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ALDEHYDES KETONES CARBOXYLIC ACIDS

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XII ALDEHYDES

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Aldehydes Ketones Carboxylic Acids

CBSE – XIITH

Recap

ALDEHYDES AND KETONES

- **General formula :** $C_nH_{2n}O$ having $\rangle C{=}O$ group.
  - **Aldehydes :** $\begin{matrix}R\\H\end{matrix}\rangle C{=}O$; where R = H, alkyl or aryl.
  - **Ketones :** $\begin{matrix}R\\R\end{matrix}\rangle C{=}O$; where R = alkyl or aryl.
- **Nomenclature :** The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending –'*ic*' of acid with aldehyde.
  – The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –'*e*' with –'*al*' and –'*one*' respectively.
- **Structure :** The C-atom of carbonyl group is sp^2 hybridised and forms three σ-bonds and one π-bond with O atom. Carbonyl carbon with three atoms attached to it lie in a same plane with bond angle 120° (trigonal coplanar structure) and π-electron cloud lies above and below of this plane.
- **Preparation :**
  - **Oxidation of alcohols :**

$$RCH_2OH + [O] \xrightarrow[H_2SO_4\,(dil.)]{K_2Cr_2O_7} RCHO + H_2O$$

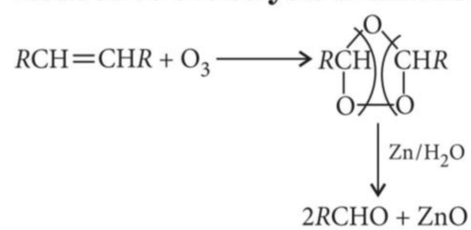
$$R_2CHOH + [O] \xrightarrow[H_2SO_4\,(dil.)]{K_2Cr_2O_7} R-\overset{O}{\overset{\|}{C}}-R + H_2O$$

  - **Catalytic dehydrogenation of alcohols :**

$$RCH_2OH \xrightarrow[573\,K]{Cu} RCHO + H_2\uparrow$$

$$R_2CHOH \xrightarrow[573\,K]{Cu} R_2CO + H_2\uparrow$$

  - **Reductive ozonolysis of alkenes :**



  - **Rosenmund reduction :**

$$RCOCl + H_2 \xrightarrow[\text{boiling xylene}]{Pd\text{-}BaSO_4,\,S} RCHO + HCl$$

  - **Reduction of nitriles :**

$$RC{\equiv}N \xrightarrow[(ii)\ H_2O]{(i)\ AlH(i\text{-}Bu)_2} RCHO$$

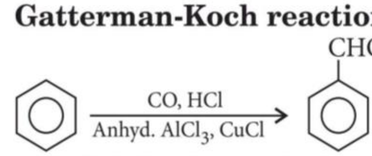
$$RC{\equiv}N \xrightarrow[(ii)\ H_3O^+]{(i)\ R'MgX/\text{dry ether}} RCOR'$$

$$RC{\equiv}N \xrightarrow[\text{Dry ether},\ (ii)\ H_3O^+]{(i)\ SnCl_2 + HCl} RCHO + NH_4Cl$$
(Stephen reduction)

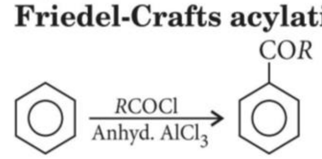
  - **From esters :**

$$RCOOR \xrightarrow[(ii)\ H_2O]{(i)\ \text{DIBAL-H, 195 K}} RCHO$$

  - **Gatterman-Koch reaction :**



  - **Friedel-Crafts acylation :**



  - **From alkynes :**

$$-C{\equiv}C- \xrightarrow[HgSO_4,\ 333\,K]{dil.\ H_2SO_4} RCHO \text{ or } RCOR$$

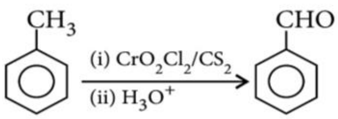
$$-C\equiv C- \xrightarrow[H_2O_2/OH^-]{B_2H_6,\ THF} RCHO \text{ or } RCOR$$

▶ **Oxidation of 1,2-glycols :**

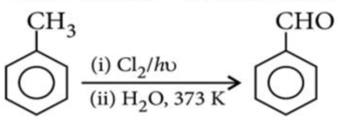
$$R-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-R' + Pb(OOCCH_3)_4 \longrightarrow RCHO + R'CHO$$

$$R_2\overset{OH}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}R'_2 \xrightarrow{[O]} RCOR + R'COR'$$

▶ **Etard reaction :**



▶ **Side chain chlorination :**



- **Physical properties :**
  - ▶ **Physical state :** Lower members of aldehydes and ketones (upto C_{10}) are colourless, volatile liquids except formaldehyde which is gas at ordinary temperature.
  - – Higher members of aldehydes and ketones are solids with fruity odour.
  - – Lower aldehydes have unpleasant odour but ketones possess pleasant smell.
  - ▶ **Boiling points :** The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses due to weak dipole-dipole interactions.
  - – Their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
  - – Among isomeric aldehydes and ketones, ketones have slightly higher boiling points due to the presence of two electron releasing alkyl groups which make carbonyl group more polar.
  - ▶ **Solubility :** Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water. However, solubility decreases with increase in molecular weight.
  - – Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger benzene ring.
  - – All carbonyl compounds are fairly soluble in organic solvents.

- **Chemical properties :**
  - ▶ **Nucleophilic addition reactions :**

$$>C=O \xrightarrow{HCN} >C<^{CN}_{OH}$$

Cyanohydrin

$$>C=O \xrightarrow{NaHSO_3} >C<^{SO_3Na}_{OH}$$

Bisulphite

$$>C=O \xrightarrow[(ii)\ H_3O^+]{(i)\ RMgX} >C<^{R}_{OH}$$

$$>C=O \xrightarrow[\text{dry HCl}]{\underset{CH_2OH}{\overset{CH_2OH}{|}}} >C<^{O-CH_2}_{O-CH_2}$$

$$>C=O \xrightarrow[\text{dry HCl}]{ROH} >C<^{OR}_{OH} \xrightarrow[\text{dry HCl}]{ROH} >C<^{OR}_{OR}$$

Hemiacetal   Acetal

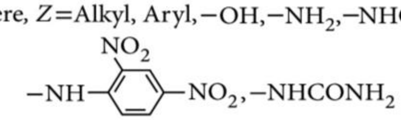
  - ▶ **Nucleophilic addition-elimination reactions :**

$$>C=O \xrightarrow[(ii)\ \Delta]{(i)\ NH_3} >C=NH$$

Imine

$$>C=O \xrightarrow[(ii)\ \Delta]{(i)\ NH_2-Z} >C=N-Z$$

[where, Z=Alkyl, Aryl, $-OH$, $-NH_2$, $-NHC_6H_5$,



]

