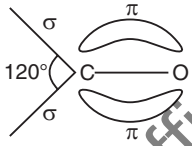
Aldehyde (where R=H or any alkyl, aryl or aralkyl group)

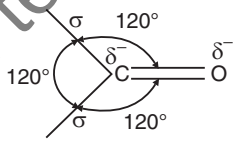


Ketone (where R and R' may be same or different alkyl, aryl or aralkyl group)

- **Structure of Carbonyl Group :**

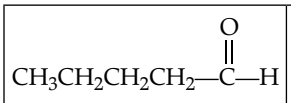
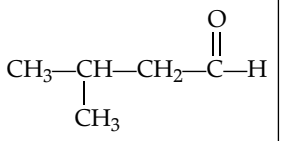
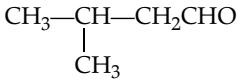
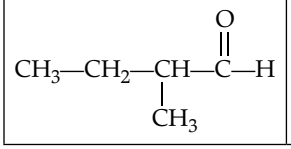
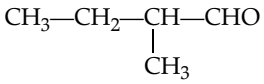




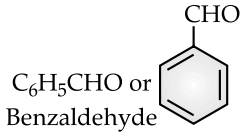
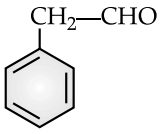
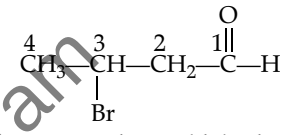
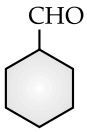
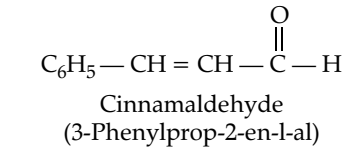
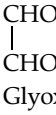
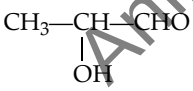
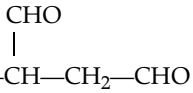
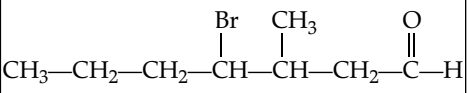
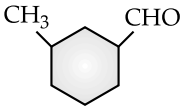
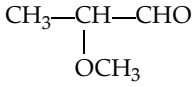
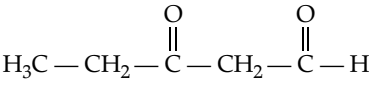
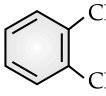
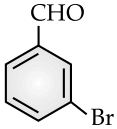
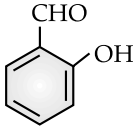


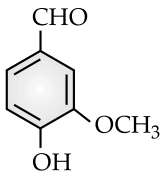
- Aldehydes are those compounds in which carbonyl group is attached to either two hydrogen atoms or one hydrogen atom and one carbon containing group such as alkyl or aryl group with hydrogen atom. *e.g.*, CH_3CHO, C_2H_5CHO, C_6H_5CHO etc.
- Ketones are those compounds in which carbonyl group is attached with two alkyl or two aryl or one alkyl and one aryl group *e.g.*, CH_3COCH_3, $CH_3COC_6H_5$, $C_6H_5COC_6H_5$ etc.
- **Nomenclature of Aldehydes and Ketones :**

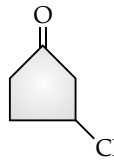
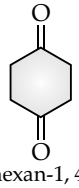
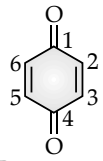
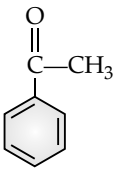
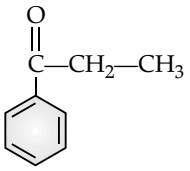
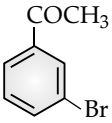
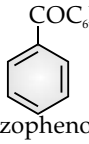
Aldehydes	**General formula :** $R—\overset{\overset{O}{\|}}{C}—H$, where $R = C_nH_{2n+1}$		
Structural formula	**Condensed formula**	**Common name**	**IUPAC name**
$H—\overset{\overset{O}{\|}}{C}—H$	HCHO	Formaldehyde	Methanal
$CH_3—\overset{\overset{O}{\|}}{C}—H$	CH_3CHO	Acetaldehyde	Ethanal
$CH_3CH_2—\overset{\overset{O}{\|}}{C}—H$	CH_3CH_2CHO	Propionaldehyde	Propanal
$CH_3CH_2CH_2—\overset{\overset{O}{\|}}{C}—H$	$CH_3CH_2CH_2CHO$	Butyraldehyde	Butanal
$CH_3—\underset{\underset{CH_3}{\|}}{CH}—\overset{\overset{O}{\|}}{C}—H$	$CH_3—\underset{\underset{CH_3}{\|}}{CH}—CHO$	Isobutyraldehyde	2-Methylpropanal

	$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
		Isovaleraldehyde	3-Methylbutanal
		α-Methylbutyraldehyde	2-Methylbutanal

Nomenclature of Some Important Aldehydes (With Common Names)

 C_6H_5CHO or Benzaldehyde	 Phenylacetaldehyde (2-Phenylethanal)	 β-Bromobutyraldehyde (3-Bromobutanal)
$CH_2 = CH - CHO$ Acrolein (Prop-2-en-1-al)	$CH_3 - CH = CH - CHO$ Crotonaldehyde (But-2-en-1-al)	 Pent-2-enal
 (Cyclohexanecarbaldehyde)	 4-Nitrobenzaldehyde (4-Nitrophenylcarbaldehyde)	 Cinnamaldehyde (3-Phenylprop-2-en-l-al)  Glyoxal (Ethane-1, 2-dial)
 2-Hydroxypropanal	 Propan- 1, 2, 3-tricarbaldehyde	 4-Bromo-3-methylheptanal
 γ-Methylcyclohexanecar-baldehyde (3-Methylcyclohexanecar-baldehyde)	 α- Methoxypropionaldehyde (2- Methoxypropanal)	 3-Oxopentanal
 Phthaldehyde (Benzene-1, 2-dicarbaldehyde)	 *m*- Bromobenzaldehyde (3- Bromobenzaldehyde)	 (Salicylaldehyde) 2-Hydroxybenzaldehyde

 Meta methoxy parahydroxy benzaldehyde (Vanilin) **or** 4-Hydroxy-3-methoxy benzaldehyde		

Ketones	**General formula :** $R—\overset{\overset{O}{\|\|}}{C}—R'$ and $R' = C_{n'}H_{2n'+1}$ ($n = n'$, $n \neq n'$)		
Structural Formula	**Condensed formula**	**Common name**	**IUPAC name**
$CH_3—\overset{\overset{O}{\|\|}}{C}—CH_3$	CH_3COCH_3	Acetone	Propanone
$CH_3—\overset{\overset{O}{\|\|}}{C}—CH_2—CH_3$	$CH_3COCH_2CH_3$	Ethyl methyl ketone	Butan-2-one or Butanone
$CH_3—\overset{\overset{O}{\|\|}}{C}—CH_2—CH_2—CH_3$	$CH_3COCH_2CH_2CH_3$	Methyl *n*-Propyl ketone	Pentan-2-one
$CH_3—CH(CH_3)—\overset{\overset{O}{\|\|}}{C}—CH(CH_3)—CH_3$	$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2, 4-Dimethyl pentan-3-one
$CH_3—CH_2—\overset{\overset{O}{\|\|}}{C}—CH_2—CH_3$	$CH_3CH_2COCH_2CH_3$	Diethyl ketone	Pentan-3-one
$CH_3—CH(CH_3)—\overset{\overset{O}{\|\|}}{C}—CH_3$	$(CH_3)_2CHCOCH_3$	Isopropyl methyl ketone	3-Methylbutan-2-one
$CH_3—C(CH_3)=CH—\overset{\overset{O}{\|\|}}{C}—CH_3$	$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one
 β-Methylcyclopentanone (3-Methylcyclopentanone)	$CH_3—\overset{\overset{O}{\|\|}}{C}—\overset{\overset{O}{\|\|}}{C}—OH$ Pyruvic acid (2-Oxopropanoic acid)  Cyclohexan-1, 4-dione	$CH_3—\overset{\overset{O}{\|\|}}{C}—\overset{\overset{O}{\|\|}}{C}—CH_3$ Diacetyl (Butane-2-3-dione)	 p-Benzoquinone (Cyclohexan-2, 5-diene-1, 4-dione)
 Acetophenone (Phenylethanone)	 1-Phenylpropan-1-one	 *m*-Bromoacetophenone 1-(3-Bromophenyl) ethanone	 Benzophenone (Diphenylmethanone)

➢ **Methods of preparation of Aldehydes and Ketones :**

(a) Preparation of Aldehydes :

(i) By oxidation of primary alcohols : Aldehydes can be prepared by the oxidation of primary alcohols.

$$\underset{\text{1° Alcohol}}{RCH_2OH} + [O] \xrightarrow[\text{or } KMnO_4]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Aldehyde}}{R-CHO} + H_2O$$

$$\underset{\text{1° Alcohol}}{R-CH_2-OH} \xrightarrow{PCC/CH_2Cl_2} \underset{\text{Aldehyde}}{R-CHO}$$

(ii) By dehydrogenation of alcohols :

$$\underset{\text{1° Alcohol}}{R-CH_2-OH} \xrightarrow[573K]{Cu} \underset{\text{Aldehyde}}{RCHO} + H_2$$

(iii) From hydrocarbons : From hydrocarbons aldehydes can be prepared either by ozonolysis or by hydration of alkenes.

(a) By ozonolysis of alkenes :

$$\underset{\text{Alkene}}{R-CH=CH-R'} + O_3 \longrightarrow R-CH\begin{matrix}O\\ \diagup\diagdown\\ O\quad O\end{matrix}CH-R' \xrightarrow[-ZnO]{H_2O,\,Zn} \underset{\text{Aldehyde}}{R-CHO} + R'-CHO$$

(b) By hydration of alkynes :

$$\underset{\substack{\text{Ethyne}\\ \text{(Acetylene)}}}{CH\equiv CH} + H_2O \xrightarrow[333K]{H_2SO_4/HgSO_4} \underset{\text{Unstable}}{\left[CH_2=CH(OH)\right]} \rightarrow \underset{\substack{\text{Ethanal}\\ \text{(Acetaldehyde)}}}{CH_3-CHO}$$

(iv) From acyl chloride :

$$\underset{\text{Acyl chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + H_2 \xrightarrow[\substack{\text{Rosenmund}\\ \text{Reduction}}]{Pd\text{-}BaSO_4,S} \underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + HCl$$

$$\underset{\text{Acetyl chloride}}{CH_3-\overset{O}{\overset{\|}{C}}-Cl} + H_2 \xrightarrow{Pd\text{-}BaSO_4,S} \underset{\text{Acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + HCl$$

(v) From nitriles and esters :

$$SnCl_2 + 2HCl \rightarrow SnCl_4 + 2(H)$$

$$R-C\equiv N + HCl + 2(H) \rightarrow R-CH=NH.HCl \xrightarrow[-NH_4Cl]{+H_2O} \underset{\text{Aldehyde}}{RCHO}$$

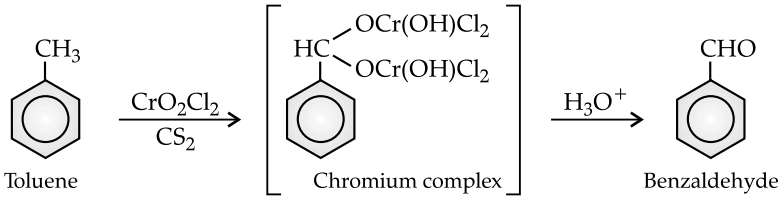
$$\underset{\text{Aldehyde}}{R-CHO} \xleftarrow[2.\,H_2O]{1.\,AlH(i\text{-}Bu)_2} R-CN$$

$$CH_3-CH=CH-CH_2-CH_2-CN \xrightarrow[2.\,H_2O]{AlH(i\text{-}Bu)_2} CH_3-CH=CH-CH_2-CH_2-CHO$$

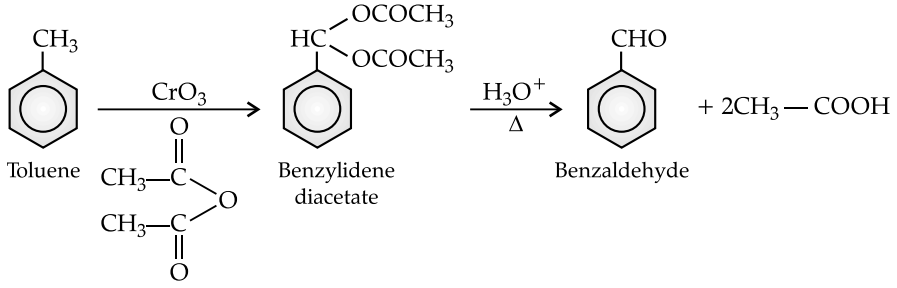
$$CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[2.\,H_2O]{1.\,DIBAL\text{–}H\ at\ -78°C} \underset{\text{Aldehyde}}{CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-H}$$

(b) Preparation of Benzaldehyde :

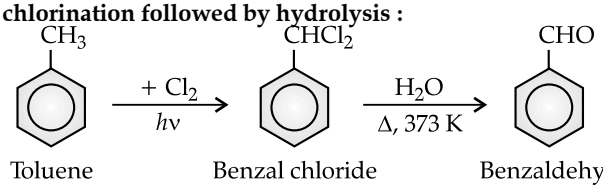
(i) By oxidation of toluene :



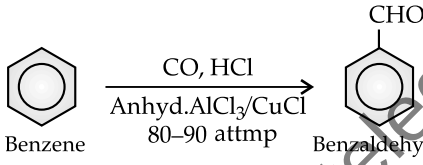
This reaction is called *Etard reaction.*



(ii) By side chain chlorination followed by hydrolysis :

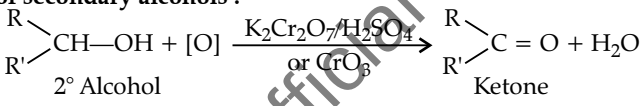


(iii) By Gattermann - Koch reaction :

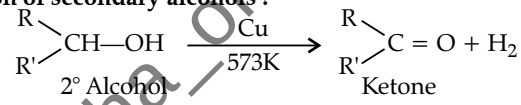


(c) Preparation of Ketones :

(i) By oxidation of secondary alcohols :

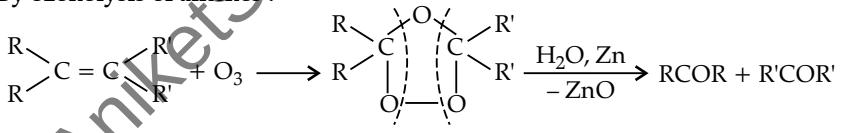


(ii) By dehydrogenation of secondary alcohols :

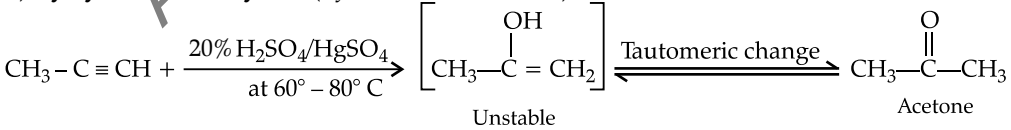


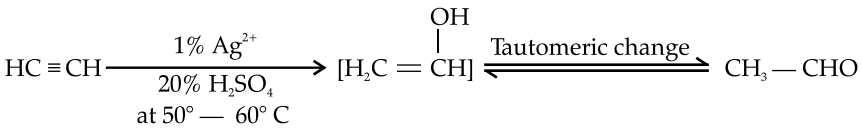
(iii) From Hydrocarbons :

(1) By ozonolysis of alkenes :

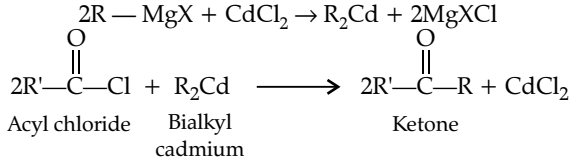


(iv) By hydration of alkynes : (By Kucherov's reaction)

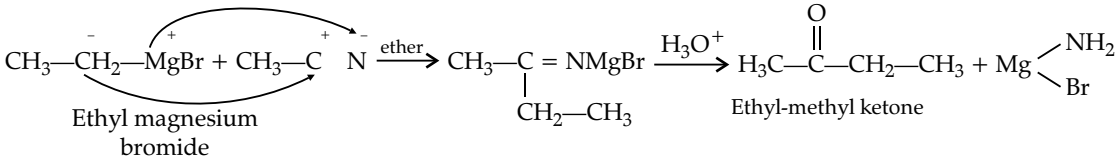




(v) From acyl chlorides :

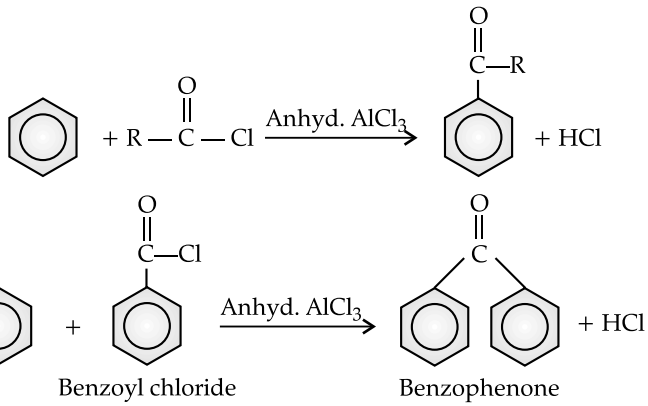


(vi) From nitriles :

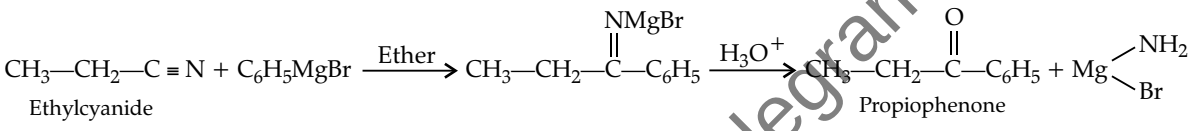


(d) Preparation of Aromatic ketones :

(i) By Friedel-Crafts acylation :



(ii) From nitriles :



➢ **Physical properties of Aldehydes and Ketones :**

(i) Most of the aldehydes (except formaldehyde which is a gas) are liquids at room temperature. The lower ketones are colourless liquids and have a pleasant smell.