  - ▶ **Oxidation :**

$$\underset{H}{\overset{R}{>}}C=O \xrightarrow{K_2Cr_2O_7/H^+} RCOOH$$

$$\underset{H}{\overset{R}{>}}C=O \xrightarrow[\text{Tollens' reagent}]{2[Ag(NH_3)_2]^+OH^-} RCOO^- + 2Ag\downarrow$$

Silver mirror test (Only aldehydes)

$$\underset{H}{\overset{R}{>}}C=O \xrightarrow[\text{+ Rochelle salt}]{2Cu^{2+},\ 5OH^-} RCOO^- + \underset{\text{red ppt.}}{Cu_2O\downarrow}$$

Fehling's solution test (Only aldehydes)

$$\underset{H}{\overset{R}{>}}C=O \xrightarrow[\text{+ sodium citrate}]{CuO \text{ or } Cu(OH)_2} RCOO^- + \underset{\text{Red ppt.}}{Cu_2O}$$

Benedict's solution test (Only aldehydes)

▶ **Reduction :**

$$R(R')C{=}O \xrightarrow[\text{Pt or Pd}]{H_2/\text{Ni or}} R(R')CHOH$$

$$R(R')C{=}O \xrightarrow{LiAlH_4 \text{ or } NaBH_4} R(R')CHOH$$

$$R(R')C{=}O \xrightarrow[\text{Clemmensen reduction}]{\text{Zn-Hg/HCl}} R(R')CH_2$$

$$R(R')C{=}O \xrightarrow{\text{HI/Red P, 423 K}} R(R')CH_2$$

$$R(R')C{=}O \xrightarrow[\text{Wolff-Kishner reduction}]{NH_2{-}NH_2/KOH} R(R')CH_2$$

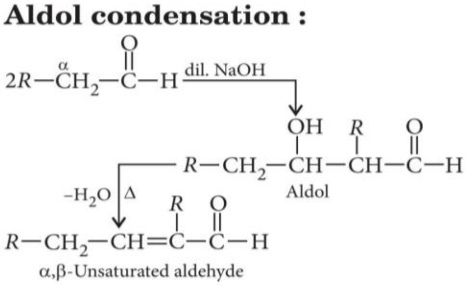
▶ **Haloform reaction :**

$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$

$RCOCH_3 + 3NaOI \longrightarrow RCOONa + \underset{\text{Iodoform (yellow ppt.)}}{CHI_3\downarrow} + 2NaOH$

(Given by compounds having CH_3CO— group or $CH_3CH(OH)$— group).

▶ **Aldol condensation :**



(aldehydes and ketones having at least one α-hydrogen)

– **Intramolecular aldol condensation :** It takes place in diketones and give rise to cyclic products.

– **Cross aldol condensation :** Aldol condensation is carried out between two different aldehydes and/or ketones and if both of them contain α-hydrogen atoms, it gives a mixture of four products.

▶ **Cannizzaro reaction :**

$$\underset{\text{Formaldehyde}}{HCHO + HCHO} \xrightarrow{\text{conc. KOH}} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Potassium formate}}{HCO\overset{-}{O}\overset{+}{K}}$$

(aldehydes which do not have an α-hydrogen atom)

▶ **Cross Cannizzaro reaction :**

$$C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}H + H{-}\overset{O}{\overset{\|}{C}}{-}H \xrightarrow{\Delta,\ OH^-} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. formate}}{HCO\overset{-}{O}\overset{+}{Na}}$$

– **Intramolecular Cannizzaro reaction:** It is given by dialdehydes having no α-hydrogen atoms.

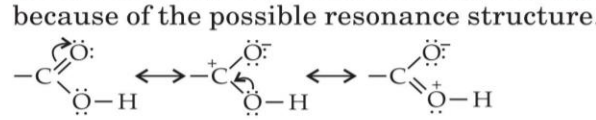
▶ **Electrophilic substitution reactions :** Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta* directing group.

▶ **Distinction between aldehydes and ketones :**

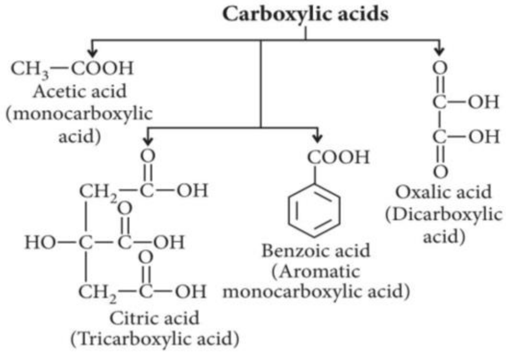
Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Silver mirror	No silver mirror
2,4-dinitrophenyl-hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.

CARBOXYLIC ACIDS

- **General Formula :** $C_nH_{2n}O_2$ having —COOH group.
  $RCOOH$ where, R=H or alkyl or aryl.
- **Nomenclature :** The common names end with the suffix –'*ic acid*' and have been derived from Latin or Greek names of their natural sources.
  – In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending –'*e*' in the name of the corresponding alkane with –'*oic* acid'. In numbering the carbon chain, the carboxylic carbon is numbered one.
- **Structure :** In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.



- **Classification :** They are classified as mono, di, tri and polycarboxylic acids depending upon the number of carboxyl groups present in a molecule.



- Aliphatic monocarboxylic acids and aliphatic esters are known as *functional isomers*. Some higher aliphatic monocarboxylic acids (C_{12}—C_{18}) are known as *fatty acids* because they occur in natural fats as esters of glycerol, *e.g.*, palmitic acid and stearic acid are obtained on hydrolysis of fats.

- **Preparation :**

$$\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow[K_2Cr_2O_7 + \text{dil. } H_2SO_4]{\text{Oxidation, alk. } KMnO_4,\ H_3O^+ \text{ or } CrO_3-H_2SO_4} RCOOH$$

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow[K_2Cr_2O_7 + \text{dil. } H_2SO_4 \text{ or Fehling's solution or Tollens' reagent}]{\text{Oxidation}} RCOOH$$

$$\underset{\text{Alkyl Cyanide}}{RCN} \xrightarrow[\text{Mineral acid HCl, } H_2SO_4\text{, etc.}]{\text{Hydrolysis}} RCOOH$$

$$\underset{\text{Alkyl Cyanide}}{RCN} \xrightarrow[\text{Alkali NaOH or KOH}]{\text{Hydrolysis}} RCOONa \xrightarrow{HCl} RCOOH$$

$$\underset{\text{Grignard reagent}}{RMgX} \xrightarrow[\text{dry ether}]{CO_2 \text{ (dry ice)}} RCOOH$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow[\Delta]{H_3O^+} RCOOH$$

$$\underset{\text{Acyl halide}}{RCOCl} \xrightarrow[\text{or, (i) } OH^-/H_2O \text{ (ii) } H_3O^+]{H_2O} RCOOH$$