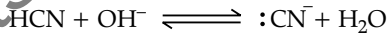
(ii) Both of these have relatively high b.p. as compared to hydrocarbons of comparable molecular masses due to presence of polar carbonyl group. But they have lower b.p. than alcohols of comparable molecular masses.

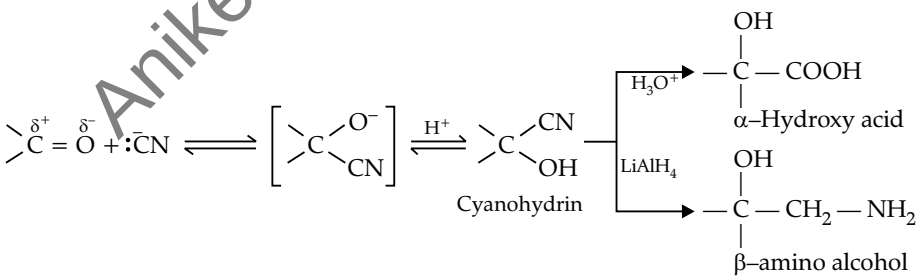
(iii) The lower members of aldehydes and ketones (up to four carbon atoms) are soluble in water due to hydrogen bonding capacity.

➢ **Chemical properties of Aldehydes and Ketones :** Aldehydes and ketones are highly reactive compounds. Both undergo nucleophilic addition reaction.

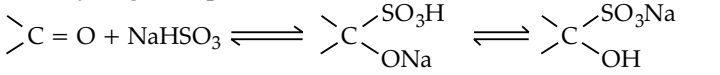
Some important nucleophilic addition reactions :

(i) Addition of hydrogen cyanide (HCN) :

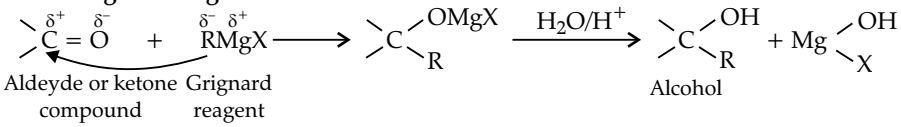




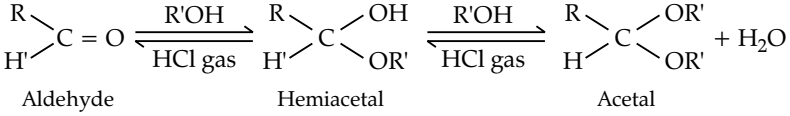
(ii) Addition to sodium hydrogen sulphite :



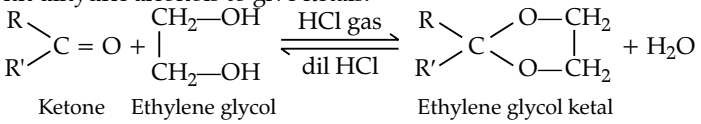
(iii) Addition of Grignard reagent :



(iv) Addition of alcohols :

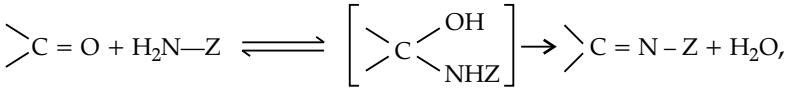


Ketones react with dihydric alcohols to give ketals.



Ketone Ethylene glycol Ethylene glycol ketal

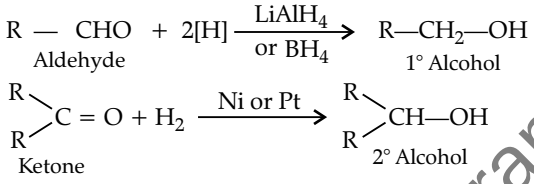
(v) Addition of ammonia and its derivatives :



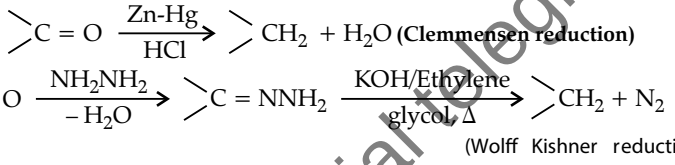
where Z = Alkyl, aryl, OH, NH_2 C_6H_5NH, NH_2CONH_2 etc.

➢ **Reduction :**

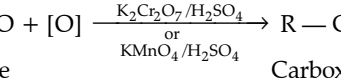
(i) Reduction to alcohols :



(ii) Reduction to hydrocarbons :

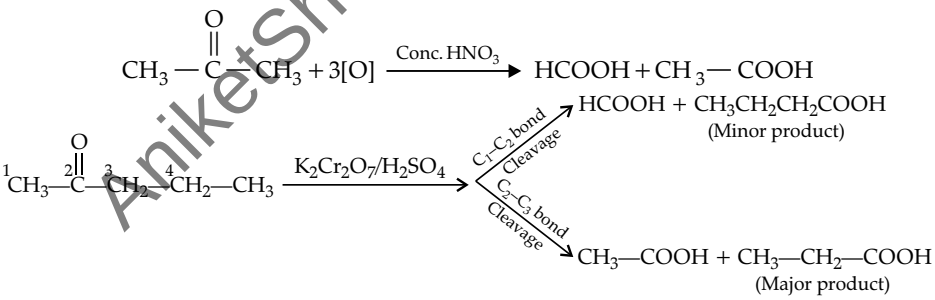


➢ **Oxidation :** Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents or mild oxidising agent like Tollen's reagent or Fehling's solution.



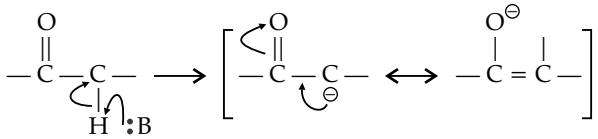
Aldehyde Carboxylic acid

Ketones undergo oxidation under vigorous conditions with cleavage of carbon bond.

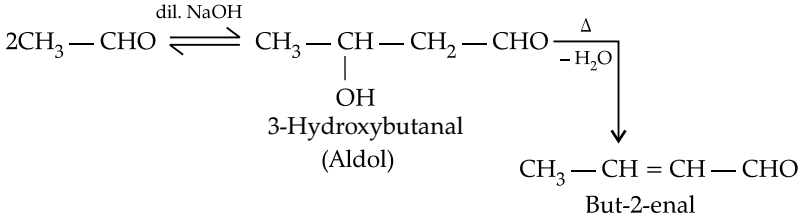


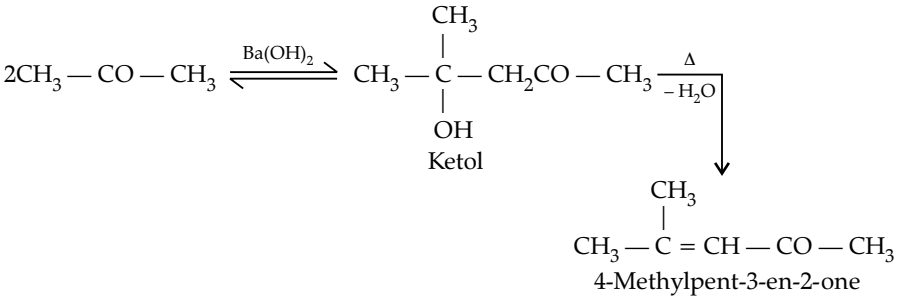
➢ **Reaction due to α-hydrogen:**

α-hydrogen in aldehydes and ketones is acidic in nature due to strong electron withdrawing effect of carbonyl group. As a result aldehydes and ketones undergo a number of reactions.

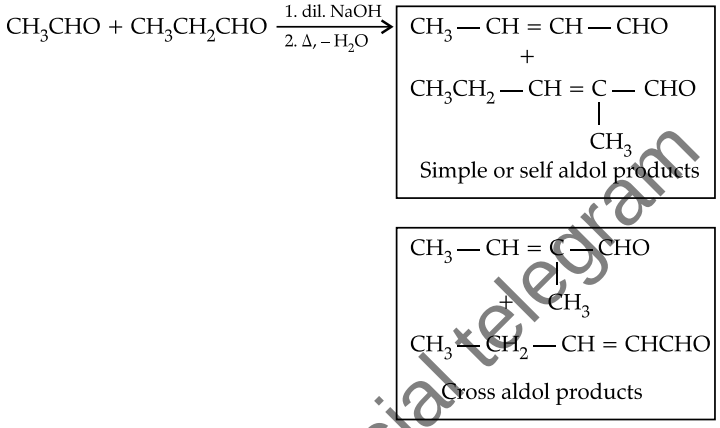


(i) Aldol condensation : Aldehydes and ketones having at least one α-hydrogen react in presence of dilute alkali to form β-hydroxy aldehyde (aldol) or β-hydroxy ketones (ketol).

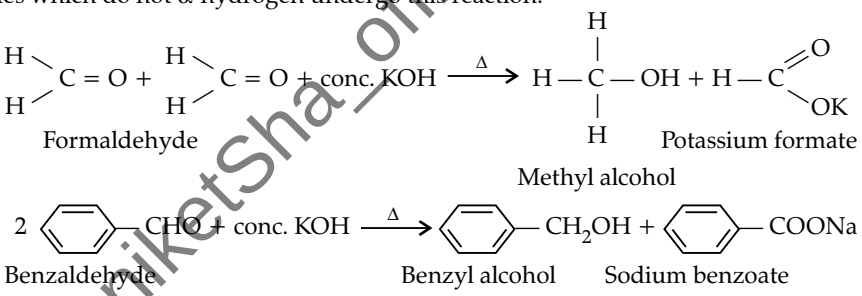




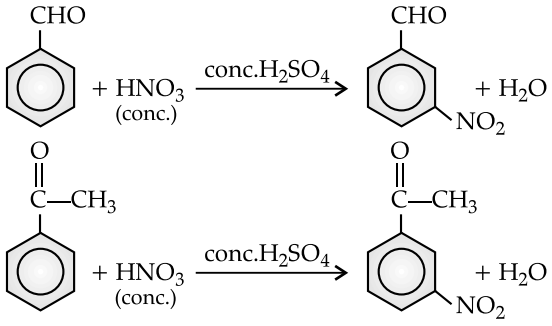
(ii) Cross aldol condensation : When two different aldehydes and/or ketones undergo aldol condensation, it is called cross aldol condensation.



(iii) Cannizzaro Reaction : Aldehydes undergo self oxidation and reduction on heating with conc. alkali. The aldehydes which do not α-hydrogen undergo this reaction.



(iv) Electrophilic substitution reaction :



➢ **Test for aldehydes and ketones :**

(i) Both form coloured compounds with 2, 4-dinitrophenylhydrazine.

(ii) Both gives iodoform test when one α-hydrogen is present.

(iii) Aldehydes restore pink colour of Schiff's base. Ketones does not give any colour.

(iv) Fehling's test : Aliphatic aldehydes reduce the Fehling solution to red cuprous oxide.

$$R — CHO + 2CuO + 5OH^- \rightarrow R — COOH + Cu_2O\downarrow + 3H_2O$$

(red ppt.)

Ketones does not give any precipitate.

(v) Ketones are not oxidised by Tollen's reagent.

Aldehydes form silver mirror with ammonical silver nitrate (Tollen's reagent) solution.

$$R-CHO + 2[Ag(NH_3)_2]^+ \xrightarrow{OH^-} R-COOH + 2Ag + H_2O + 4NH_3$$

(Silver mirror)

Know the Terms

- **Hydroformylation :** In this process, alkenes give aldehydes by the reaction of hydrogen and CO.
- **Collin's Reagent :** This reagent can be prepared by mixing pyridine (C_5H_5N), CrO_3 and HCl in the presence of dichloromethane. This reagent is used to prepare aldehydes by controlled oxidation process.
- **Baeyer-Villiger Oxidation :** In this process, when ketones are treated with peroxy acids (peracetic acid) *e.g.*, in the presence of an acid catalyst give carboxylic esters by insertion of esters.
- **MPV-Reduction :** It is Meerwein Ponndorf Verely reduction. In this process, ketones are reduced to secondary alcohols with isopropyl alcohol in the presence of aluminium isopropoxide.

Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple choice Questions:

Q. 1. The reagent which does not react with both, acetone and benzaldehyde.

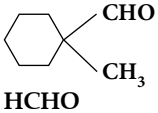
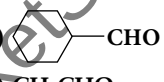
(a) Sodium hydrogen sulphite
(b) Phenyl hydrazine
(c) Fehlings' solution
(d) Grignard reagent

R **[NCERT Exemp. Q. 5, page 169]**

Ans. Correct option : (c)

Explanation : Fehlings' solution oxidizes aliphatic aldehydes very easily but does not react with acetone and benzaldehyde.

Q. 2. Cannizzaro reaction is not given by _____

(a)  **(b)** 

(c) HCHO **(d) CH_3CHO**

A **[NCERT Exemp. Q. 6, page 169]**

Ans. Correct option : (a)

Explanation : CH_3CHO will not give Cannizzaro reaction because it contains α-hydrogen while other three compounds have no α-hydrogen. Hence, they will give Cannizzaro reaction.

Q. 3. Compounds A and C in the following reaction are :

$$CH_3CHO \xrightarrow[(ii)H_2O]{(i)CH_3MgBr_4} (A) \xrightarrow{H_2SO_4.A} (B) \xrightarrow[\text{oxidation}]{\text{Hydroboration}} (C)$$

(a) identical **(b) positional isomers**
(c) functional isomers **(d) optical isomers**

A **[NCERT Exemp. Q. 9, page 170]**

Ans. Correct option : (b)

Explanation :

$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} \underset{\substack{\text{Propa—2—ol}\\(A)}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH} \xrightarrow[\text{Dehydration}]{H_2SO_4\ .A} \underset{\substack{\text{Propena}\\(B)}}{CH_3-\underset{\displaystyle H}{\underset{|}{C}}-OH_2}$$

$$\xrightarrow[(ii)\ H_2O_2\ /\ OH^\circ]{(i)\ BH_3} \underset{\substack{\text{Propa—1—ol}\\(C)}}{CH_3-CH_2-CH_2OH} \quad \text{(Hydroboration Oxidation)}$$

Q. 4. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution?

(a) Butan-1-ol **(b) Butan-2-ol**
(c) Both of these **(d) None of these**

A **[NCERT Exemp. Q. 11, page 170]**

Ans. Correct option : (b)

Explanation :

$$\underset{\substack{|\\OH\\\text{Butan-2-ol}}}{CH_3CH_2CHCH_3} \xrightarrow[KMnO_4]{alk} \underset{\text{Butanone}}{CH_3CH_2COCH_3}$$

Q. 5. In Clemmensen reduction carbonyl compound is treated with

(a) zinc amalgam + HCl
(b) sodium amalgam + HCl
(c) zinc amalgam + nitric acid
(d) sodium amalgam + HNO_3

R **[NCERT Exemp. Q. 12, page 170]**

Ans. Correct option : (a)

Explanation : Clemmensen reduction is used to convert carbonyl group to CH_2 group as follows :

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

Zinc amalgam and HCl act as reagent in this reaction.

B. Match the following :

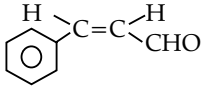
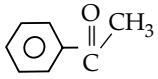
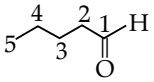
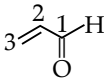
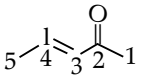
Q. 1. Match the species given in Column I with those mentioned in Column II.

S. No.	Column I	S. No	Column II
(i)	Cinnamaldehyde	(a)	Pentanal
(ii)	Acetophenone	(b)	Prop-2-enal
(iii)	Valeraldehyde	(c)	4-Methylpent-3-en-2-one
(iv)	Acrolein	(d)	3-Phenylprop-2-enal
(v)	Mesityl oxide	(e)	1-Phenylethanone

[NCERT Exemp. Q. 38, Page 174]

Ans. (i) ↔ (d)
(ii) ↔ (e)
(iii) ↔ (a)
(iv) ↔ (b)
(v) ↔ (c)

Explanation :

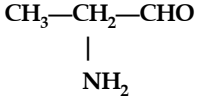
(Common names	Structure	(IUPAC names)
(i) Cinnamaldehyde		3-Phenylprop-2-enal
(ii) Acetophenone		1-Phenylethanone
(iii) Valeraldehyde		Pentanal
(iv) Acrolein		prop-2-enal
(v) Mesityl oxide		4-Methylpent-3-en-2-one

C. Answer the following :

Q. 1. Write the IUPAC name of the following :
$CH_3 – CH_2 – CHO$ **A [CBSE Comptt. OD 2015]**

Ans. Propanal. **1**
[CBSE Marking Scheme 2015]

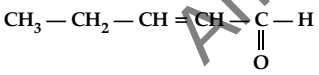
Q. 2. Write the IUPAC name of



A [CBSE OD 2014]

Ans. 2-Aminopropanal. **1**
[CBSE Marking Scheme 2014]

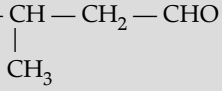
AI Q. 3. Write the IUPAC name of :



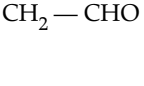
A [CBSE OD 2012]

Ans. Pent-2-en-1-al. **1**
[CBSE Marking Scheme 2012]

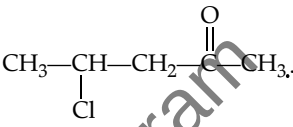
Q. 4. Draw the structure of 3-methylpentanal.
A [CBSE Comptt. Delhi 2015]

Ans.  **1**
[CBSE Marking Scheme 2015]

Q. 5. Write the structure of 3-methylbutanal.
A [CBSE Delhi 2013]

Ans.  **1**

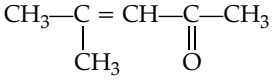
Q. 6. Write the structure of 4-chloropentan-2-one.
A [CBSE Delhi 2013]

Ans.  **1**

Q. 7. Write the structure of p-methyl benzaldehyde molecule. **A [CBSE Delhi 2013]**

Ans.  **1**
[CBSE Marking Scheme 2013]

Q. 8. Draw the structure of the compound named 4-methyl pent-3-en-2-one
A [CBSE Comptt. Delhi 2013]

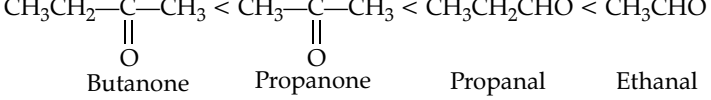
Ans.  **1**

AI Q. 9. What type of aldehydes undergo cannizaro reaction?
U [CBSE Comptt. Delhi Set-1, 2, 3 2017; DDE]

Ans. Having no α-hydrogen **1**
[CBSE Marking Scheme 2017]

AI Q. 10. Arrange the following compounds in an increasing order of their reactivity in nucleophilic addition reactions : ethanal, propanal, propanone, butanone. **U [CBSE Delhi 2012]**

Ans. Increasing order of reactivity :



Butanone Propanone Propanal Ethanal **1**

Q. 11. An aromatic organic compound 'A' with molecular formula C_8H_8O gives positive DNP and iodoform tests. It neither reduces Tollens' reagent nor does it decolourise bromine water. Write the structure of 'A'. **A [CBSE Comptt. Delhi/OD 2018]**

Ans. $C_6H_5COCH_3$ **1**
[CBSE Marking Scheme 2018]

Detailed Answer:

'A' gives positive DNP test. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' reagent, 'A' must be a ketone. 'A' responds to iodoform test. Therefore, it should be a methyl ketone. The molecular formula of 'A' indicates high degree of unsaturation, yet it does not decolourisee bromine water. This indicates the presence of unsaturation due to an aromatic ring. The molecular formula of 'A' indicates that it should be phenyl methyl ketone (acetophenone). **1**

Q. 12. $(CH_3)_3C$-CHO does not undergo aldol condensation. Comment A&E **[CBSE SQP 2017]**

Ans. No α-H is present **1**

[CBSE Marking Scheme 2017]

Q. 13. Out of $CH_3CH_2COCH_2CH_3$ and $CH_3CH_2CH_2COCH_3$ which gives iodoform test. A&E **[CBSE OD 2014]**

Ans. $CH_3CH_2CH_2COCH_3$ will give iodoform test as it has a terminal Ketomethyl group. **1**

AI **Q. 14. Give the chemical test to distinguish between the following pairs of compounds.**

(i) Propanal and propanone.