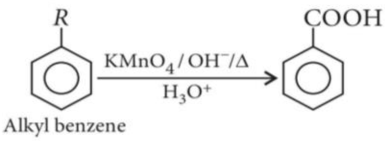
$$\underset{\text{Acid anhydride}}{(RCO)_2O} \xrightarrow{H_2O} RCOOH$$

$$\underset{\text{Ester}}{RCOOR'} \xrightarrow{H_3O^+,\ \Delta} RCOOH$$

$$\underset{\text{Ester}}{RCOOR'} \xrightarrow{NaOH,\ H_3O^+} RCOOH$$

$$\underset{\text{Alkene}}{RCH{=}CHR} \xrightarrow[\Delta,\ H_3O^+]{KMnO_4/OH^-} RCOOH$$

$$\underset{\text{Alkyne}}{RC{\equiv}CR} \xrightarrow[\Delta,\ H_3O^+]{KMnO_4/OH^-} RCOOH$$

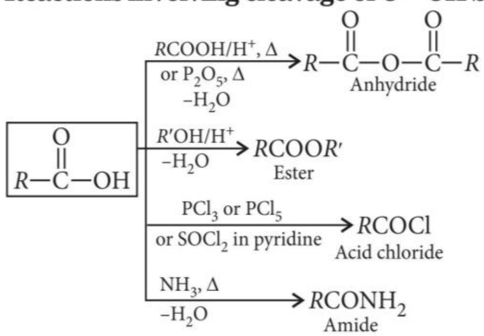


- **Physical Properties :**
  - ▶ **Physical state :** The lower fatty acids upto C_9 are colourless liquids. The higher ones are colourless waxy solids.
  - ▶ **Odour :** The first three members have a sharp pungent odour. The middle ones, C_4 to C_9, have an odour of rancid butter. The higher members do not possess any smell.
  - ▶ **Solubility :** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.
    - The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.
    - Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water.
    - Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.
  - ▶ **Boiling points :** Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses due to more extensive association of their molecules through intermolecular hydrogen bonding. The H-bonds are not broken completely even in the vapour phase.

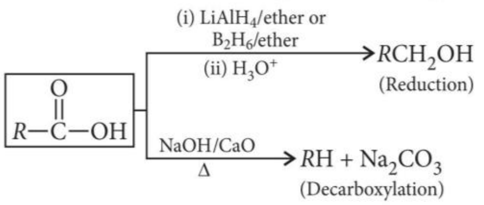
- **Chemical reactions :**
  - ▶ **Reactions involving cleavage of O—H bond :**

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Na_2CO_3} RCOONa + CO_2 + H_2O$$
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaHCO_3} RCOONa + CO_2 + H_2O$$
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Na} RCOONa + 1/2\, H_2$$
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaOH} RCOONa + H_2O$$

- **Reactions involving cleavage of C—OH bond:**



- **Reactions involving —COOH group :**

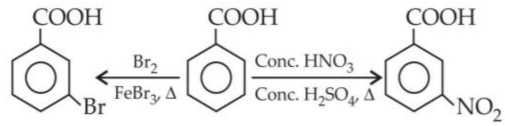


- **Hell—Volhard—Zelinsky reaction :**

$$RCH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red P}} R-\underset{\underset{X}{|}}{CH}-COOH$$

α-Halocarboxylic acid

- **Ring substitution in aromatic acids :** Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a *deactivating* and *meta* directing group.



- **Distinction test between phenol and carboxylic acid :**

Test	Phenol	Carboxylic acid
$NaHCO_3$ test	No reaction	Brisk effervescence of CO_2 gas.
$FeCl_3$ test	Violet colour	Buff coloured ppt.

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.*

Trend Analysis

List of Concepts	2018	2019		2020	
	D/OD	D	OD	D	OD
Conversions	1 Q (2 marks)	1 Q (2 marks)	1 Q (2 marks)	-	-
Writing the structure of product in the reaction	1 Q (3 marks)	1 Q (2 mark) 2 Q (3 marks)	1 Q (2 marks)	1 Q (1 mark) 2 Q (3 marks)	1 Q (2 marks)
Give reasons	1 Q (2 marks)	-	1 Q (2 marks)	3 Q (1 marks)	1 Q (2 marks)
Chemical Tests to distinguish between	-	-	1 Q (1 mark)	1 Q (2 marks)	1 Q (1 mark) 1 Q (3 marks)
Miscellaneous Type	1 Q (3 marks)	-	-	-	1 Q (1 mark) 1 Q (2 marks)

TOPIC-1
Aldehydes and Ketones

Revision Notes

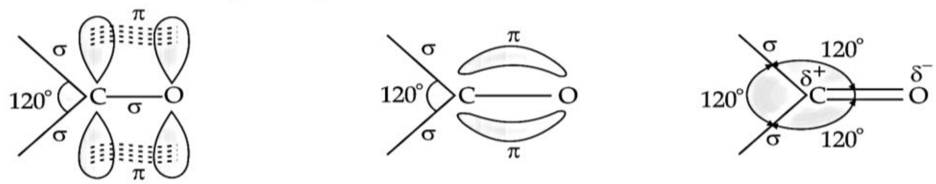
- **Carbonyl group :** The functional group >C=O is called carbonyl group. Organic compounds containing carbonyl group are aldehydes and ketones. The general formulae of these compounds are

$$\underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H} \qquad \underset{\text{Ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-R'}$$

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. *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
$CH_3CH_2CH_2CH_2-\overset{\overset{O}{\|\|}}{C}-H$	$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde	Pentanal
$CH_3-\underset{\underset{CH_3}{\|}}{CH}-CH_2-\overset{\overset{O}{\|\|}}{C}-H$	$CH_3-\underset{\underset{CH_3}{\|}}{CH}-CH_2CHO$	Isovaleraldehyde	3-Methylbutanal
$CH_3-CH_2-\underset{\underset{CH_3}{\|}}{CH}-\overset{\overset{O}{\|\|}}{C}-H$	$CH_3-CH_2-\underset{\underset{CH_3}{\|}}{CH}-CHO$	α-Methylbutyraldehyde	2-Methylbutanal

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

$CH_3-\overset{O}{\overset{\parallel}{C}}-CH_2-CH_2-CH_3$	$CH_3COCH_2CH_2CH_3$	Methyl *n*-Propyl ketone	Pentan-2-one
$CH_3-\underset{CH_3}{\underset{\mid}{CH}}-\overset{O}{\overset{\parallel}{C}}-\underset{CH_3}{\underset{\mid}{CH}}-CH_3$	$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2, 4-Dimethyl pentan-3-one
$CH_3-CH_2-\overset{O}{\overset{\parallel}{C}}-CH_2-CH_3$	$CH_3CH_2COCH_2CH_3$	Diethyl ketone	Pentan-3-one
$CH_3-\underset{CH_3}{\underset{\mid}{CH}}-\overset{O}{\overset{\parallel}{C}}-CH_3$	$(CH_3)_2CHCOCH_3$	Isopropyl methyl ketone	3-Methylbutan-2-one
$CH_3-\underset{CH_3}{\underset{\mid}{C}}=CH-\overset{O}{\overset{\parallel}{C}}-CH_3$	$(CH_3)_2C=CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

➢ **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.