(ii) Benzaldehyde and Benzoic acid.

A **[CBSE Delhi 2012]**

Ans. (i) Propanal gives silver mirror on reaction with Tollen's reagent while propanone does not give. ½

(ii) Benzoic acid evolves CO_2 gas with $NaHCO_3$ while benzaldehyde does not evolve CO_2. ½

Commonly Made Error

- In several cases, only the name of the test is given, the reagents used and the observations are not written.

Short Answer Type Questions (2 marks each)

Q. 1. Name the reagents used in the following reactions :

(i) $CH_3 - CO - CH_3 \xrightarrow{?} CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$

(ii) $C_6H_5 - CH_2 - CH_3 \xrightarrow{?} C_6H_5 - COO^-K^+$

R **[CBSE Delhi 2015]**

Ans. (i) $LiAlH_4$/ $NaBH_4$ /H_2, Pt **1**

(ii) $KMnO_4$, KOH **1**

[CBSE Marking Scheme 2015]

Commonly Made Error

- Many students were not able to identify all the reagents correctly. Some students forget to mention the conditions.

Answering Tip

- Study organic reactions by writing the equations. Catalysts and conditions should be properly indicated.

Q. 2. Write the reagents required in the following reactions :

(i) $CH_2 = CH - CH_2OH \xrightarrow{?} CH_2 = CH - CHO$

(ii) $CH_3 - COOH \xrightarrow{?} CH_3 - CONH_2$ R

OR

Arrange the following compounds in increasing order of their property as indicated :

(i) CH_3COCH_3, $C_6H_5COCH_3$, CH_3CHO **(reactivity towards nucleophilic addition reaction)**

(ii) $Cl - CH_2 - COOH$, $F - CH_2 - COOH$, $CH_3 - COOH$ **(acidic character)**

U **[CBSE OD Set-1, 2, 3, 2015]**

Ans. (i) PCC / Cu at 573 K **1**

(ii) NH_3, Δ(heat) **1**

OR

(i) $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$. **1**

(ii) $CH_3COOH < Cl - CH_2 - COOH < F - CH_2 - COOH$ **1**

Commonly Made Error

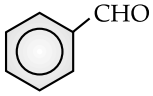
- Many students were not able to identify all the reagents correctly. Some students forget to mention the conditions.

Answering Tip

- Practise reactions by repeated writing. Learn complete reactions with reagents.

Q. 3. Complete the following reactions :

(i) $2H-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow{\text{Conc. KOH}}$

(ii)  $\xrightarrow[273 - 283\ K]{HNO_3 / H_2SO_4}$

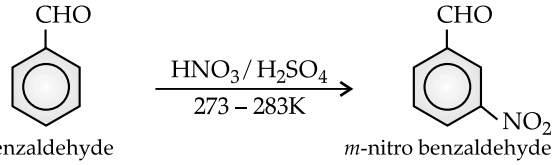
A **[CBSE Delhi 2013]**

Ans. (i)

$2H-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow{\text{Conc. KOH}} H-\underset{\displaystyle H}{\underset{|}{C}}-OH + HCOOK$

Methanal — Methanol — (Cannizzaro reaction) **1**

(ii)



Benzaldehyde — *m*-nitro benzaldehyde **1**

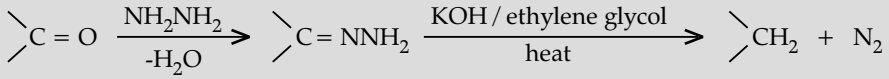
AI **Q. 4. Write the equations involved in the following reactions:**

(i) Wolff-Kishner reduction

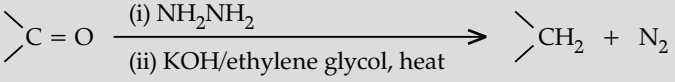
(ii) Etard reaction

R **[CBSE Delhi Set-1 2017]**

Ans. (i) Wolff-Kishner reduction :

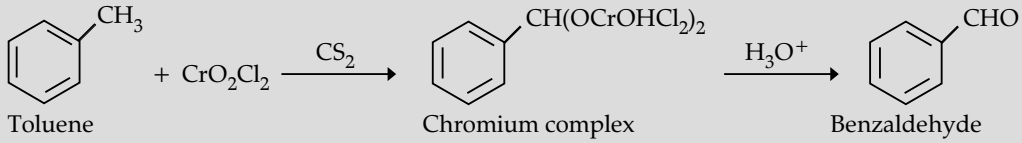


OR



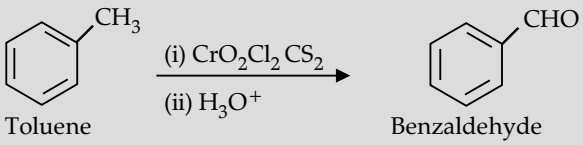
1

(ii) Etard reaction :



1

OR



[CBSE Marking Scheme 2017]

Answering Tip

- Mention the reagents and conditions involved in the reaction.

AI Q. 5. Give simple chemical test to distinguish between the following pairs of compounds.

(i) Ethanal and propanal

(ii) Benzoic acid and phenol. **A [CBSE Delhi 2013]**

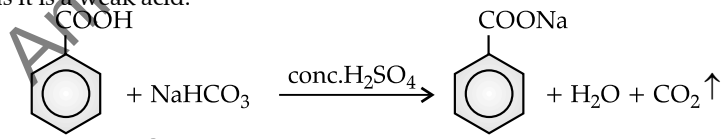
Ans. (i) Iodoform test : Ethanal gives this test due to the presence of CH_3CO group

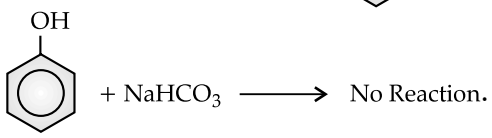
$CH_3CHO + 4NaOH + 3I_2 \rightarrow \underset{\text{Iodoform}}{CHI_3} + HCOONa + 3NaI + 3H_2O$ (yellow ppt)

Ethanal

$CH_3CH_2CHO + 4NaOH + 3I_2 \rightarrow$ No reaction. **1**

(ii) Sodium bicarbonate test : Benzoic acid gives brisk effervescence of CO_2 when react with $NaHCO_3$, while phenol does not give it, as it is a weak acid.





1

Answering Tip

- Mention the test and the observations in each case.

Q. 6. Write the structures and IUPAC names of the cross aldol condensation products only of ethanal and propanal. **A [CBSE SQP 2018-2019]**

Ans. (i) 2-Methylbut-2-enal ½

½

(ii) Pent-2-enal ½

$CH_3 - CH_2 - CH = CH - CHO$ ½

[CBSE Marking Scheme 2018]

Long Answer Type Questions-I (3 marks each)

Q. 1. Predict the products of the following reactions :

(i) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\overset{\|}{C}}}-H \xrightarrow[\text{(ii) KOH/Glycol, } \Delta]{\text{(i) } H_2N-NH_2} ?$

(ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} ? + ?$

(iii) $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} ?$

A [CBSE Delhi 2015]

Ans. (i) $CH_3CH_2CH_3$ **1**

(ii) $C_6H_5COONa + CHI_3$ **½+ ½**

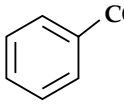
(iii) CH_4 **1**

[CBSE Marking Scheme 2015]

Q. 2. Predict the products of the following reactions :

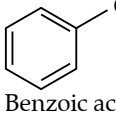
(i) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\overset{\|}{C}}}-H \xrightarrow{H_2N-NH_2} ?$

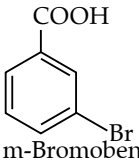
(ii) $C_6H_5-CH_3 \xrightarrow[\text{(b) } H^+]{\text{(a) } KMnO_4/KOH} ?$

(iii)  $\xrightarrow{Br_2/FeBr_3} ?$

A [CBSE OD 2015]

Ans. (i) $(CH_3)_2C=N-NH_2$ **1**

(ii) 
Benzoic acid **1**

(iii) 
m-Bromobenzoic acid **1**

Q. 3. Write the structure of the main products of following reactions :

(i)  $+ C_6H_5COCl \xrightarrow[CS_2]{\text{Anhy. } AlCl_3}$

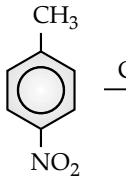
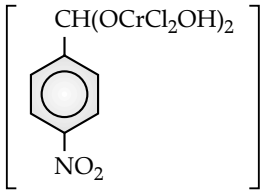
(ii) $H_3C-C\equiv C-H \xrightarrow{Hg^{2+}, H_2SO_4}$

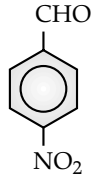
(iii)  $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CrO_2Cl_2}$

A [CBSE Delhi 2012]

Ans. (i)  + HCl **1**
Benzophenone

(ii) $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$ **1**
Acetone

(iii)  $\xrightarrow{CrO_2Cl_2}$ 

$\xrightarrow{H_3O^+}$  **1**
p-nitrobenzaldehyde

AI Q. 4. How will you bring about the following conversions :

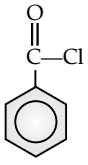
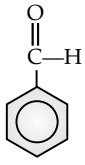
(i) Propanone to propane

(ii) Benzoyl chloride to benzaldehyde.

(iii) Ethanal to but-2-enal.

A [CBSE Delhi 2013]

Ans. (i) $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \xrightarrow[Zn(Hg) + HCl\ (Conc.)]{Clemmensen\ Reduction} CH_3-CH_2-CH_3$ **1**
Propanone → Propane

(ii)  $\xrightarrow[+ H_2]{BaSO_4/Pd}$  **1**
Benzoyl chloride → Benzaldehyde

(iii) $2CH_3-CHO \xrightarrow[Aldol\ Condensation]{Dil.NaOH} CH_3-\underset{\displaystyle OH}{CH}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$ **1**
Ethanal → 3-hydroxybutanal → But-2-enal

Q. 5. (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 Tollens' test whereas isomer (B) does not give Tollens' test but gives positive Iodoform test. Isomers (A) and (B) on reduction with Zn(Hg)/ conc. HCl give the same product (D).

(a) Write the structures of (A), (B), (C) and (D).

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

A **[CBSE Delhi/OD 2018]**

Ans. (a) A = $CH_3CH_2CH_2CHO$ ½
B = $CH_3COCH_2CH_3$ ½
C = $(CH_3)_2CHCHO$ ½
D = $CH_3CH_2CH_2CH_3$ ½

(b) B **1**

[CBSE Marking Scheme 2018]

Detailed Answer:

(b) (B) as ketones are less reactive towards addition of HCN than aldehydes and alkane due to higher hinderance caused by steric effect and inductive effect. **1**

Long Answer Type Questions-II (5 marks each)

AI **Q. 1. (i) How will you convert the following :**

(a) Propanone to propan-2-ol

(b) Ethanal to 2-hydroxy propanoic acid

(c) Toluene to benzoic acid

(ii) Distinguish the following pairs of compounds :

(a) Pentan-2-one and pentan-2-one

(b) Ethanal and propanal

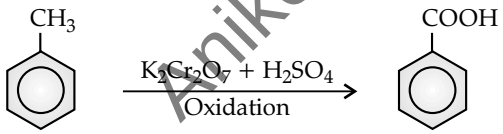
A **[CBSE OD 2013]**

Ans. (i)

(a) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (Propanone) $\xrightarrow[\text{Reduction}]{LiAlH_4}$ $CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$ (Propan-2-ol) **1**

(b) $H_3C-\overset{\overset{H}{|}}{C}=O + HCN \longrightarrow H_3C-\overset{\overset{H}{|}}{\underset{\underset{CN}{|}}{C}}-OH \xrightarrow[HCl]{H_2O} CH_3-\overset{\overset{H}{|}}{\underset{\underset{COOH}{|}}{C}}-OH$ **1**

Ethanal — 2-Hydroxy propanoic acid

(c)  **1**

Toluene — Benzoic acid

(ii) (a) Pentane -2-one gives yellow ppt of iodoform in Iodoform test, while pentane-3-one does not give it.

$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3 + 3NaOI \longrightarrow CH_3CH_2CH_2COONa + \underset{\text{(Yellow ppt)}}{CHI_3\downarrow} + 2NaOH$ **1**

(b) Ethanal will give iodoform test, while propanal will not give it.

$CH_3CHO + 3NaOI \longrightarrow \underset{\text{(yellow ppt)}}{CHI_3\downarrow} + HCOONa + 2NaOH$ **1**

Commonly Made Error

- **(ii)** Correct observations are not written in some cases although the tests given are correct.

AI **Q. 2. (i) Write the structures of A, B, C, D and E in the following reactions:**

$C_6H_6 \xrightarrow[\text{Anhyd.}AlCl_3]{CH_3COCl} A \xrightarrow{Zn-Hg/Conc.HCl} B \xrightarrow[(ii)\ H_3O^+]{(i)\ KMnO_4-KOH,D} C$

$A \xrightarrow{NaOH} D + E$

OR

(i) Write the chemical equation for the reaction involved in Cannizzaro reaction.

(ii) Draw the structure of the semicarbazone of ethanal.

(iii) Why pK_a of $F-CH_2-COOH$ is lower than that of $Cl-CH_2-COOH$?

(iv) Write the product in the following reaction

$$CH_3-CH=CH-CH_2CN \xrightarrow[(ii)\ H_2O]{(i)\ DIBAL\text{-}H} ?$$

(v) How can you distinguish between propanal and propanone ? A **[CBSE Delhi 2016]**

Ans. (i) $C_6H_6 \xrightarrow[\text{Anhyd. } AlCl_3]{CH_3COCl}$ Acetophenone (A) $\xrightarrow{\text{Zn-Hg/Conc. HCl}}$ Ethylbenzene (B) $\xrightarrow[H^+]{KMnO_4-KOH}$ Benzoic acid (C) **1 × 5**

Acetophenone (A) $\xrightarrow{NaOH}$ Sodium benzoate (D) + $CHI_3\downarrow$ Iodoform (yellow ppt.) (E)

OR

(i) $2HCHO \xrightarrow{\text{Conc. NaOH}} CH_3OH + HCOONa$ (or any other example) **1**

(ii) $CH_3-CH=N-NH-CO-NH_2$ **1**

(iii) In FCH_2-COOH, fluorine is more electron withdrawing and has stronger -I effect than chlorine in $ClCH_2-COOH$. So, FCH_2COOH is more acidic than $ClCH_2COOH$ hence its pK_a value is lesser than $ClCH_2COOH$. **1**

(iv) $CH_3-CH=CH-CH_2-CN \xrightarrow[(ii)\ H_2O]{(i)\ DIBAL-H} CH_3-CH=CH-CH_2-CHO$ **1**

Pent-3-enenitrile Pent-3-ene-1-al

(v) Propanal and propanone can be differentiated by Tollen's reagent *i.e.* propanal will give silver mirror but propanone will not.

$CH_3-CH_2-CHO + 2[Ag(NH_3)_2]^+ \rightarrow CH_3-CH_2-COO^- + 2Ag\downarrow + H_2O + 4NH_3$ (or any other correct test) **1**

(Silver mirror)

[CBSE Marking Scheme 2016]

AI **Q. 3. (i) Write the structures of A and B in the following reactions :**

(a) $CH_3COCl \xrightarrow{H_2,Pd-BaSO_4} A \xrightarrow{H_2N-OH} B.$

(b) $CH_3MgBr \xrightarrow[2.\ H_3O^+]{1.\ CO_2} A \xrightarrow{PCl_5} B.$

(ii) Distinguish between :

(a) $C_6H_5-COCH_3$ **and** C_6H_5-CHO, **(b)** CH_3COOH **and** $HCOOH$.

(iii) Arrange the following in the increasing order of their boiling points :

CH_3CHO, CH_3COOH, CH_3CH_2OH.

OR

(i) Write the chemical reaction involved in Wolff-Kishner reduction.

(ii) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction :

$C_6H_5COCH_3$, CH_3-CHO, CH_3COCH_3

(iii) Why carboxylic acid does not give reactions of carbonyl group ?

(iv) Write the product in the following reaction

$$CH_3CH_2CH=CH-CH_2CN \xrightarrow[2.\ H_2O]{1.\ (i-Bu)_2AlH} ?$$

(v) A and B are two functional isomers of compound C_3H_6O. On heating with NaOH and I_2, isomer B forms yellow precipitate of iodoform whereas isomer A does not form any precipitate. Write the formulae of A and B.

A **[CBSE OD 2016]**

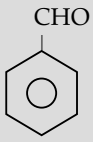
Ans. (i) (a) $CH_3COCl \xrightarrow{H_2, Pd-BaSO_4} \underset{[A]}{CH_3CHO} + HCl \xrightarrow{H_2N-OH} \underset{[B]}{CH_3-CH=N-OH}$ ½ + ½

Acetaldehyde — Acetaldoxime

(b) $CH_3MgBr \xrightarrow[2.H_3O^+]{1.\ CO_2} \underset{[A]}{CH_3COOH} \xrightarrow{PCl_5} \underset{[B]}{CH_3COCl} + HCl + POCl_3$ ½ + ½

Acetic acid — Acetyl chloride

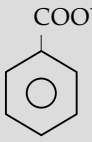
(ii) (a) C_6H_5 – CHO being an aldehyde reduces Tollen's reagent to give shining silver mirror whereas $C_6H_5COCH_3$ being a ketone does not.



$+ 2[Ag(NH_3)_2]^+ + 3OH^-$

Tollen's reagent

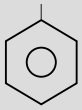
Benzaldehyde



$+ 2Ag + 4NH_3 + 2H_2O$

Silver mirror

Benzoate ion



$\xrightarrow[\text{reagent}]{\text{Tollens}}$ No silver mirror **1**

(b) HCOOH gives silver mirror test with Tollen's reagent whereas ethanoic acid does not.

$HCOOH + 2[Ag(NH_3)_2]^+ + 2OH^- \rightarrow 2Ag\downarrow + 2H_2O + CO_2 + 4NH_3$

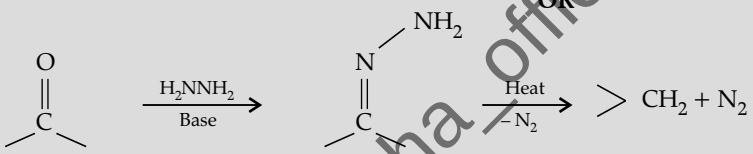
Silver mirror

$CH_3COOH \xrightarrow[\text{reagent}]{\text{Tollen's}}$ No silver mirror (or any other correct test) **1**

(iii) $CH_3CHO < CH_3CH_2OH < CH_3COOH$ **1**

OR

(i)



$\xrightarrow[\text{Base}]{H_2NNH_2}$ $\xrightarrow[-N_2]{\text{Heat}}$ $CH_2 + N_2$ **1**

(ii) $C_6H_5COCH_3 < CH_3-COCH_3 < CH_3CHO$ **1**

(iii) Because of resonance in carboxylic group the Carbonyl group loses a double bound character. **1**

(iv) $CH_3CH_2CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-H$ **1**

(v) A : CH_3CH_2CHO

B : CH_3COCH_3 ½+½

[CBSE Marking Scheme 2016]

Commonly Made Error

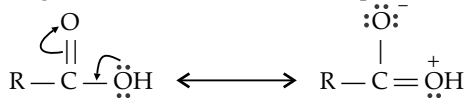
- Students forget to mention the observation in the answers.

Answering Tips

- Specify the reagents involved in distinguishing each compound followed by observation in each case.
- Be careful while writing the structures as the answer must correspond to the question.

Detailed Answer :

(iii) Carboxylic acids do not give reactions of carbonyl groups as it enters into resonance with lone pair present on O of –COOH groups thereby making the carbon atoms less electrophilic. **1**



(v) $CH_3CH_2CHO + NaOH + I_2 \rightarrow$ No yellow precipitate ½

Propanal

$\underset{[A]}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + 3NaOH + 4I_2 \xrightarrow{\Delta} \underset{\text{Yellow precipitate}}{CHI_3} + 3NaI + CH_3COONa + 3H_2O$ ½

Acetone [B]

AI **Q 4. (i) What is meant by the following terms ? Give an example of the reaction in each case.**

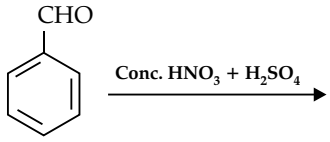
(a) Aldol

(b) Semicarbazone

(ii) Complete the following :

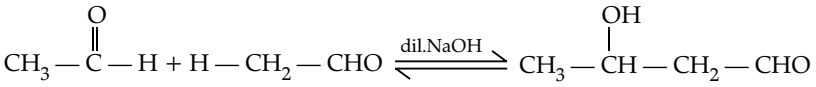
(a) $CH_3COCl \xrightarrow{H_2, Pd-BaSO_2}$

(b) $CH_3—CH = CH—CN \xrightarrow{DiBAL-H}$

(c) 

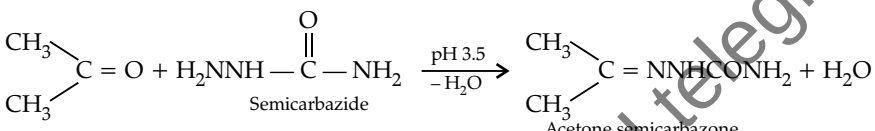
R + A **[CBSE Comptt. Delhi 2016]**

Ans. (i) (a) Aldol : Two molecules of aldehydes containing a minimum one α-hydrogen atom on treatment with dilute alkali undergo condensation to form aldol (β-hydroxy aldehydes).



3-Hydroxy butanal (Aldol) **1**

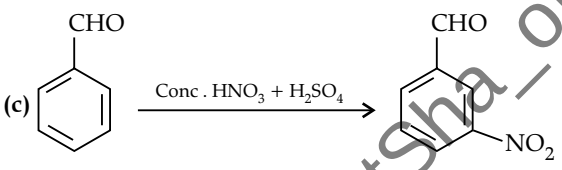
(b) Semicarbazone : Derivative of aldehydes and ketones produced by the action of semicarbazide on them in weak acid.



Acetone semicarbazone **1**

(ii) (a) $CH_3COCl \xrightarrow{H_2, Pd/BaSO_4} CH_3CHO + HCl$

(b) $CH_3—CH = CH—CN \xrightarrow{DiBAL-H} CH_3CH=CH—CHO$ **3**

(c) 

Commonly Made Error

- Writing just the name of the test and not the reagent.

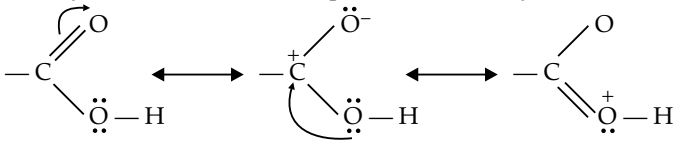
Answering Tips

- Mention the reagents/conditions involved in a chemical reaction.
- Give appropriate chemical reactions to support the explanation of name reactions.

TOPIC-2
Carboxylic Acids

Revision Notes

- Carboxylic acids are those compounds which have —C(=O)—OH group. The carboxyl group is made up of carboxyl, >C=O and hydroxyl, –OH group, hence, its name is carboxyl group.
- **Structure of carboxyl group :** The bonds to the carboxyl carbon lie in one plane separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon due to possible resonance structure.

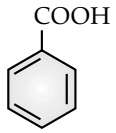


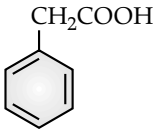
➢ **Nomenclature of carboxylic acids :** Derived by replacing terminal 'e' of the alkane with 'oic acid'.

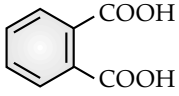
Carboxylic acids **Structural formula**	**General formula :** $R-\overset{\overset{O}{\|}}{C}-OH$, where $R = C_nH_{2n+1}$		
	Condensed formula	**Common name**	**IUPAC name**
$R-\overset{\overset{O}{\|}}{C}-OH$	HCOOH	Formic acid	Methanoic acid
$CH_3-\overset{\overset{O}{\|}}{C}-OH$	CH_3COOH	Acetic acid	Ethanoic acid
$CH_3CH_2-\overset{\overset{O}{\|}}{C}-OH$	CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH$	$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$CH_3-\underset{\underset{CH_3}{\|}}{CH}-\overset{\overset{O}{\|}}{C}-OH$	$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid

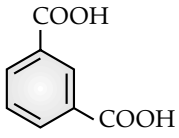
Dicarboxylic Acids

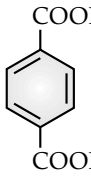
$\begin{matrix}COOH\\\|\\COOH\end{matrix}$ (Oxalic acid) Ethane-1, 2-dioic acid	$CH_2\begin{matrix}\diagup COOH\\\diagdown COOH\end{matrix}$ (Malonic acid) Propane-1, 3-dioic acid	$\begin{matrix}CH_2COOH\\\|\\CH_2COOH\end{matrix}$ (Succinic acid) Butane-1, 4-dioic acid	$CH_2\begin{matrix}\diagup CH_2COOH\\\diagdown CH_2COOH\end{matrix}$ (Glutaric acid) Pentane-1, 5-dioic acid
$\begin{matrix}CH_2CH_2COOH\\\|\\CH_2CH_2COOH\end{matrix}$ (Adipic acid) Hexane-1, 6-dioic acid	$\begin{matrix}CH_2-COOH\\\|\\CH-COOH\\\|\\CH_2-COOH\end{matrix}$ Propane-1, 2- 3-tricarboxylic acid	$CH_3-CH=CH-COOH$ (Crotonic acid) But-2-enoic acid	$\begin{matrix}OH\\\|\\CH_3-CH-COOH\end{matrix}$ (Lactic acid) 2-Hydroxypropanoic acid


Benzoic acid or Benzene carboxylic acid


Phenylacetic acid or 2-Phenylethanoic acid


Phthalic acid or Benzene-1, 2-dicarboxylic acid


Isophthalic acid or Benzene-1, 3-dicarboxylic acid


Terephthalic acid or Benzene-1, 4-dicarboxylic acid

➢ **Methods of preparation of Carboxylic acids :**

(i) By oxidation of primary alcohols and aldehydes :

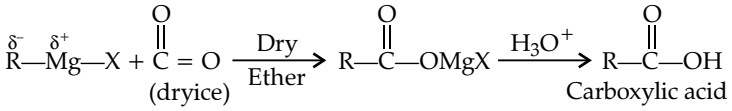
$$\underset{1^\circ\text{ Alcohol}}{R-CH_2-OH} \xrightarrow[(ii)\ H_3O^+]{(i)\ Alk.KMnO_4} \underset{\text{Carboxylic acid}}{R-COOH}$$

$$\underset{\text{Aldehyde}}{R-CHO} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Carboxylic acid}}{R-COOH}$$

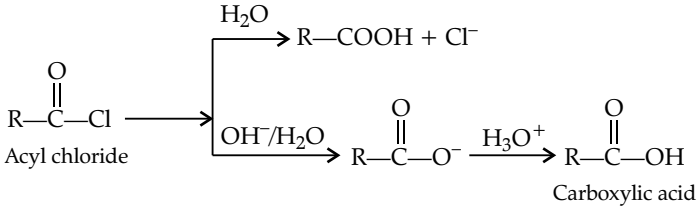
(ii) From alkyl cyanides and amides :

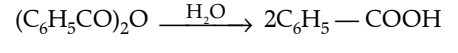
$$R-C\equiv N \xrightarrow[H_2O]{H_3O^+} \underset{\text{acid amide}}{R-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow[H_2O]{H_3O^+} \underset{\text{Carboxylic acid}}{R-\overset{\overset{O}{\|}}{C}-OH}$$

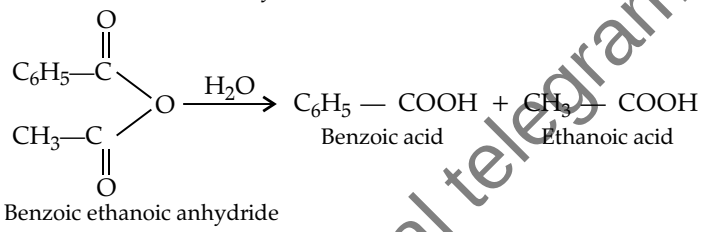
(iii) From Grignard reagent :



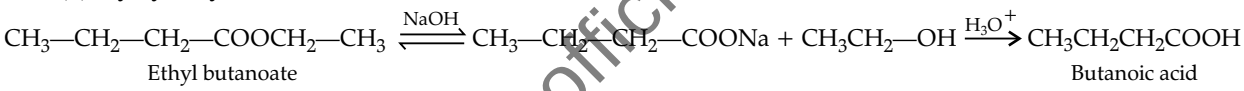
(iv) From hydrolysis of acyl halide and acid anhydrides :







(v) By hydrolysis of esters :



- **Physical properties of Carboxylic acids :**
  - **(i)** Lower members are colourless liquid with pungent smell, while higher members are odourless waxy solid. Benzoic acid is a crystalline solid.
  - **(ii)** First four members are water miscible due to tendency to form hydrogen bond. Higher acids are insoluble.
  - **(iii)** Carboxylic acids have higher boiling point due to their ability to form intermolecular hydrogen bonding.
  - **(iv)** Carboxylic acid with even number of carbon atoms have higher melting points than those with odd number of carbon atoms above or below it.
- **Chemical Properties :** Chemical properties of carboxylic acids are classified as follows :
  - **(i) Reaction involving cleavage of O — H bond :** Reactions with metal alkalies :

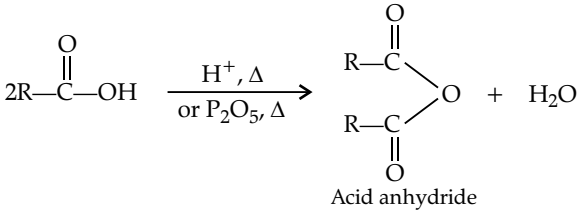
$$2R — COOH + 2Na \rightarrow 2R — COONa + H_2$$

Sodium Carboxylate

$$R — COOH + NaOH \rightarrow R — COONa + H_2O$$

$$R — COOH + NaHCO_3 \rightarrow R — COONa + H_2O + CO_2 \uparrow$$

  - **(ii) Reactions involving cleavage of C — OH Bond :**
    - **(a) Formation of anhydride :**



    - **(b) Esterification :**

$$R — COOH + R' — OH \rightleftharpoons R — COOR' + H_2O$$

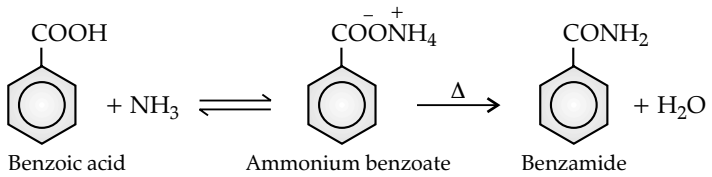
    - **(c) Reaction with PCl_5, PCl_3 and $SOCl_2$**

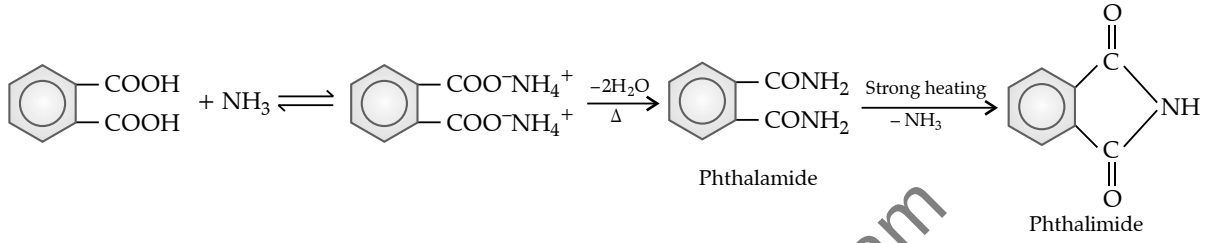
$$R — COOH + PCl_5 \rightarrow \underset{\text{acyl chloride}}{RCOCl} + POCl_3 + HCl$$

$$R — COOH + SOCl_2 \rightarrow RCOCl + SO_2 \uparrow + HCl \uparrow$$

(d) Reaction with ammonia :

$$\underset{\text{Carboxylic acid}}{R-COOH} + NH_3 \rightleftharpoons R-COO-NH_4 \xrightarrow[-H_2O]{\Delta} \underset{\text{Amide}}{R-CONH_2}$$





(iii) Reduction involving –COOH group :

(a) Reduction :

$$R-COOH \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4\ /\ \text{ether or } B_2H_6} \underset{1^\circ\text{ – Alcohol}}{R-CH_2-OH}$$

(b) Decarboxylation :

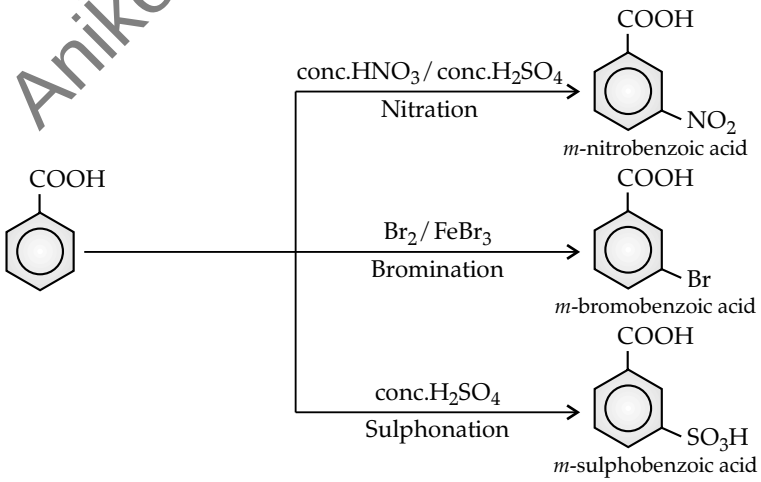
$$\underset{\text{Sodium carboxylate}}{R-COONa} \xrightarrow[\Delta]{NaOH \text{ and } CaO} R-H + Na_2CO_3$$

(c) Halogenation :

$$R-CH_2-COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2\ /\ \text{Red P}} \underset{(X = Cl, Br)}{R-\underset{\displaystyle X}{\underset{|}{C}}H-COOH}$$

This reaction is known as Hell-Volhard Zelinsky reaction.