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

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

(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 of alkenes or by hydration of alkynes.

(a) By ozonolysis of alkenes :

$$\underset{\text{Alkene}}{R-CH=CH-R'} + O_3 \longrightarrow R-CH\overset{O}{\underset{O-O}{\langle\ \rangle}}CH-R' \xrightarrow[-ZnO]{H_2O,\ Zn} \underset{\text{Aldehyde}}{R-CHO + R'-CHO}$$

(b) By hydration of alkynes :

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

(iv) From acyl chloride :

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

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

(v) From nitriles and esters :

$SnCl_2 + 2HCl \rightarrow SnCl_4 + 2[H]$

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

Stephen reaction :

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

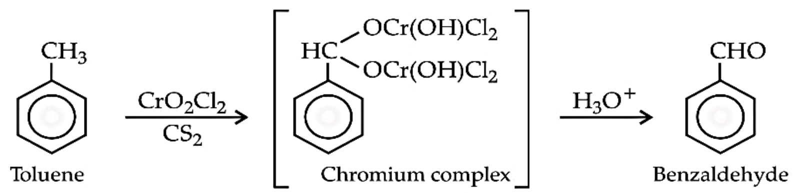
$$CH_3-CH=CH-CH_2-CH_2-CN \xrightarrow[2.\ H_2O]{AlH(i\text{-}Bu)_2} CH_3-CH=CH-CH_2-CH_2-CHO$$

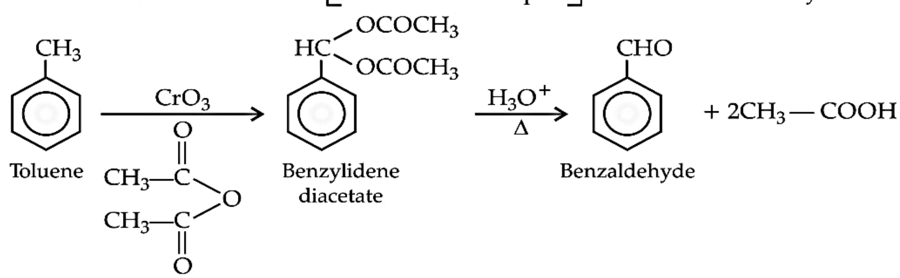
$$CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[2.\ H_2O]{1.\ DIBAL-H\ at\ -78^\circ C} \underset{\text{Aldehyde}}{CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-H}$$

(b) Preparation of Benzaldehyde :

(i) By oxidation of toluene :

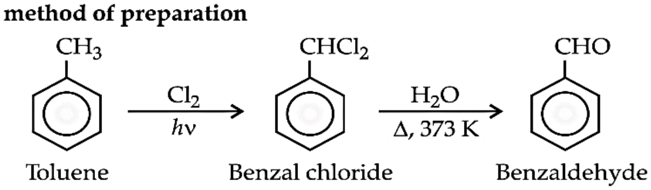
Etard reaction :



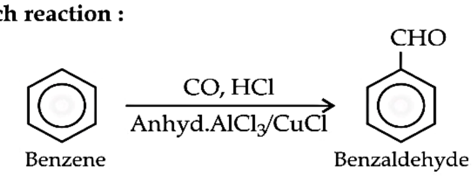


(ii) By side chain chlorination followed by hydrolysis :

Commercial method of preparation



(iii) By Gattermann - Koch reaction :



(c) Preparation of Ketones :

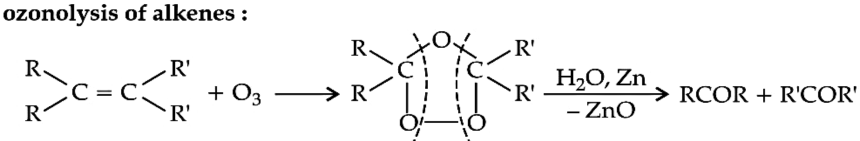
(i) By oxidation of secondary alcohols :

$$\underset{2^\circ\ \text{Alcohol}}{\begin{matrix}R\\R'\end{matrix}\!>CH-OH} + [O] \xrightarrow[\text{or } CrO_3]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Ketone}}{\begin{matrix}R\\R'\end{matrix}\!>C=O} + H_2O$$

(ii) By dehydrogenation of secondary alcohols :

$$\underset{2^\circ\ \text{Alcohol}}{\begin{matrix}R\\R'\end{matrix}\!>CH-OH} \xrightarrow[573K]{Cu} \underset{\text{Ketone}}{\begin{matrix}R\\R'\end{matrix}\!>C=O} + H_2$$

(iii) By ozonolysis of alkenes :



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

$$CH_3-C\equiv CH + \xrightarrow[\text{at } 60^\circ - 80^\circ C]{20\%\ H_2SO_4/HgSO_4} \underset{\text{Unstable}}{\left[CH_3-\overset{\overset{OH}{|}}{C}=CH_2\right]} \underset{}{\overset{\text{Tautomeric change}}{\rightleftharpoons}} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{||}}{C}-CH_3}$$

$$HC\equiv CH \xrightarrow[\substack{20\%\ H_2SO_4 \\ \text{at } 50^\circ - 60^\circ C}]{1\%\ Ag^+} [H_2C=\overset{\overset{OH}{|}}{C}H] \overset{\text{Tautomeric change}}{\rightleftharpoons} CH_3-CHO$$

(v) From acyl chlorides :

$$2R-MgX + CdCl_2 \rightarrow R_2Cd + 2MgXCl$$

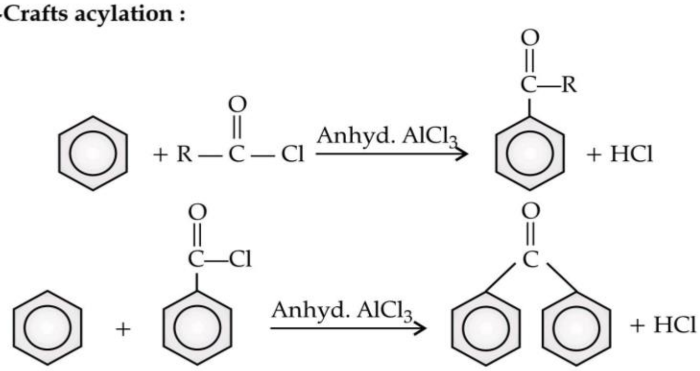
$$\underset{\text{Acyl chloride}}{2R'-\overset{\overset{O}{||}}{C}-Cl} + \underset{\text{Bialkyl cadmium}}{R_2Cd} \longrightarrow \underset{\text{Ketone}}{2R'-\overset{\overset{O}{||}}{C}-R} + CdCl_2$$