(iv) Ring Substitution Reaction :



➢ **Tests for Carboxylic acid :**

(i) Litmus test : It turns blue litmus to red.

(ii) Sodium bicarbonate test : When they react with $NaHCO_3$, evolve CO_2 gas with brisk effervescence.

$$\underset{\text{Carboxylic acid}}{RCOOH} + NaHCO_3 \rightarrow \underset{\text{Sodium carboxylate}}{RCOONa} + H_2O + CO_2 \uparrow$$

(iii) Ester formation test : On heating with ethanol (alcohol) in the presence of conc. H_2SO_4, they give fruity smell of ester.

$$R-COOH + R'-OH \xrightarrow{H_2SO_4} RCOOR' + H_2O$$

Carboxylic Acid — Fruity smell (Ester)

➢ **Test to distinguish between formic acid and acetic acid :**

(i) Tollens' reagent test : Formic acid reduces Tollen's reagent to metallic silver but acetic acid does not.

$$HCOOH + 2[Ag(NH_3)_2]^+ + 2OH^- \rightarrow \underset{\text{(Silver mirror)}}{2Ag\downarrow} + CO_2\uparrow + 2H_2O + 4NH_3$$

(ii) $HgCl_2$ Test : Formic acid reduces $HgCl_2$ to give white ppt. of Hg_2Cl_2 while acetic acid does not give this test.

$$\underset{\text{Formic acid}}{HCOOH} + 2\underset{\text{Mercuric chloride}}{HgCl_2} \longrightarrow \underset{\text{Mercurous chloride (white ppt)}}{Hg_2Cl_2\downarrow} + 2HCl + CO_2\uparrow$$

Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple choice Questions:

Q. 1. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these conditions?

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

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

(c) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + CH_2$

(d) $CH_3-\overset{O}{\overset{\|}{C}}-OH + H-\overset{O}{\overset{\|}{C}}-H$

R [NCERT Exemp. Q. 1., Page 168]

Ans. Correct option : (b)

Explanation :

$$CH_3CH_2C \equiv CH + H_2O \xrightarrow{H^+, Hg^{2+}} CH_3CH_2C = CH_2 \rightleftharpoons CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

(OH)

Q. 2. The correct order of increasing acidic strength is :

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

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

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

(d) Chloroacetic acid < Acetic acid < Phenol < Ethanol. U [NCERT Exemp. Q. 3., Page 168]

Ans. Correct option : (c)

Explanation : Phenol is more stable than alcohol due to formation of more stable conjugate base after removal of H^+ from phenol.

$$CH_3CH_2OH < \text{C}_6\text{H}_5\text{OH} < CH_3-\overset{O}{\overset{\|}{C}}-OH < Cl-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

Whereas, carboxylic acid is more acidic than acetic acid due to formation of more stable conjugate base after removal of H^+ as compared to phenol.

$$\text{C}_6\text{H}_5\text{OH} \xrightarrow{-H^+} \text{C}_6\text{H}_5\text{O}^-$$

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

Q. 3. Which is the most suitable reagent for the following conversion?

$$CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

(a) Tollens' reagent

(b) Benzoyl peroxide

(c) I_2 and NaOH solution

(d) Sn and NaOH solution

U [NCERT Exemp. Q. 10., Page 170]

Ans. Correct option : (a)

Explanation :

$$CH_3CH=CH-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{I_2+NaOH} CH_3CH=CHCH_2-\overset{O}{\overset{\|}{C}}-ONa + CHI_3$$

$$CH_3CH=CHCH_2-\overset{O}{\overset{\|}{C}}-OH \xleftarrow{H_2O}$$

B. Match the following:

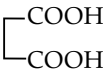
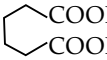
Q. 1. Match the species given in Column I with those mentioned in Column II.

S. No.	Column I	S. No	Column II
(i)	Phthalic acid	(a)	Hexane-1,6-dioic acid
(ii)	Oxalic acid	(b)	Benzene-1,2-dicarboxylic acid
(iii)	Succinic acid	(c)	Pentane-1,5-dioic acid
(iv)	Adipic acid	(d)	Butane-1,4-dioic acid
(v)	Glutaric acid	(e)	Ethane-1,2-dioic acid

[NCERT Exemp. Q. 39, Page 174]

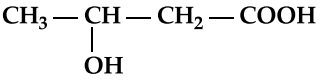
Ans. **(i)** → (b) **(ii)** → (e)
(iii) → (d) **(iv)** → (a)
(v) → (c)

Explanation :

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

C. Answer the following :

Q. 1. Write IUPAC name of :

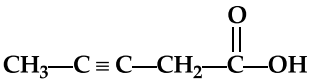


A **[CBSE Delhi 2014]**

Ans. 3-Hydroxybutanoic acid/3-hydroxybutan-1-oic acid. **1**

[CBSE Marking Scheme 2014]

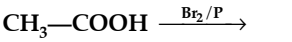
Q. 2. Write the IUPAC name of :



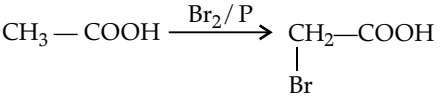
A **[CBSE Delhi 2011]**

Ans. Pent-3-yne-1-oic acid. **1**

Q. 3. Complete the following reaction :

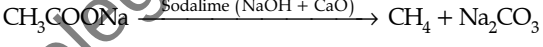


A **[CBSE Delhi 2013]**

Ans.  **1**

Q. 4. Illustrate the decarboxylation reaction giving a suitable example : C **[CBSE Delhi 2012]**

Ans. Decarboxylation refers to the reaction in which carboxylic acid loose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime, *e.g.*, ½



½

Short Answer Type Questions (2 marks each)

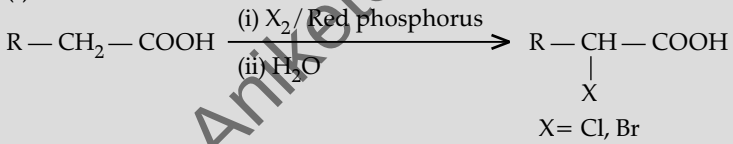
Q. 1. Write the reactions involved in the following:

(i) Hell-Volhard Zelinsky reaction

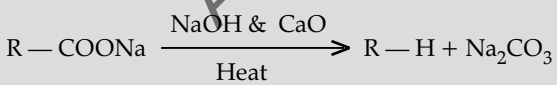
(ii) Decarboxylation reaction

R **[CBSE Delhi Set-2 2017]**

Ans. (i)



1

(ii) 

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[CBSE Marking Scheme 2017]

Answering Tip

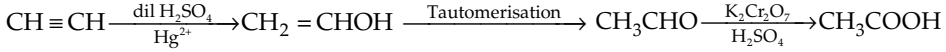
- Write the reagents involved in the reactions. The equations should be balanced and all side products should be mentioned.

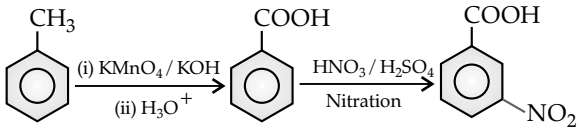
Q. 2. How will you carry out the following conversions ?

(i) Acetylene to acetic acid

(ii) Toluene to *m*-nitro benzoic acid.

A **[CBSE Delhi 2013]**

Ans. (i)  **1**

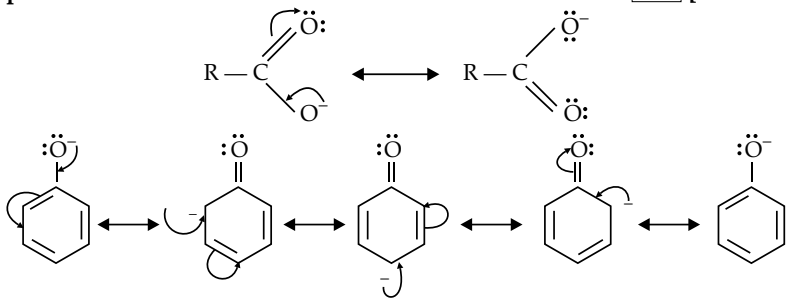
(ii)  **1**

Answering Tip

- Mention the name of reagents/ conditions involved in each step of conversion.

Q. 3. Although phenoxide ion has more number of resonating structures than carboxylate ion carboxylic acid is a stronger acid than phenol. Give two reasons. A&E **[CBSE Delhi 2013; NCERT]**

Ans.



(i) Phenoxide ion has non-equivalent resonance structures in which the negative charge is at the lesser electronegative carbon atom whereas in case of carboxylate ion both the resonating structures are equivalent. **1**

(ii) The negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion whereas in phenoxide ion, the negative charge less effectively delocalises over one oxygen atom and less electronegative carbon atoms. So, the carboxylate ion is more resonance stabilised than phenoxide ion. Thus, the release of proton from carboxylic acid is much easier than from phenol. Hence, carboxylic acid is a stronger acid than phenol. **1**

Answering Tip

- Draw all the possible resonating structures of phenoxide ion and carboxylate ion in support of the reasons.

Q. 4. Do the following conversions in not more that two steps:

(i) Propene to Acetone

(ii) Propanoic acid to 2-hydroxypropanoic acid A **[CBSE Foreign Set-1, 2, 3 2017]**

Ans. (i)

$$CH_3CH{=}CH_2 \xrightarrow[H^+]{H_2O} CH_3CH(OH)CH_3 \xrightarrow[CrO_3]{[O]} CH_3COCH_3$$ **1**

(ii)

$$CH_3CH_2COOH \xrightarrow{Br_2/\text{ Red P}} CH_3CH(Br)COOH \xrightarrow[(ii)\ H^+]{(i)\text{ aq KOH or NaOH}} CH_3CH\,(OH)COOH$$ **1**

(or any other suitable method)

[CBSE Marking Scheme 2017]

Commonly Made Error

- Some students wrote more than two reactions.

Answering Tip

- Read the question carefully.

AI **Q. 5. How do you convert the following ?**

(a) Ethanal to Propanone

(b) Toluene to Benzoic acid A

OR

Account for the following :

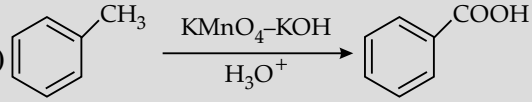
(a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.

(b) pKa value of 4-nitrobenzoic acid is lower than that of benzoic acid. A&E **[CBSE Delhi/OD 2018]**

Ans. (a)

$$CH_3CHO \xrightarrow{(i)\ CH_3MgBr,\ \text{Dry ether}\ (ii)\ H_2O/H^+} CH_3CH(OH)CH_3 \xrightarrow{CrO_3} CH_3COCH_3$$ **1**

(b)



1

OR

(a) because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group **1**

(b) Nitro group is an electron withdrawing group (-I effect) so it stabilises the carboxylate anion and strengthens the acid / Due to the presence of an electron withdrawing Nitro group (-I effect). **1**

[CBSE Marking Scheme 2018]

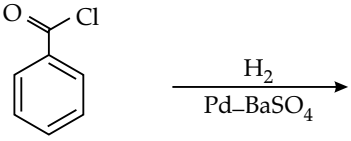
Detailed Answer:

(a) Because — COOH group present in aromatic carboxylic acids is an electron withdrawing group causing deactivation of benzene ring. This results in the bonding of anhydrous $AlCl_3$ with carboxyl group. Hence, electrophilic substitution i.e., Friedel-Crafts reaction does not occur in aromatic carboxylic acids. **1**

(b) As 4-nitrobenzoic acid contains $–NO_2$ group which is an electron withdrawing group resulting in higher acidity than benzoic acid. Greater is the acidic character lower is the pKa value. Thus, pKa value of 4-nitrobenzoic acid is lower than that of benzoic acid. **1**

Q. 6. Identify the reaction and write the IUPAC name of the product formed:

(a) $CH_3–CH_2–COOH \xrightarrow{\text{(i) } Br_2/\text{Red phosphorous}}$

(b)  $\xrightarrow[Pd–BaSO_4]{H_2}$

A **[CBSE SQP 2018-2019]**

Ans. (a) Reaction : Hell-Volhard- Zelinsky reaction. ½

IUPAC : 2-Bromopropanoic acid. ½

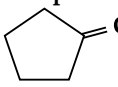
(b) Reaction : Rosenmund reduction reaction. ½

IUPAC : Benzaldehyde. ½

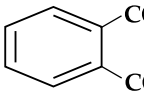
[CBSE Marking Scheme 2018]

Long Answer Type Questions-I **(3 marks each)**

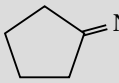
Q. 1. Complete the following reactions :

(i)  **+ H_2N—OH** ⟶

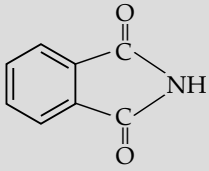
(ii)  $\xrightarrow[\Delta]{KMnO_4,\ H_2SO_4}$

(iii)  **+ NH_3** $\xrightarrow{\text{Strong heating}}$

A **[CBSE SQP 2018-2019]**

Ans. (i)  **1**

(ii) $HOOC–CH_2–CH_2–CH_2–CH_2–COOH$ **1**

(iii)  **1**

[CBSE Marking Scheme 2018]

AI **Q. 2. (i) Account for the following :**

(a) $Cl—CH_2COOH$ is a stronger acid than CH_3COOH.

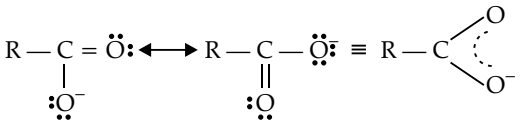
(b) Carboxylic acids do not give reactions of carbonyl group.

(ii) Write the chemical equation to illustrate the following name reaction :

(a) Rosenmund reduction. A&E + R **[CBSE OD/Delhi 2014]**

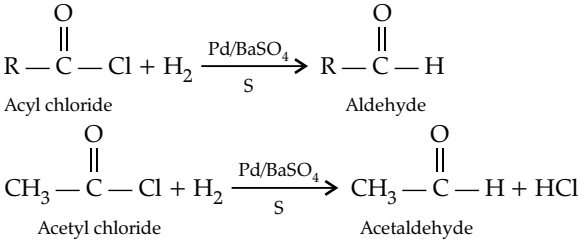
Ans. (i) (a) Cl-CH_2COOH has lower pk_a value than acetic acid. Also, Cl group is an electron withdrawing creating less electron density on oxygen of carboxylic acid making the release of proton easier than acetate ion. Hence, $Cl–CH_2COOH$ is a stronger acid than CH_3COOH. **1**

(b) The carbonyl group in –COOH is inert and does not show nucleophilic addition reaction like carbonyl compound due to resonance stabilisation of carboxylate ion :



1

(ii) (a) Rosenmund reaction :



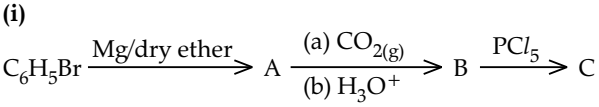
1

Commonly Made Error

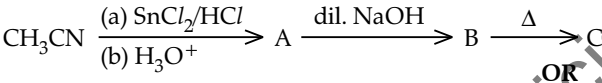
- Some candidates failed to mention the catalyst i.e. Pd and $BaSO_4$ while a few used 2[H] for reduction instead of H_2.

AI Q. 3. Write structures of compounds A, B and C in each of the following reactions:

(i)



(ii)



OR

Do the following conversions in not more than two steps:

(i) Benzoic acid to benzaldehyde

(ii) Ethyl benzene to Benzoic acid

(iii) Propanone to Propene

A [CBSE Delhi Set-1, 2, 3 2017]

Ans. (i) C_6H_5MgBr B: C_6H_5COOH C: C_6H_5COCl ½ × 3

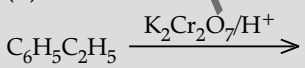
(ii) A: CH_3CHO B: $CH_3CH(OH)CH_2CHO$ C: $CH_3CH=CHCHO$ ½ × 3

OR

(i)

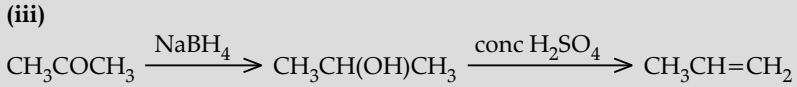
1

(ii)



1

(iii)



1

(or any other correct method)

[CBSE Marking Scheme 2017]

Q. 4.Give reasons :

(i) Propanone is less reactive than ethanal towards nucleophilic addition reactions.

(ii) O_2N - CH_2 - COOH has lower pKa value than CH_3COOH.

(iii) $(CH_3)_2CH$ - CHO undergoes aldol condensation whereas $(CH_3)_3C$ - CHO does not.

A&E [CBSE Foreign Set-1, 2, 3 2017]

Ans. (i) Due to steric hindrance and +I effect caused by two alkyl groups in propanone. ½ + ½

(ii) Due to electron withdrawing nature of $-NO_2$ group which increases the acidic strength and decreases the pK_a value. **1**

(iii) $(CH_3)_2CH$-CHO has one α -H atom whereas α -H atom is absent in $(CH_3)_3C$-CHO. **1**

[CBSE Marking Scheme 2017]

Detailed Answer:

(i) As alkyl group is an electron releasing group (+I inductive effect), electron releasing power of two alkyl groups in propanone is higher than that of one alkyl group in ethanal. The reduced positive

charge on carbon in propanone discourages the attack of nucleophiles making propanone less reactive than ethanal. Also, presence of two alkyl groups increases the steric hindrance to the attack of nucleophile reducing the reactivity of carbonyl. Thus, propanone is less reactive than ethanal towards nucleophilic addition reactions. **1**

(iii) Aldol condensation occurs due to presence of α -hydrogen. As $(CH_3)_2CH–CHO$ has one α - H atom whereas $(CH_3)_3C$-CHO does not have α - H atom. Thus, $(CH_3)_2CH–CHO$ undergoes aldol condensation whereas $(CH_3)_3C–CHO$ does not. **1**

A **Q. 5. (i) What happens when $CH_3 – O – CH_3$ is heated with HI?**

(ii) Explain mechanism for hydration of acid catalyzed ethene:

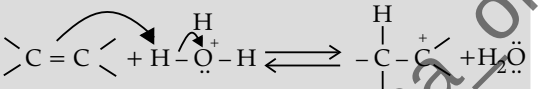
$$CH_2= CH_2 + H_2O \xrightarrow{H^+} CH_3–CH_2–OH$$

A **[CBSE Comptt. Delhi Set 1, 2, 3 2017]**

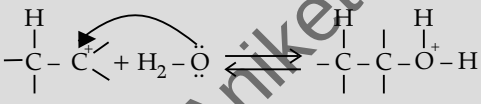
Ans. (i) $CH_3– O– CH_3 + HI \longrightarrow CH_3–OH + CH_3–I$ **1**

(ii) Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

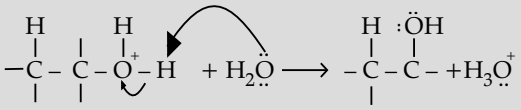
$H_2O + H^+ \rightarrow H_3O^+$

 ½

Nucleophilic attack of water on carbocation.