(vi) From nitriles :

$$\underset{\text{Ethyl magnesium bromide}}{CH_3-\overset{\delta^-}{C}H_2-\overset{\delta^+}{M}gBr} + CH_3-\overset{\delta^+}{C}\equiv\overset{\delta^-}{N} \xrightarrow{\text{ether}} CH_3-\underset{\underset{CH_2-CH_3}{|}}{C}=NMgBr \xrightarrow{H_3O^+} \underset{\text{Ethylmethyl ketone}}{H_3C-\overset{\overset{O}{||}}{C}-CH_2-CH_3} + Mg\begin{matrix} NH_2 \\ Br \end{matrix}$$

(d) Preparation of Aromatic ketones :

(i) By Friedel-Crafts acylation :



Benzoyl chloride   Benzophenone

(ii) From nitriles :

$$\underset{\text{Ethyl cyanide}}{CH_3-CH_2-C\equiv N} + C_6H_5MgBr \xrightarrow{\text{Ether}} CH_3-CH_2-\overset{\overset{NMgBr}{||}}{C}-C_6H_5 \xrightarrow{H_3O^+} \underset{\text{Propiophenone}}{CH_3-CH_2-\overset{\overset{O}{||}}{C}-C_6H_5} + Mg\begin{matrix} NH_2 \\ Br \end{matrix}$$

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

  Nucleophilic addition reactions :

  (i) Addition of hydrogen cyanide (HCN) :

$$HCN + OH^- \rightleftharpoons :\bar{C}N + H_2O$$

$$>\overset{\delta+}{C}=\overset{\delta-}{O} + :\bar{C}N \rightleftharpoons \left[>C<^{O^-}_{CN}\right] \xrightleftharpoons{H^+} >C<^{CN}_{OH}\ \text{(Cyanohydrin)}$$

$$>C<^{CN}_{OH} \xrightarrow{H_3O^+} -\underset{|}{\overset{OH}{\overset{|}{C}}}-COOH \quad \alpha\text{–Hydroxy acid}$$

$$>C<^{CN}_{OH} \xrightarrow{LiAlH_4} -\underset{|}{\overset{OH}{\overset{|}{C}}}-CH_2-NH_2 \quad \beta\text{–amino alcohol}$$

(ii) Addition to sodium hydrogen sulphite :

$$>C=O + NaHSO_3 \rightleftharpoons >C<^{SO_3H}_{ONa} \rightleftharpoons >C<^{SO_3Na}_{OH}$$

Bisulphite (addition compound)

(iii) Addition of Grignard reagent :

$$>\overset{\delta+}{C}=\overset{\delta-}{O} + \overset{\delta-}{R}\overset{\delta+}{MgX} \longrightarrow >C<^{OMgX}_{R} \xrightarrow{H_2O/H^+} >C<^{OH}_{R} + Mg<^{OH}_{X}$$

Aldeyde or ketone compound; Grignard reagent; Alcohol

(iv) Addition of alcohols :

$$\underset{H'}{\overset{R}{>}}C=O \underset{\text{HCl gas}}{\overset{R'OH}{\rightleftharpoons}} \underset{H'}{\overset{R}{>}}C<^{OH}_{OR'} \underset{\text{HCl gas}}{\overset{R'OH}{\rightleftharpoons}} \underset{H}{\overset{R}{>}}C<^{OR'}_{OR'} + H_2O$$

Aldehyde; Hemiacetal; Acetal

Ketones react with dihydric alcohols to give ketals.

$$\underset{R'}{\overset{R}{>}}C=O + \begin{matrix}CH_2-OH\\ |\\ CH_2-OH\end{matrix} \underset{\text{dil HCl}}{\overset{\text{HCl gas}}{\rightleftharpoons}} \underset{R'}{\overset{R}{>}}C<\begin{matrix}O-CH_2\\ |\\ O-CH_2\end{matrix} + H_2O$$

Ketone; Ethylene glycol; Ethylene glycol ketal

(v) Addition of ammonia and its derivatives :

$$>C=O + H_2N-Z \rightleftharpoons \left[>C<^{OH}_{NHZ}\right] \rightarrow >C=N-Z + H_2O,$$

where Z = Alkyl, aryl, –OH, $-NH_2$ C_6H_5NH-, $-NHCONH_2$ etc.

➢ **Reduction :**

(i) Reduction to alcohols :

$$\underset{\text{Aldehyde}}{R-CHO} + 2[H] \xrightarrow[NaBH_4]{LiAlH_4} \underset{1^\circ\ \text{Alcohol}}{R-CH_2-OH}$$

$$\underset{\text{Ketone}}{\underset{R}{\overset{R}{>}}C=O} + H_2 \xrightarrow{\text{Ni or Pt}} \underset{2^\circ\ \text{Alcohol}}{\underset{R}{\overset{R}{>}}CH-OH}$$

(ii) Reduction to hydrocarbons :

$$>C=O \xrightarrow[HCl]{Zn-Hg} >CH_2 + H_2O \ \textbf{(Clemmensen reduction)}$$

$$>C=O \xrightarrow[-H_2O]{NH_2NH_2} >C=NNH_2 \xrightarrow[\text{glycol, }\Delta]{\text{KOH/Ethylene}} >CH_2 + N_2$$

(Wolff-Kishner reduction)

➢ **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.

$$\underset{\text{Aldehyde}}{R-CHO} + [O] \xrightarrow[KMnO_4/H_2SO_4]{K_2Cr_2O_7/H_2SO_4 \text{ or}} \underset{\text{Carboxylic acid}}{R-COOH}$$

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

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 3[O] \xrightarrow{\text{Conc. } HNO_3} HCOOH + CH_3-COOH$$

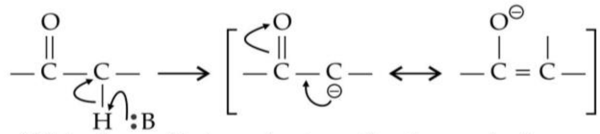
$$\overset{1}{C}H_3-\overset{\overset{O}{\|}}{\overset{2}{C}}-\overset{3}{C}H_2-\overset{4}{C}H_2-CH_3 \xrightarrow{K_2Cr_2O_7/H_2SO_4}$$

$\xrightarrow{C_1-C_2 \text{ bond Cleavage}} HCOOH + CH_3CH_2CH_2COOH$ (Minor product)

$\xrightarrow{C_2-C_3 \text{ bond Cleavage}} CH_3-COOH + CH_3-CH_2-COOH$ (Major product)

➢ **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 aldehydes (aldol) or β-hydroxy ketones (ketol).