 ½

Deprotonation to form an alcohol.



1

[CBSE Marking Scheme 2017]

AI **Q. 6. An alcohol A ($C_4H_{10}O$) on oxidation with acidified potassium dichromate gives acid B($C_4H_8O_2$). Compound A when dehydrated with conc. H_2SO_4 at 443 K gives compound C. Treatment of C with aqueous H_2SO_4 gives compound D ($C_4H_{10}O$) which is an isomer of A. Compound D is resistant to oxidation but compound A can be easily oxidised. Identify A, B, C and D. Name the type of isomerism exhibited by A and D.**

A **[CBSE SQP 2018-2019]**

Ans. A : $CH_3–CH(CH_3)–CH_2–OH$ **1**

B : $CH_3–CH(CH_3)–COOH$ ½

C : $CH_3–CH=CH_2\ CH_3$ ½

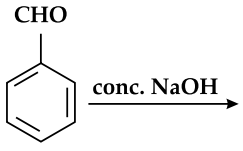
D : $CH_3–C(CH_3)(OH)–CH_3$ ½

A and D are position isomers. ½

[CBSE Marking Scheme 2018]

Long Answer Type Questions-II **(5 marks each)**

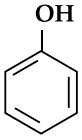
Q. 1. (i) Complete the following equations :

(a) 

(b) $CH_3COCH_3 \xrightarrow{LiAlH_4}$

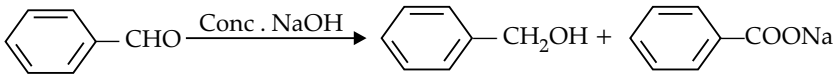
(c) $CH_3 – COOH \xrightarrow[(b)\ H_2O]{(a)\ Cl_2/P}$

(ii) Distinguish between :

(a) CH_3COOH **and** 

(b) $CH_3 – CHO$ **and** $CH_3 – C(=O) – CH_3$

A **[CBSE Comptt. Delhi 2016]**

Ans. (i) (a)  **1**

(b) $2[H] + CH_3COCH_3 \xrightarrow{LiAlH_4} CH_3CH(OH)CH_3$ **1**

(c) $CH_3 - COOH \xrightarrow[(ii)\ H_2O]{(i)\ Cl_2/\text{Red phosphorus}} \underset{Cl}{CH_2} - COOH$ **1**

(ii) (a) When CH_3COOH is added to an aqueous solution of sodium carbonate, brisk effervescence of CO_2 is evolved.

$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$ **1**

Carboxylic acid — Sodium carboxylate

Phenol do not give this test.

(b) When CH_3CHO is heated with Tollen's reagent, they form silver mirror while CH_3COCH_3 does not.

$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3\ OH^- \longrightarrow CH_3 - COO^- + 2\ Ag\downarrow + 2H_2O + 4NH_3$

Tollens' reagent — (Silver mirror)

(or any other suitable test) **1**

AI Q. 2. (i) Describe the following giving chemical equations :

(a) De-carboxylation reaction

(b) Friedel-Crafts reaction

(ii) How will you bring about the following conversions ?

(a) Benzoic acid to Benzaldehyde

(b) Benzene to m-Nitroacetophenone

(c) Ethanol to 3-Hydroxybutanal

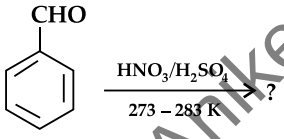
OR

(i) Describe the following reactions :

(a) Acetylation (b) Aldol condensation

(ii) Write the main product in the following equations :

(a) $CH_3 - \underset{\underset{O}{\|}}{C} - CH_3 \xrightarrow{LiAlH_4} ?$

(b) 

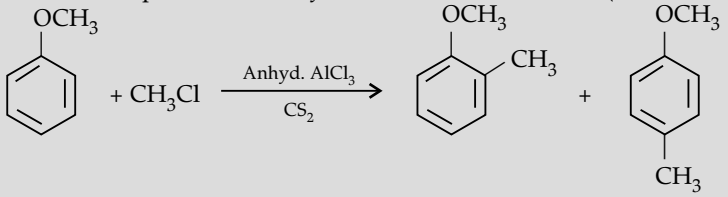
(c) $CH_3 - COOH \xrightarrow{PCl_5} ?$

R + A **[CBSE Comptt. Delhi 2015]**

Ans. (i) (a) Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO).

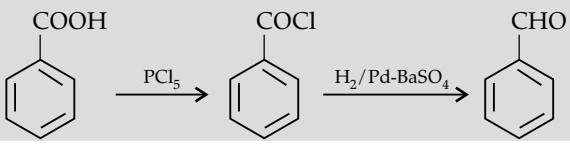
$R - COONa \xrightarrow[Heat]{NaOH\ \&\ CaO} R - H + Na_2CO_3$ **1**

(b) When the alkyl / acyl group is introduced at ortho and para positions by reaction with alkyl halide / acyl halide in the presence of anhydrous aluminium chloride (a Lewis acid) as catalyst.

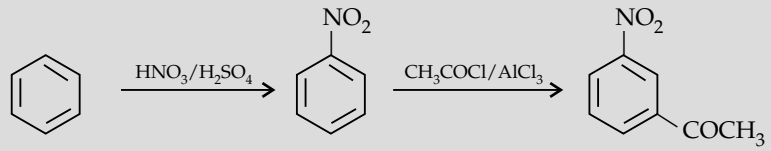


1

(Note : Award full marks if correct equation is given)

(ii) (a)  **1**

(b)



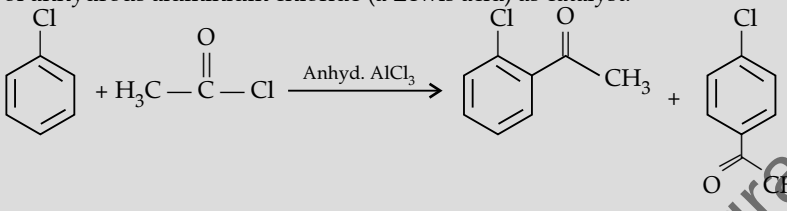
Benzene Nitrobenzene m-Nitroacetophenone **1**

(c) $CH_3CH_2OH \xrightarrow{CrO_3} CH_3-CHO \xrightarrow{\text{dil. NaOH}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$

(or any other correct method) **1**

OR

(i) (a) When the acyl groups are introduced at ortho and para positions by reaction with acyl halide in the presence of anhydrous aluminium chloride (a Lewis acid) as catalyst.



1

(b) Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol), respectively.

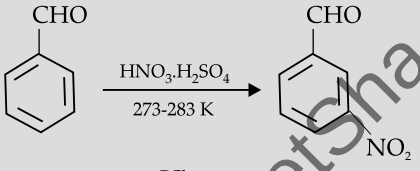
$$2CH_3-CHO \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$$

1

(Note : Award full marks if correct equation is given)

(ii) (a) $CH_3-\underset{\underset{OH}{||}}{CH}-CH_3 \xrightarrow{LiAlH_4} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$ **1**

(b)



1

(c) $CH_3COOH \xrightarrow{PCl_5} CH_3COCl$ **1**

[CBSE Marking Scheme 2015]

Q. 3. (i) Draw the structures of the following :

(a) p-Methylbenzaldehyde,

(b) 4-Methylpent-3-en-2-one.

(ii) Give chemical tests to distinguish between the following pairs of compounds :

(a) Benzoic acid and Ethyl benzoate,

(b) Benzaldehyde and Acetophenone

(c) Phenol and Benzoic acid.

OR

(i) Draw the structures of the following derivatives :

(a) Propanone oxime,

(b) Semicarbazone of CH_3CHO.

(ii) How will you convert ethanal into the following compounds ? Give the chemical equations involved.

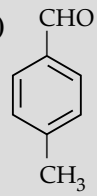
(a) $CH_3—CH_3$

(b) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$

(c) CH_3CH_2OH

A **[CBSE Comptt. OD 2015]**

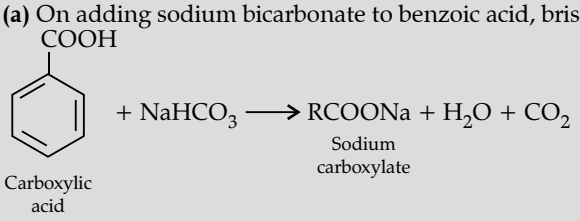
Ans. (i) (a)



1

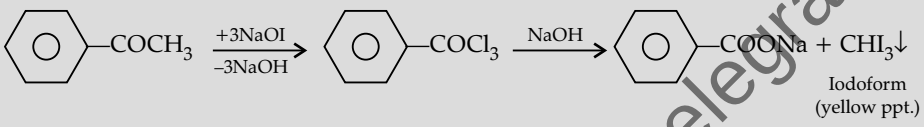
(b) $(CH_3)_2C = CHCOCH_3$ **1**

(ii) (a) On adding sodium bicarbonate to benzoic acid, brisk effervescence of CO_2 is evolved.



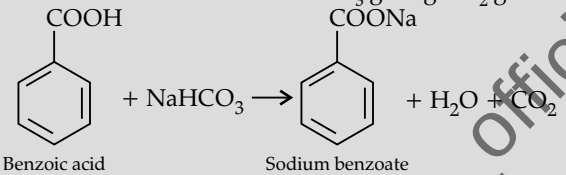
Whereas ethylbenzoate does not. **1**

(b) Acetophenone having at least one $-CH_3$ group on heating with alkaline solution of iodine forms yellow coloured precipitate of iodoform.



Whereas benzaldehyde does not **1**

(c) Benzoic acid reacts with $NaHCO_3$ giving CO_2 gas with effervescence whereas phenol does not.



1

OR

(i) (a) $CH_3-C(CH_3)=N-OH$ **1**

(b) $CH_3-C(H)=N-NH-\overset{\overset{O}{\|}}{C}-NH_2$ **1**

(ii) (a) $CH_3CHO \xrightarrow[\text{conc HCl}]{\text{Zn–Hg}} CH_3-CH_3$ **1**

(b)

$$2CH_3-CHO \xrightleftharpoons{\text{dil. NaOH}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$$

1

(c) $CH_3CHO \xrightarrow{LiAlH_4} CH_3CH_2OH$ **1**

[CBSE Marking Scheme 2015]

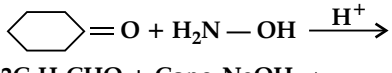
Commonly Made Error

- Writing just the name of the test and not the reagent.

Answering Tips

- Specify the reagents involved in distinguishing each compound followed by the response of each.
- Mention the reagents involved in a chemical reaction.

Q. 4. (i) Write the products of the following reactions :

(a)  **1**

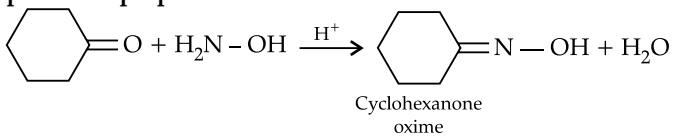
(b) $2C_6H_5CHO + \text{Conc. NaOH} \rightarrow$

(c) $CH_3COOH \xrightarrow{Cl_2/P}$

(ii) Give, simple chemical tests to distinguish between the following pairs of compounds :

(a) Benzaldehyde and benzoic acid

(b) Propanal and propanone. A **[CBSE Delhi 2014]**

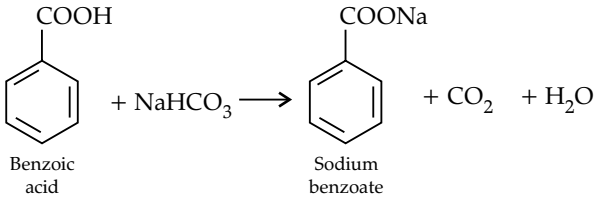
Ans. (i) (a) 

1

(b) $2C_6H_5OH + Conc.NaOH \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sodium benzoate}}{C_6H_5COONa}$ **1**

(c) $CH_3COOH \xrightarrow{Cl_2/P} \underset{\text{2–Chloro-ethanoic acid}}{Cl - CH_2 - COOH} + HCl$ **1**

(ii) (a) Benzoic acid reacts with $NaHCO_3$ to give brisk effervescence of CO_2 while benzaldehyde does not.



1

(b) Propanal being aldehyde when heated with Tollen's reagent to give silver mirror but propanone being a ketone does not.

$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow \underset{}{CH_3CH_2COO^-} + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$ **1**

AI **Q. 5. (i) Account for the following :**

(a) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.

(b) Carboxylic acid is stronger acid than phenol.

(ii) Write chemical reactions to illustrate the following name reactions :

(a) Wolff Kishner reduction

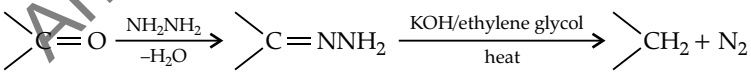
(b) Aldol condensation

(c) Cannizzaro reaction. A&E + R **[CBSE Delhi 2014]**

Ans. (i) (a) Because the positive charge on carbonyl carbon of CH_3CHO decreases to a lesser extent due to one electron releasing (+I effect) CH_3 group as compared to CH_3COCH_3 (two electron releasing CH_3 group) and hence more reactive. **1**

(b) Because carboxylate ion (conjugate base) is more resonance stabilized than phenoxide ion. **1**

(ii) (a)



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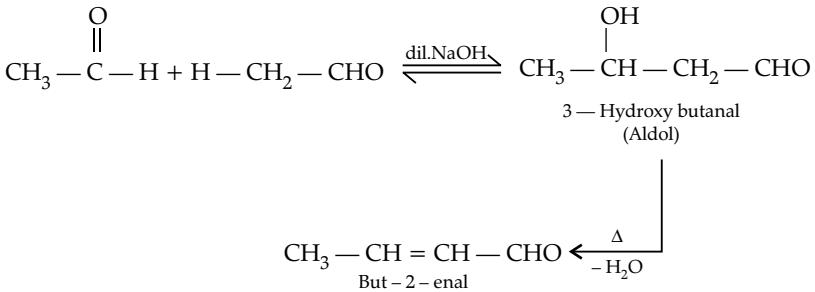
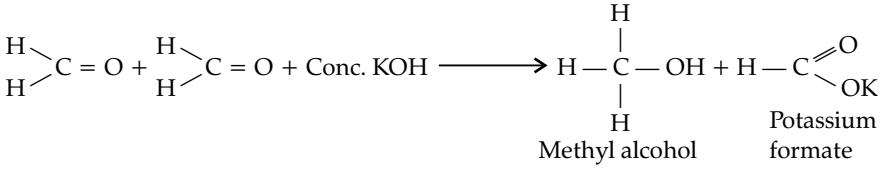
(b)



1

(c)



1

Answering Tip

- Read the questions carefully and do not forget to attempt the sub-parts of the questions.

Q. 6. (i) Illustrate the following name reactions giving suitable example in each case :

(a) Clemmensen reduction

(b) Hell Volhard-Zelinsky reaction.

(ii) How are the following conversions carried out ?

(a) Ethylcyanide to ethanoic acid,

(b) Butan-1- ol to butanoic acid,

(c) Benzoic acid to m-bromobenzoic acid.

R + A **[CBSE OD 2012]**

Ans. (i) (a) Clemmensen reduction : The carbonyl group of aldehydes and ketones is reduced to $—CH_2$ group on treatment with zinc amalgam and concentrated HCl **1**

$$>C=O \xrightarrow[\text{Conc. HCl}]{\text{Zn(Hg)}} >CH_2$$

(b) Hell Volhard-Zelinsky reaction : Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of red phosphorus to give α-halo-carboxylic acids. **1**

$$R—CH_2—COOH \xrightarrow[(X = Cl, Br)]{X_2/P} R—\underset{\displaystyle X}{\underset{|}{CH}}—COOH$$

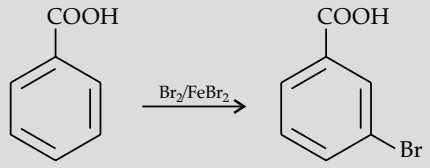
(Or by any other suitable method)

(Note : *Award full marks for correct chemical equation; award ½ mark if only correct statement is written*)

(ii) (a) $CH_3CH_2CN \xrightarrow{H_3O^+} CH_3CH_2COOH \xrightarrow[\Delta]{NH_3} CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow{KMnO_4} CH_3COOH$ **1**

(b) $CH_3—CH_2—CH_2—CH_2—OH \xrightarrow{KMnO_4} CH_3CH_2CH_2COOH$ **1**

(c)



1

(Or any other suitable method can be used for each conversion) [CBSE Marking Scheme 2012]

Commonly Made Error

- **(i) (a)** For Clemmensen's reduction, the correct condition for the reaction is not given by many candidates.

Answering Tips

- Mention the reagents/conditions involved in a chemical reaction.
- Give appropriate chemical reactions to support the explanation of name reactions.

Q. 7. (i) Write a suitable chemical equation to complete each of the following transformations :

(a) Butan-1-ol to butanoic acid

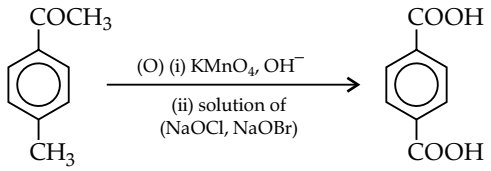
(b) 4-Methyl acetophenone to benzene-1, 4-dicarboxylic acid

(ii) An organic compound with molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1,2-benzene dicarboxylic acid. Identify the compound.

A **[CBSE Delhi 2012; NCERT]**

Ans. (i) (a) $\underset{\text{Butan-1-ol}}{CH_3—CH_2—CH_2—CH_2OH} \xrightarrow[KMnO_4]{(O)} CH_3CH_2CH_2CHO \xrightarrow[KMnO_4]{(O)} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$ **1**

(b)



4-methyl acetophenone — Benzene - 1, 4-dicarboxylic acid

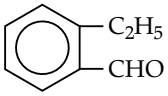
1

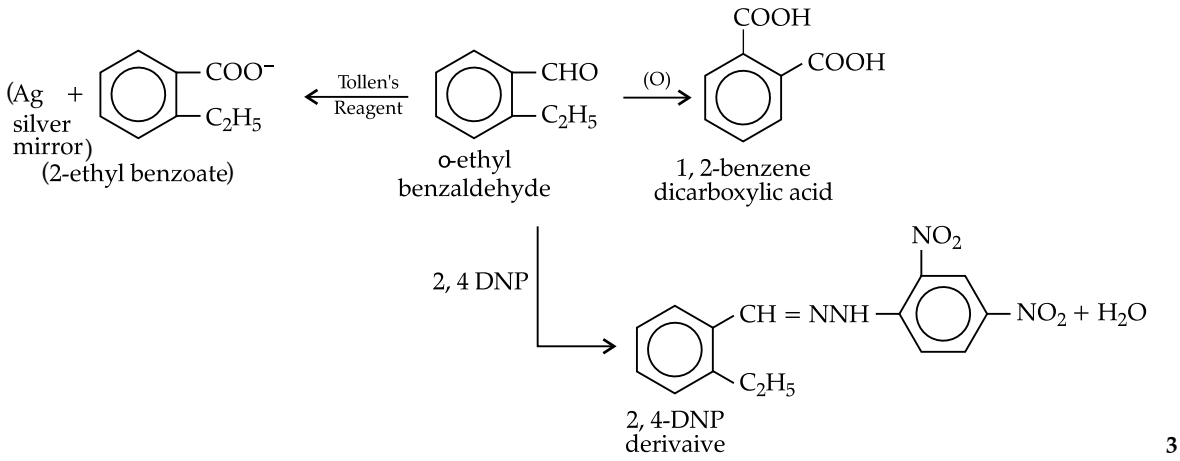
(ii) (a) It is an aldehyde or ketone as it forms 2, 4-DNP derivative.

(b) As the compound reduces Tollen's reagent and undergoes Cannizzaro reaction, it is an aldehyde and not a ketone.

(c) On vigrous oxidation, it gives 1, 2-benzenedicarboxylic acid. So, it must have an alkyl group at ortho position with respect to CHO group on the benzene ring.

(d) Molecular formula suggests that it should be 2-ethyl benzaldehyde.





3

Commonly Made Error

- Students get confused in aromatic reactions and are not able to analyse that the given molecular formula will form aromatic rings.

Q. 8. (i) Give a plausible explanation for each one of the following :

(a) Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol.

(b) There are two -NH_2 groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

(ii) Carry out the following conversions in not more than two steps :

(a) Phenyl magnesium bromide to benzoic acid.

(b) Acetaldehyde to But-2-enal.

(c) Benzene to m-Nitroacetophenone. A&E + A

OR

(i) Give a simple chemical test to distinguish between the pair of organic compounds :
Ethanal and Propanal

(ii) Name and complete the following chemical reaction :
$RCH_2COOH \xrightarrow{(i)X_2/red\,P\,(ii)H_2O}$

(iii) Draw the structures of the following derivatives :

(a) The 2, 4-Dinitrophenylhydrazone of benzaldehyde,

(b) Acetaldehyde dimethyl acetal

(c) Cyclopropanone oxime. A **[CBSE SQP 2016]**

Ans. (i) (a) The delocalisation of benzene electrons contributes little towards the stability of phenoxide ion. The carboxylate ion is much more resonance stabilized than phenoxide ion. So, it is easier to lose a proton than phenol. Hence, carboxylic acid is a stronger acid than phenol. **1**

(b) Semicarbazide has two —NH_2 groups. One of them, which is directly attached to C=O is involved in resonance. Thus, electron density on this group decreases and it does not act as a nucleophile. In contrast, the lone pair of electrons on the other —NH_2 group is available for nucleophilic attack. **1**

(ii) (a) $PhMgBr + O{=}C{=}O \rightarrow PhCOOMgBr \xrightarrow{H_2O} PhCOOH$ **1**

(b) $2CH_3CHO \xrightarrow{OH^-} CH_3CH(OH)—CH_2CHO \xrightarrow{Heat} CH_3CH{=}CH—CHO$ **1**

(c) $C_6H_6 \xrightarrow{(CH_3CO)_2O/Anhy\ AlCl_3} PhCOCH_3$

$\xrightarrow[Or\ CH_3COCl/AlCl_3]{conc.H_2SO_4+conc.HNO_3} m\text{–}NO_2C_6H_4COCH_3$ **1**

OR

(i) Ethanal and propanal can be distinguished by Iodoform test.

Ethanal gives a yellow precipitate of iodoform with an alkaline solution of NaOH. Propanal does not gives this test. **1**

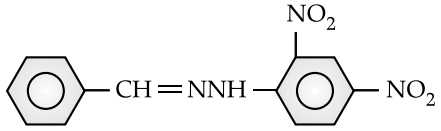
$CH_3CHO + 4NaOI \xrightarrow{NaOH/I_2} CHI_3 + HCOONa + 2NaOH$

(ii) $RCH_2COOH \xrightarrow{(i)X_2\,red\,P\,(ii)H_2O} RCH(X)COOH$ ½

α-Halo carboxylic acid

The name of the reaction is Hell-Volhard-Zelinsky reaction. ½

(iii) (a)



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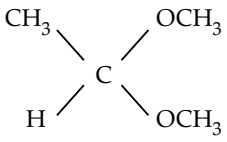
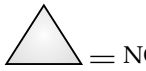
(b)



1

(c)



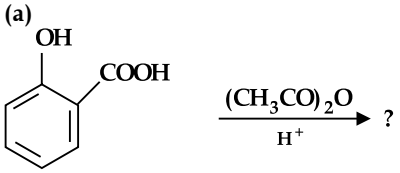
1

Answering Tips

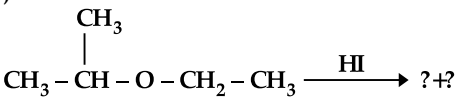
- Write the reagents involved in the conversions and distinguish between type of questions.
- Draw the structure neatly avoiding over-writing.

Q. 9. (i) Write the product(s) in the following reactions:

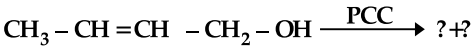
(a)



(b)



(c)



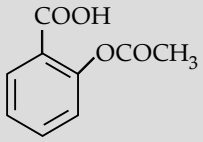
(ii) Give simple chemical tests to distinguish between the following pairs of compounds:

(a) Ethanol and Phenol

(b) Propanol and 2-methylpropan -2-ol

A **[CBSE Delhi Set-1, 2, 3 2017]**

Ans. (i) (a)



1

(b) $(CH_3)_2$ CHOH and CH_3 CH_2I **1**

(c) $CH_3CH{=}CHCHO$ **1**

(ii) (a) Add neutral $FeCl_3$ to both the compounds, phenol gives violet complex. **1**

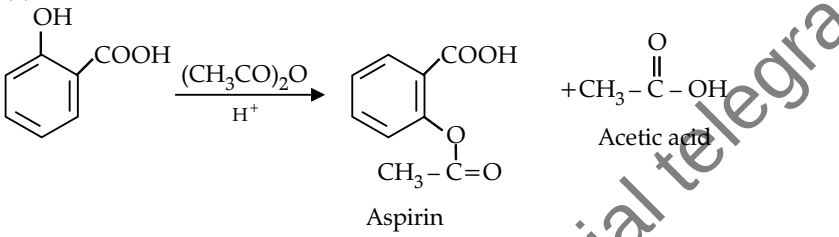
(b) Add anhy $ZnCl_2$ and conc. HCl to both the compounds, 2-methyl propan-2-ol gives turbidity immediately. **1**

(or any other correct test)

[CBSE Marking Scheme 2017]

Detailed Answer:

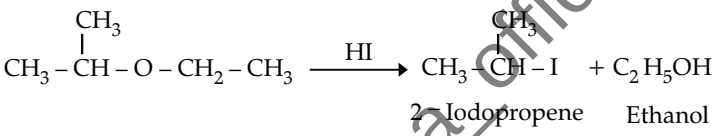
(i) (a)



Aspirin Acetic acid

1

(b)



2– Iodopropene Ethanol

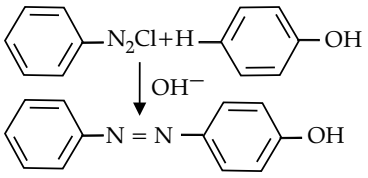
1

(c)

But – 2 – enal

1

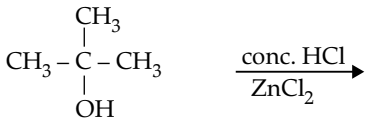
(ii) (a) Test : Coupling Ethanol Negative test : Phenol Positive test :



Orange $+Cl^- + H_2O$

(b) By Lucas test

Propanol Turbidity appears from heating after longtime



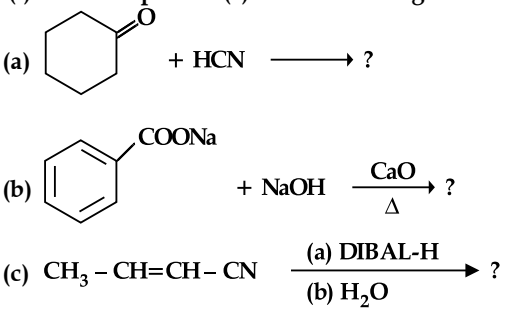
2- Methylpropan-2-ol Turbidity appears very quickly

2

Answering Tip

- Students should understand the observations for different organic reactions. They should mention colour or precipitate properly.

Q. 10. (i) Write the product(s) in the following reactions :



(ii) Give simple chemical tests to distinguish between the following pairs of compounds:

(a) Butanal and Butan-2-one

(b) Benzoic acid and Phenol A

OR

(i) Write the reactions involved in the following:

(a) Etard reaction

(b) Stephen reduction

(ii) How will you convert the following in not more than two steps :

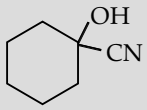
(a) Benzoic acid to Benzaldehyde

(b) Acetophenone to Benzoic acid

(c) Ethanoic acid to 2-Hydroxyethanoic acid

R + A **[CBSE OD Set-1, 2, 3 2017]**

Ans. (i) (a)



1

(b)

1

(c) $CH_3–CH=CH–CHO$ **1**

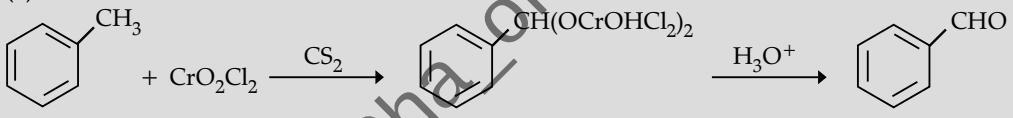
(ii) (a) Tollen's reagent test : Add ammoniacal solution of silver nitrate (Tollen's Reagent) in both the solutions. Butanal gives silver mirror whereas Butan-2-one does not. **1**

(b) Add neutral $FeCl_3$ in both the solution, phenol forms violet colour but benzoic acid does not. **1**

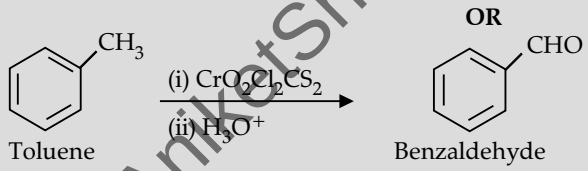
(or any other correct test)

OR

(i) (a) Etard reaction



OR



Toluene Benzaldehyde **1**

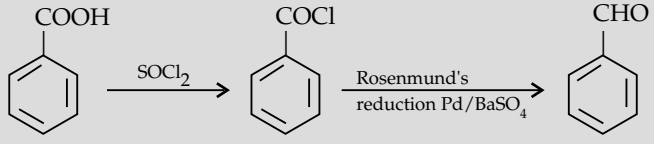
(b) Stephen reaction

$$RCN + SnCl_2 + HCl \longrightarrow RCH=NH \xrightarrow{H_3O^+} RCHO$$ **1**

OR

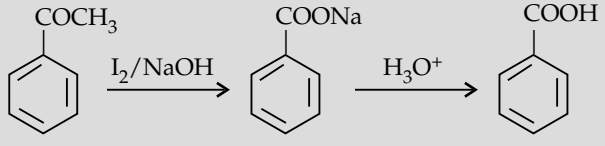
$$RCN \xrightarrow[(ii)\ H_3O^+]{(i)\ SnCl_2+HCl} RCHO$$

(ii) (a)



Benzoic acid Benzoyl chloride Benzaldehyde **1**

(b)



Acetophenone Sodium benzoate Benzoic acid **1**

(c)

$$CH_3COOH \xrightarrow{Cl_2/P} \underset{\displaystyle Cl}{\overset{|}{CH_2}}COOH \xrightarrow{KOH(Aq)} \underset{\displaystyle OH}{\overset{|}{CH_2}}COOH$$

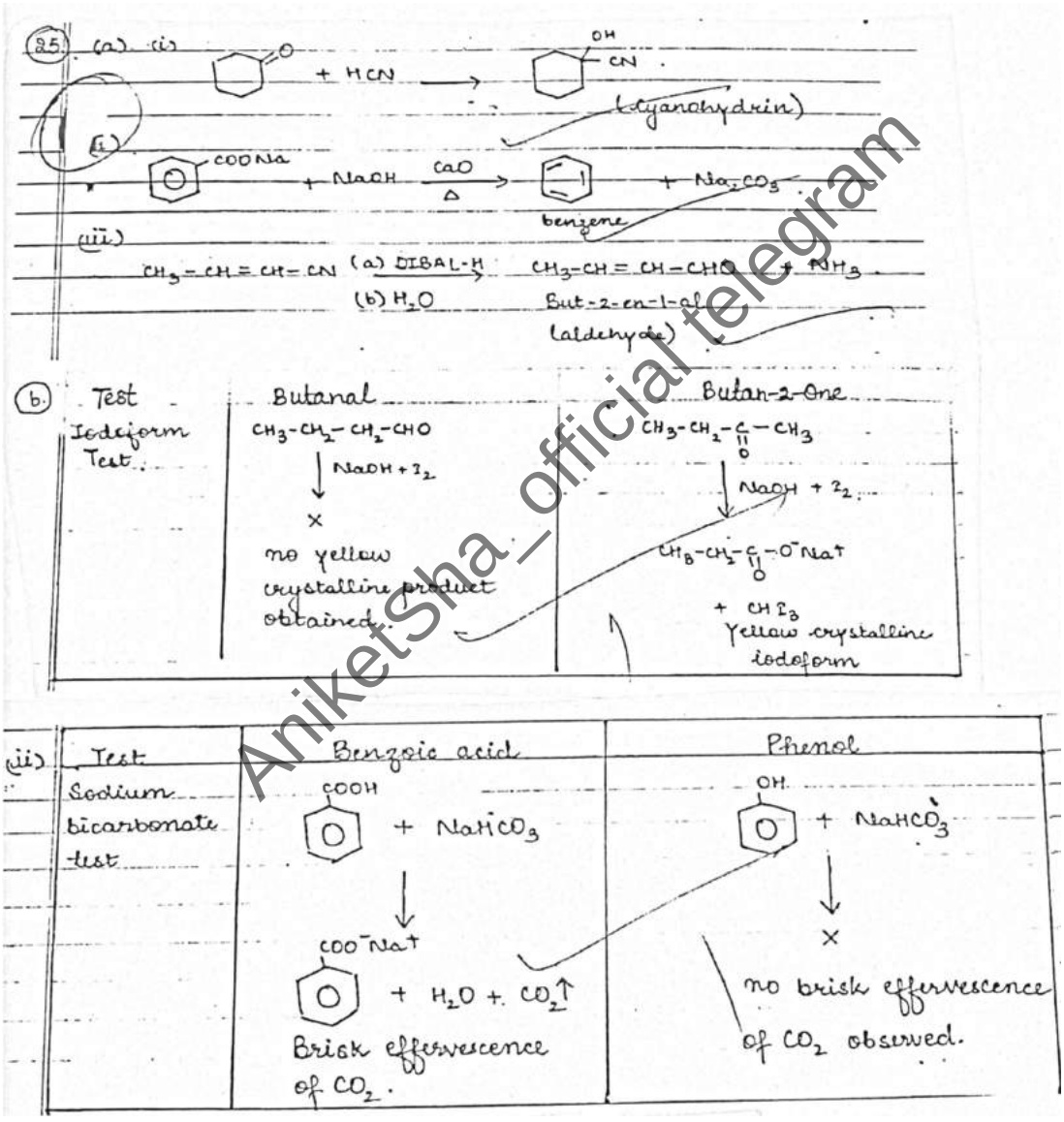
1

(or any other correct method)
[CBSE Marking Scheme 2017]

OR

Answering Tip

- Write each step of the chemical reaction. Mention the reagents involved in each step.



5

[Topper's Answer 2017]

Q. 11. (i) Account for the following :

(a) Propanal is more reactive than propanone towards nucleophilic reagents.

(b) Electrophilic substitution in benzoic acid takes place at meta position.

(c) Carboxylic acids do not give characteristic reactions of carbonyl group.