$$2CH_3-CHO \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

3-Hydroxybutanal (Aldol) → But-2-enal

$$2CH_3-CO-CH_3 \overset{Ba(OH)_2}{\rightleftharpoons} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CO-CH_3 \xrightarrow[-H_2O]{\Delta} CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CO-CH_3$$

Ketol → 4-Methylpent-3-en-2-one

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

$$CH_3CHO + CH_3CH_2CHO \xrightarrow[2.\ \Delta,\ -H_2O]{1.\ \text{dil. NaOH}}$$

$CH_3-CH=CH-CHO$ + $CH_3CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CHO$

Simple or self aldol products

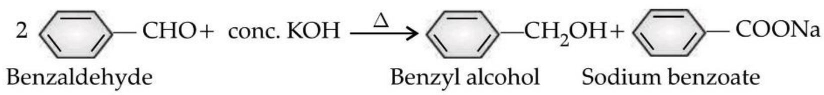
$CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CHO$ + $CH_3-CH_2-CH=CHCHO$

Cross aldol products

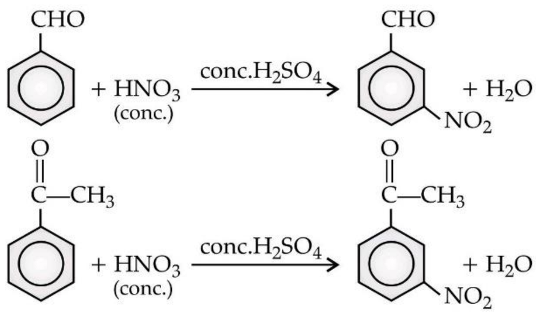
(iii) Cannizzaro Reaction : Aldehydes undergo self oxidation and reduction on heating with conc. alkali. The aldehydes which do not have α-hydrogen undergo this reaction.

$$H_2C{=}O + H_2C{=}O + \text{conc. KOH} \xrightarrow{\Delta} H{-}CH_2{-}OH + H{-}C(=O){-}OK$$

Formaldehyde — Methyl alcohol — Potassium formate



(iv) Electrophilic substitution reaction :



➢ **Test for Aldehydes and Ketones :**

(i) Both give iodoform test when one α-hydrogen is present.

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

$$R-CHO + 2CuO + 5OH^- \rightarrow R-COOH + \underset{\text{(red ppt.)}}{Cu_2O\downarrow} + 3H_2O$$

Aromatic aldehydes do not respond to this test.

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

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

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

Mnemonics

- **Concept:** To distinguish Aldehydes from Ketones. Detection tests - Tollen's and Fehling's
- **Mnemonic:** TASty FAAli Redbrown IMeLY
- **Interpretation:** TASty ⟶ Tollen's test, Aldehyde group, Silver mirror
  FAAli ⟶ Fehling's test, Aliphatic Aldehyde
  Red brown ⟶ Red brown ppt in Fehling's test
  IMeLY ⟶ Iodoform test, Methyl group Linked to -C=O- group, Yellow ppt
- **Concept:** Canniest's Reaction
- **Mnemonic:** CRAKN Reviews
- **Interpretation:** Canizzaro Reaction is given by Aldehydes and Ketones having no a-H atom.

Know the Terms

➢ **Tollen's Reagent :** Ammonical silver nitrate solution with which aldehydes give confirmatory silver mirror test.

➢ **Fehling's Solution :** Fehling A (aq. Copper sulphate) solution + Fehling B solution (alk. Sodium potassium tartarate). Aliphatic aldehydes reduce it to give reddish brown precipitate, which is a confirmatory test for aliphatic aldehydes.

- **Aldol Condensation:** Aldehydes and ketones with α-hydrogen in presence of dil alkali form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol).
- **Cannizzaro Reaction:** Aldehydes which do not contain α-hydrogen undergo self oxidation and reduction on heating with conc. alkali resulting in an alcohol and a carboxylic acid.

How is it done on the GREENBOARD?

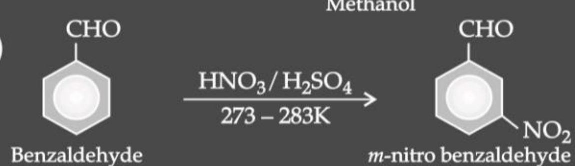
Q. Complete the following reactions :

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

(ii) 

Solutions:

STEP I: (i) $\underset{\text{Methanal}}{2H{-}\overset{O}{\overset{\|}{C}}{-}H} \xrightarrow{\text{Conc. KOH}} \underset{\text{Methanol}}{H{-}\overset{H}{\underset{H}{C}}{-}OH} + HCOOK$

STEP II: (ii) 

Objective Type Questions (1 mark each)

[A] MULTIPLE CHOICE QUESTIONS :

Q. 1. 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** U

Ans. Correct option : (b)

Explanation : Butan-2-ol is secondary alcohol which on oxidation with alkaline $KMnO_4$ solution gives butanone (ketone).

$$\underset{\text{Butan-2-ol}}{\begin{matrix}CH_3CH_2\\CH_3\end{matrix}\!\!>CHOH} + [O] \xrightarrow{\text{alk.}KMnO_4} \underset{\text{Butanone}}{\begin{matrix}CH_3CH_2\\CH_3\end{matrix}\!\!>C{=}O} + H_2O$$

Q.2. Write the IUPAC name of

$$CH_3{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}CHO$$

(a) 1-Aminopropanaldehyde **(b) 2-Aminopropanal**
(c) 1-Aminoethan-1-al **(d) None of the above** U

Ans. Correct option : (b)

Explanation :

$$\overset{3}{C}H_3-\underset{\displaystyle NH_2}{\underset{|}{\overset{2}{C}H}}-\overset{1}{C}HO$$

2-Amino propanal

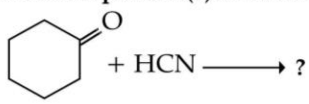
Q.3. What kind of compounds undergo Cannizaro reactions ?

(a) Ketones with no α- hydrogen
(b) Aldehydes with α- hydrogen
(c) Carboxylic acids with α- hydrogen
(d) Aldehydes with no α- hydrogen R

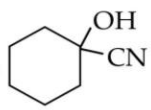
Ans. Correct option : (d)

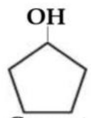
Explanation : Aldehydes with no α-hydrogen undergo Canizzaro reaction.

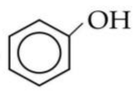
Q.4. Write the product(s) in the following reactions :



(a) No product formed

(b) 

(c) 

(d) 

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Ans. Correct option : (b)

Explanation :

It is a nucleophilic addition reaction.

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

$$CH_3CHO \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} (A) \xrightarrow{(i)\ H_2SO_4, \Delta} (B) \xrightarrow[\text{oxidation}]{\text{Hydroboration}} (C)$$

(a) identical **(b) positional isomers**

(c) functional isomers **(d) optical isomers** A

Ans. Correct option : (b)

Explanation :

$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} \underset{\substack{\text{Propan—2—ol} \\ (A)}}{CH_3—\underset{|}{\overset{}{CH}}(CH_3)—OH} \xrightarrow[\text{Dehydration}]{H_2SO_4 . \Delta}$$

$$\underset{\substack{\text{Propene} \\ (B)}}{CH_3—CH=CH_2} \xrightarrow[\text{(Hydroboration Oxidation)}]{(i)\ BH_3,\ (ii)\ H_2O_2 / OH^{\circ}} \underset{\substack{\text{Propan-1-ol} \\ (C)}}{CH_3—CH_2—CH_2OH}$$

In compound A and C, position of –OH group is changed. So, these are positional isomers.

Q.6. 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

Ans. Correct option : (a)

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

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

Q.7. The reagent which does not react with both, acetaldehyde and benzaldehyde.

(a) Sodium hydrogen sulphite

(b) Phenyl hydrazine

(c) Fehling's solution

(d) Grignard reagent R

Ans. Correct option : (c)

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

$$CH_3CHO + 2CuO + 5OH^- \rightarrow CH_3COOH + \underset{\text{Red ppt.}}{Cu_2O\downarrow} + 3H_2O$$

Aromatic aldehydes (benzaldehyde) do not react with Fehling's solution.

Q.8. $C_6H_5 – CO – CH_3 \xrightarrow{NaOH/I_2}$? + ?

(a) $C_6H_5COOH + CH_4$

(b) $C_6H_5COONa + CHI_3$

(c) $C_6H_6 + CH_3COONa + HI$

(d) $C_6H_5CH_2COOH$ R

Ans. Correct option : (b)

Explanation :

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} \xrightarrow{NaOH/I_2} C_6H_5COONa + \underset{\text{Iodoform}}{CHI_3}$$

Q.9. Predict the product of the following reaction :

$$CH_3–\underset{\substack{| \\ CH_3}}{C}=O \xrightarrow[(ii)\ KOH/Glycol, \Delta]{(i)\ H_2N–NH_2} ?$$

(a) $CH_3CH_2CH_3$ **(b) $CH_3CHOHCH_3$**

(c) CH_3CH_2CHO **(d) $CH_3CONHCH_3$** R

Ans. Correct option : (a)

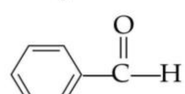
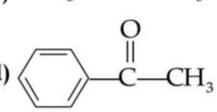
Explanation :

$$\underset{\text{acetone}}{CH_3–\underset{\substack{| \\ CH_3}}{C}=O} \xrightarrow[(ii)\ KOH/Glycol\ \Delta]{(i)\ H_2N–NH_2} \underset{\text{propane}}{CH_3–CH_2–CH_3}$$

It is a Wolff-Kishner reduction which converts $>C=O$ group into $–CH_2–$ group.

Q.10. Which of the following compounds is most reactive towards nucleophilic addition reactions ?

(a) $CH_3—\overset{\overset{O}{||}}{C}—H$ **(b)** $CH_3—\overset{\overset{O}{||}}{C}—CH_3$

(c)  **(d)**  U

Ans. Correct option : (a)

Explanation : Methyl benzaldehyde < Benzaldehyde < Propanone < Ethanal – reactivity towards nucleophilic substitution.

Aldehydes are more reactive than aliphatic ketones. Aliphatic ketones are more reactive than aromatic ketones.

The +I effect is more in ketone than in aldehyde. Thus ketone will be least reactive in nucleophilic addition reactions. The presence of electron withdrawing group increases the reactivity towards the addition while the presence of electron donating group decreases the reactivity of compound towards nucleophilic addition.

Benzaldehyde does not favour nucleophilic addition reaction due to resonance stabilisation.

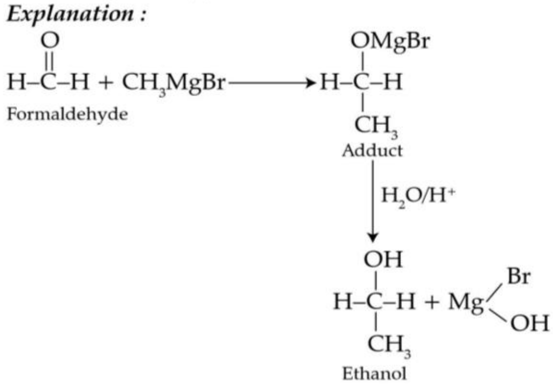
Q.11. Formaldehyde reacts with methyl magnesium bromide followed by hydrolysis to form.

(a) Methanol **(b) Ethanol**

(c) Propanol **(d) Butanol** R

Ans. Correct option : (b)

Explanation :



[B] ASSERTIONS AND REASONS

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

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

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

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

AI Q.1. Assertion (A) : Oxidation of ketones is easier than aldehydes.

Reason (R) : C–C bond of ketones is stronger than C–H bond of aldehydes.

[CBSE, Delhi Set 1, 2020]

Ans. Correct option : (d)

Explanation : Oxidation of aldehydes are easier than ketones.

AI Q. 2. Assertion (A) : Benzaldehyde is less reactive than ethanal towards nucleophilic addition reactions.

Reason (R) : Ethanal is more sterically hindered.
[CBSE, Delhi Set 3, 2020]

Ans. Correct option : (b)

Explanation : The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of carbonyl group present in ethanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance hence it is less reactive than ethanal towards nucleophilic addition reaction.

Q. 3. Assertion (A) : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason (R) : Aromatic aldehydes are almost as reactive as formaldehyde. U

Ans. Correct option : (c)

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

Q. 4. Assertion (A): Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.

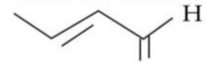
Reason (R): Both aldehydes and ketones contain a carbonyl group. R

Ans. Correct option : (d)

Explanation : Both aldehydes and ketones have carbonyl group but only aldehydes react with Tollens' reagent to give silver mirror.

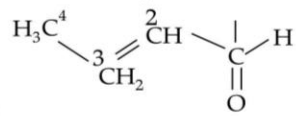
[C] VERY SHORT ANSWER TYPE QUESTIONS :

Q.1. Write the IUPAC name of



A

Ans.



IUPAC name = But-2-enal

AI Q.2. Write the IUPAC name of the following :

$CH_3 - CH_2 - CHO$ A **[CBSE Comptt. OD 2015]**

Ans. Propanal.

[CBSE Marking Scheme 2015]

AI Q.3. Write the IUPAC name of

$CH_3—CH—CHO$ with **NH_2** on the middle carbon A **[CBSE OD 2014]**

Ans. 2-Aminopropanal.

Q. 4. Draw the structure of 3-methylpentanal.

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

Ans. $CH_3 — CH_2 — CH — CH_2 — CHO$ with CH_3 on the CH

[CBSE Marking Scheme 2015]

AI Q.5. What type of aldehydes undergo cannizaro reaction?