(ii) Give simple chemical test to distinguish between the following pairs of compounds:

(a) Acetophenone and benzaldehyde

(b) Benzoic acid and ethylbenzoate A&E + A

OR

(i) Write structures of A, B, C and D in the following reaction sequence:

$$CH_3COCl \xrightarrow{H_2/\text{Pd-BaSO}_4} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta}$$
$$\downarrow CH_3MgBr/H_3O^+$$
$$D$$

(ii) Arrange the following compounds in the increasing order of their boiling points :

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, CH_3COOH

A + U **[CBSE Comptt. OD Set-1, 2, 3 2017]**

Ans (i) (a) Due to steric and +I effect of two methyl groups in propanone. **1**

(b) Because it is a deactivating group/Due to electron withdrawing carboxylic group resulting in decreased electron density at o- and p- position. **1**

(c) Due to resonance, electrophilicity of carbonyl carbon is reduced. **1**

(ii) (a) Add NaOH and I_2 to both the compounds and heat, acetophenone forms yellow ppt of iodoform. **1**

(b) Add $NaHCO_3$ solution to both the compounds, benzoic acid will give effervescence and liberates CO_2.

(Or any other suitable test) 1

Answering Tips

- Give cause and consequence of the condition.
- Name the reagents involved in the distinction of the compounds.

OR

(i) A: CH_3CHO; B: CH_3-CH(OH)-CH_2-CHO; C: CH_3-CH=CH-CHO; D: CH_3-CH(CH_3)-OH 1x4

(ii) CH_3-O-CH_3<CH_3CHO<CH_3-CH_2-OH < CH_3-COOH **1**

[CBSE Marking Scheme 2017]

Detailed Answer :

(i) (a) Propanone is sterically more hindered than propanal due to presence of alkyl group on both sides of carbonyl carbon, making them less reactive towards nucleophilic attack as both methyl groups have electron releasing tendency due to -I effect. These alkyl groups makes ketone less reactive by donating an electron to a carbonyl group. **1**

(b) –COOH is an electron withdrawing group which deactivates the benzene ring lowering the electron density at ortho and para position in comparison to meta position. Electrophiles easily attacks at meta position. Therefore, due to higher density at meta position electrophilic substitution takes place at meta position. **1**

(c) Carbonyl carbon present in ketones and aldehyde is more electrophilic than in carboxylic acids. This is due to lone pairs on oxygen atom attached to hydrogen atom in the –COOH group causing resonance thereby making the carbon atom less electrophilic. Thus, carboxylic acids do not give characteristic reaction of carbonyl group. **1**

(ii) (a) Tollen's test :

Benzaldehyde being an aldehyde reduces Tollen's reagent to give a red-brown precipitate of Cu_2O, but acetophenone being a ketone does not.

$$C_6H_5CHO + 2[Ag(NH_3)_2]^+ + 3O\bar{H} \longrightarrow C_6H_5CO\bar{O} + Ag\downarrow + 4NH_3 + 2H_2O$$ **1**

Silver mirror

(b) Sodium bicarbonate test : Acid reacts with $NaHCO_3$ to produce brisk effervescence due to evolution of CO_2 gas. As benzoic acid is an acid, it gives positive test while ethylbenzoate does not. **1**

Q. 12. (i) How will you convert:

(a) Benzene to acetophenone

(b) Propanone to 2-Methylpropan-2-ol

(ii) Give reasons:

(a) Electrophilic substitution in benzoic acid take place at meta position.

(b) Carboxylic acids are higher boiling liquids than aldehydes, ketones and alcohols of comparable molecular masses.

(c) Propanal is more reactive than propanone in nucleophilic addition reactions. A + A&E

OR

(i) Write the products of the following reaction:

(a)  $=O + NH_2 - NH - \overset{\overset{O}{\|}}{C} - NH_2 \xrightarrow{H^+}$

(b) $CH_3MgBr + CO_2 \xrightarrow[H_3O^+]{\text{Dry ether}}$

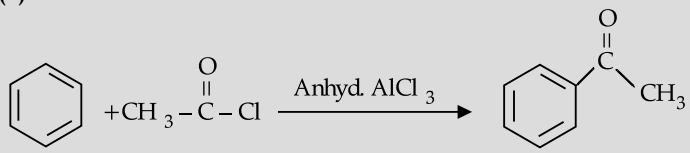
(c) $CH_3CH_2COOH + Br_2 \xrightarrow{\text{Red Phosphorus}}$

(ii) Write simple chemical tests to distinguish between the following pairs of compounds.

(a) Propanal and propanone

(b) Benzaldehyde and Benzoic acid A **[CBSE Comptt. Delhi Set-1, 2, 3 2017]**

Ans (i) (a)



(b) $CH_3CO CH_3 + CH_3MgBr \longrightarrow CH_3-C(CH_3)_2-OMgBr \xrightarrow{H_2O} CH_3-C(CH_3)_2-OH$ **2**

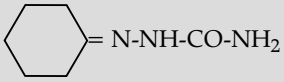
(ii) (a) Because it is a deactivating group/Due to electron withdrawing carboxylic group resulting in decreased electron density at o- and p- position. **1**

(b) Due to extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. **1**

(c) Due to steric and +I effect of two methyl groups in propanone. **1**

OR

(i) (a)



(b) CH_3COOH

(c) CH_3 — CH(Br)— COOH **1+1+1**

(ii) (a) Add ammonical solution of silver nitrate / Tollen's reagent to both the compounds, propanal will give silver mirror while propanone does not. **1**

(b) Add $NaHCO_3$ solution to both the compounds, benzoic acid will give effervescence and liberate CO_2 while benzaldehyde will not. **(Or any other suitable test) 1**

[CBSE Marking Scheme 2017]

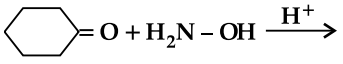
Detailed Answer:

(ii) (a) —COOH is an electron withdrawing group which deactivates the benzene ring lowering the electron density at ortho and para position in comparison to meta position. Electrophiles easily attacks at meta position. Therefore, due to higher density at meta position electrophilic substitution takes place at meta position. **1**

(b) The higher boiling point is due to polarity and carboxylic acids ability to form very strong intermolecular hydrogen bonds. **1**

(c) Propanone is sterically more hindered than propanol due to presence of alkyl group on both sides of carbonyl carbon, making them less reactive towards nucleophilic attack as both methyl groups have electron releasing tendency due to I effect. These alkyl groups make ketone less reactive by donating an electron to a carbonyl group. Hence, propanal is more reactive than propanone towards nucleophilic reagents. **1**

Q. 13. (i) Write the products of the following reactions :

(a) 

(b) $2C_6H_5CHO + \text{conc. } NaOH \longrightarrow$

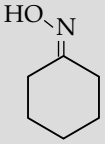
(c) $CH_3COOH \xrightarrow{Cl_2/P}$

(ii) Give simple chemical tests to distinguish between the following pairs of compounds:

(a) Benzaldehyde and Benzoic acid

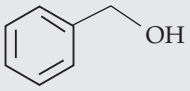
(b) Propanal and Propanone A **[CBSE SQP 2017; DDE]**

Ans (a)



1

(b)



½+½

(c) $Cl–CH_2–COOH$ **1**

(ii) (a) $NaHCO_3$ test. **1**

(b) Iodoform test./Fehling's Test/Tollen's Test **1**

[CBSE Marking Scheme 2017]

Detailed Answer :

Refer LAQ-II Ans.4. (ii)

AI **Q. 14. (i) Write the chemical reaction involved in Etard reaction.**

(ii) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction:

$CH_3 – CHO$, $C_6H_5COCH_3$, HCHO

(iii) Why pKa of $Cl — CH_2 — COOH$ is lower than the pKa of CH_3COOH?

(iv) Write the product in the following reaction.

$$CH_3CH_2CH=CH–CH_2CN \xrightarrow[2.\ H_2O]{1.\ (i\text{-}Bu)_2AlH}$$

(v) A and B are two functional isomers of compound C_3H_6O. On heating with NaOH and I_2, isomer A forms yellow precipitate of iodoform whereas isomer B does not form any precipitate. Write the formulae of A and B.

R + A&E + A **[CBSE OD Set-2 2016]**

Ans.

25:(a) Etard reaction is used to convert toluene or its derivatives into benzaldehyde and derivatives.

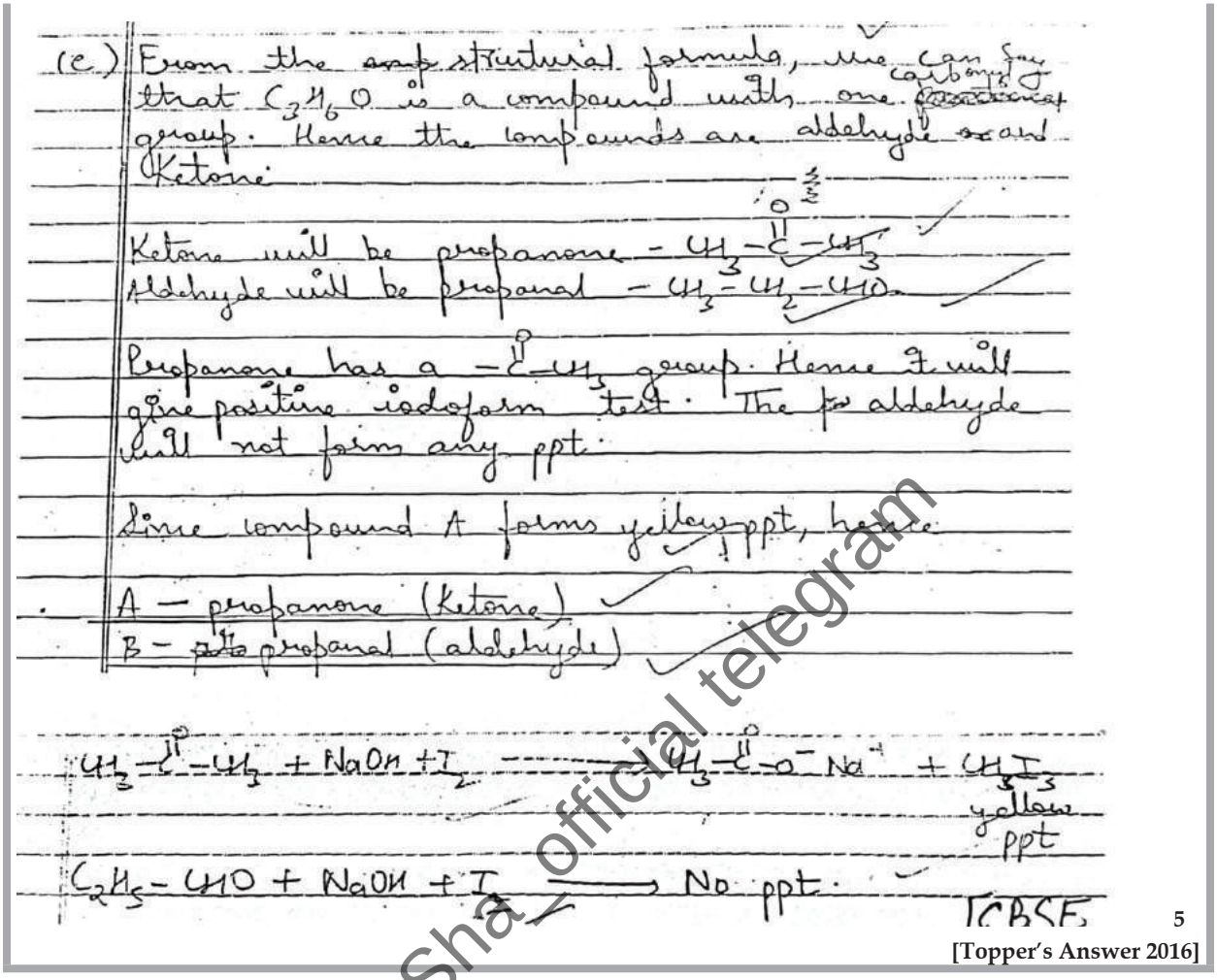
(b) $C_6H_5COCH_3 < CH_3CHO < HCHO$

The more electrophilic the carbonyl carbon, the more reactive is the compound to nucleophilic addition.

In Ketone, the +I group decreases the electrophilicity
In ethanal, the +I of $-CH_3$ is more less than that of $-C_6H_5$. Hence ethanal is more reactive than Ketone

(c) pKa of $Cl-CH_2-COOH$ is lower than ethanoic acid because 2-chloroethanoic acid is more acidic than ethanoic acid. This is because, through -I effect, the chlorine atom pulls the electron density towards itself i.e. it is electron withdrawing and stabilising the conjugate base of 2-chloroethanoic acid.

(d) $CH_3-CH_2-CH=CH-CH_2-C\equiv N \xrightarrow[2.\ H_2O]{1.\ (i\text{-}Bu)_2AlH} CH_3-CH_2-CH=CH-CH_2-CHO$



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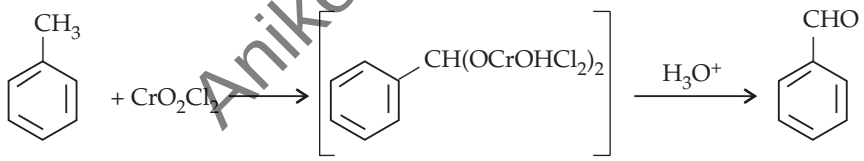
[Topper's Answer 2016]

Detailed Answer :

(i) Etard reaction :



1

(ii) $C_6H_5COCH_3 < CH_3CHO < HCHO$

The reactivity of the compound towards nucleophilic addition reaction is directly proportional to electrophilic character of carbonyl carbon. In ketone, the +I group lowers the electrophilicity. Whereas, +I of methyl group in ethanal is less than of $-C_6H_5$. Hence, ethanal is most reactive than acetophenone. **1**

(iii) –Cl being electron withdrawing group stabilizes the $ClCH_2COO^-$ anion and increases the acidic strength. Therefore, chloroacetic acid has lower pKa value than acetic acid. **1**

(iv) $CH_3CH_2CH=CH-CH_2CN \xrightarrow[2.\ H_2O]{1.\ (i\text{-}Bu)_2AlH} CH_3-CH_2-CH=CH-CH_2-CHO$

1

(v)

$$\underset{\text{A}}{\underset{\text{Propanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}} + NaOH + I_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Na} + \underset{\text{Yellow ppt.}}{CHI_3}$$

$$\underset{\text{B}}{\underset{\text{Propanal}}{C_2H_5CHO}} + NaOH + I_2 \longrightarrow \text{No ppt.}$$

1

Q. 15. (i) Give reasons :

(a) HCHO is more reactive than $CH_3 – CHO$ towards addition of HCN.

(b) pKa of $O_2N – CH_2 – COOH$ is lower than that of $CH_3 – COOH$.

(c) Alpha hydrogen of aldehydes & ketones is acidic in nature.

(ii) Give simple chemical tests to distinguish between the following pairs of compounds :

(a) Ethanal and Propanal

(b) Pentan-2-one and Pentan-3-one A&E + A

OR

(i) Write structure of the product(s) formed :

(a) $CH_3–CH_2–COOH \xrightarrow{Cl_2,\ red\ phosphorus}$

(b) $C_6H_5COCl \xrightarrow{H_2,\ Pd – BaSO_4}$

(c) $2HCHO \xrightarrow{Conc.KOH}$

(ii) How will you bring the following conversions in not more than two steps :

(a) Propanone to propene

(b) Benzyl chloride to phenyl ethanoic acid A **[CBSE Comptt. Delhi/OD 2018]**

Ans. (i) (a) Due to +I effect of methyl group in CH_3CHO. **1**

(b) due to –I effect of nitro group in nitroacetic acid. **1**

(c) Due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base. **1**

(ii) (a) Add NaOH and I_2 to both the compounds and heat, ethanal gives yellow ppt of iodoform. **1**

(b) Add NaOH and I_2 to both the compounds and heat, pentan-2-one gives yellow ppt of iodoform. **1**

OR

(i) (a) $CH_3–\underset{\displaystyle Cl}{\underset{|}{CH}}–CHO$ **1**

(b) C_6H_5CHO **1**

(c) $CH_3OH + HCOOK$ **1**

(ii) (a) $CH_3COCH_3 \xrightarrow{NaBH_4} CH_3CH(OH)CH_3 \xrightarrow{conc.\ H_2SO_4,\ 443K} CH_3–CH=CH_2$ **1**

(b) $C_6H_5CH_2Cl \xrightarrow{KCN} C_6H_5CH_2CN \xrightarrow{H_3O^+} C_6H_5CH_2COOH$ **1**

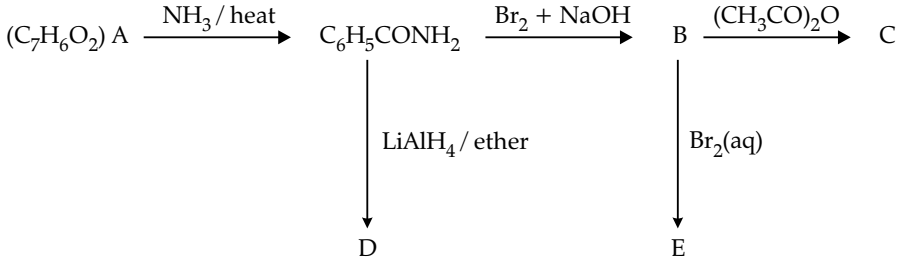
[CBSE Marking Scheme 2018]

Detailed Answer :

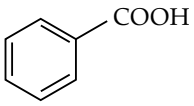
(i) (a) CH_3CHO has a comparitively bulky group attached to carbonyl group than HCHO which hinders the attack of nucleophile to some extent. Also, CH_3 group in CH_3CHO decreases the positive charge on carbonyl carbon by +I effect to some extent which doesn't take place in HCHO. Since, Nu attack is favourable with more positive charge and less hindrance at carbonyl carbon, hence HCHO is more reactive than CH_3CHO. **1**

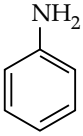
(b) Due to electron withdrawing nature of $-NO_2$ group in $O_2N–CH_2–COOH$ resulting in -I effect which increases the acidic strength and decreases the pKa value. **1**

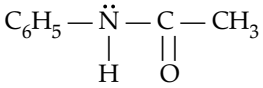
AI **Q. 16. An aromatic compound 'A' of molecular formula $C_7H_6O_2$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions :**



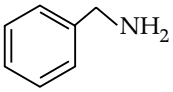
A **[CBSE OD 2015]**

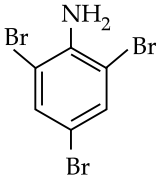
Ans. A = 

B = 

C = 

(1 each)

D = 

E = 

5

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