U **[CBSE Comptt. Delhi Set-1, 2, 3 2017; DDE]**

Ans. Having no α-hydrogen.

[CBSE Marking Scheme 2017]

Q. 6. 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. $C_6H_5COCH_3$

[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 decolourise 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).

Q. 7. $(CH_3)_3C–CHO$ does not undergo aldol condensation. Comment. A&E

Ans. No α-H is present.

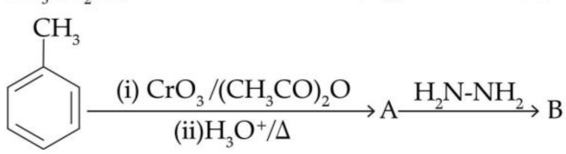
Q. 8. Out of $CH_3CH_2COCH_2CH_3$ and $CH_3CH_2CH_2COCH_3$, which gives iodoform test. A&E

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

Short Answer Type Questions-I (2 marks each)

AI Q.1. Write structures of main compounds A and B in each of the following reactions :

(i) $CH_3CH_2CN \xrightarrow{CH_3MgBr\,/\,H_3O^+} A \xrightarrow{LiAlH_4} B$

(ii) 

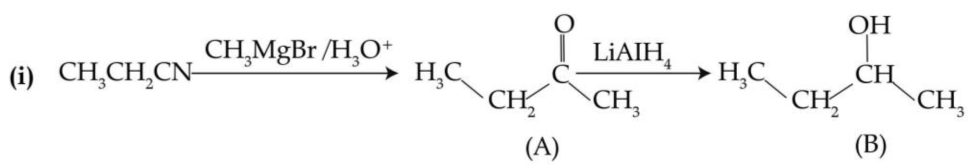
U [CBSE, Delhi Set 3, 2019]

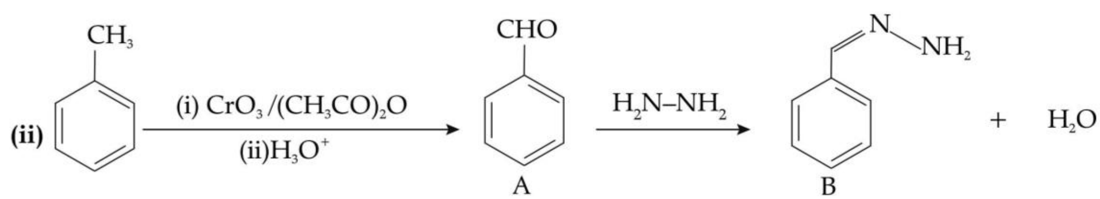
Ans. A ⇒ $CH_3CH_2CO\text{-}CH_3$, B ⇒ $CH_3CH_2\text{–}CH(CH_3)\text{–}OH$ [½ + ½]

A ⇒ C_6H_5CHO, B ⇒ $C_6H_5\text{–}CH{=}N\text{–}NH_2$ [½ + ½]

[CBSE Marking Scheme 2019]

Detailed Answer :





[2]

Q.2 Write structures of main compounds A and B in each to the following reactions:

(a) $CH_3CH_2OH \xrightarrow{PCC} A \xrightarrow{CH_3OH/dry\ HCl(g)} B$

(b) $C_6H_5COCH_3 \xrightarrow{NaOI} A + B$

U [CBSE, Delhi Set 3, 2019]

Ans. (a) A = CH_3CHO B= $CH_3CH(OH)OCH_3$

(b) A and B = CHI_3, C_6H_5COONa [½ × 4]

[CBSE Marking Scheme 2019]

Detailed Answer :

(a) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PCC} \underset{\text{Ethanal (A)}}{CH_3CHO}$ 3

$\xrightarrow{CH_3OH/dry\ HCl(s)} \underset{\text{1–methoxy ethanol (B)}}{CH_3CH(OH)OCH_3}$

(b) $\underset{\text{Acetophenone}}{C_6H_5COCH_3} \xrightarrow{NaOI} \underset{\text{Iodoform (A)}}{CHI_3} + \underset{\text{Sodium benzoate (B)}}{C_6H_5COONa}$ [2]

Commonly Made Error

- Some students give wrong products.

Answering Tip

- Do practice for organic reactions.

AI Q.3. Write the equations involved in the following reactions :

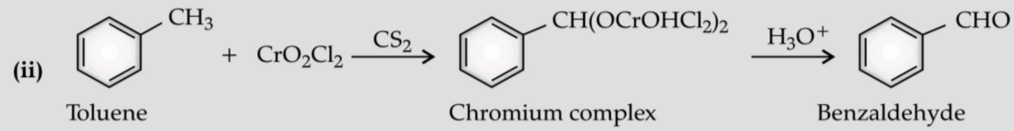
(i) Wolff-Kishner reduction

(ii) Etard reaction. R [CBSE, Delhi Set 1, 2017]

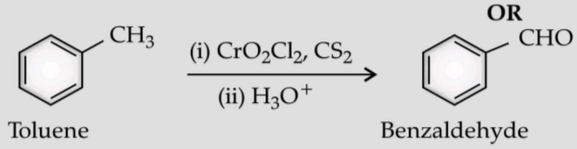
Ans. (i) $>C{=}O \xrightarrow[-H_2O]{NH_2NH_2} >C{=}NNH_2 \xrightarrow[heat]{KOH/ethylene\ glycol} >CH_2 + N_2$

OR

$>C{=}O \xrightarrow[\text{(ii) KOH/ethylene glycol, heat}]{\text{(i) }NH_2NH_2} >CH_2 + N_2$ [1]



OR



[1]

[CBSE Marking Scheme, 2017]

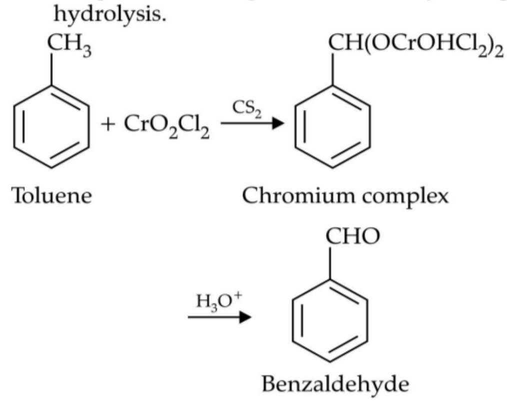
Detailed Answer :

(i) **Wolff-Kishner reduction** method is used to reduce a carbonyl compound like aldehyde or ketone to a hydrocarbon. The reduction reaction takes place when the carbonyl compound is heated with a mixture of hydrazine and a strong base like potassium hydroxide at a temperature range of 453 K to 473 K in ethylene glycol solvent.

$$>C=O \xrightarrow[-H_2O]{NH_2NH_2} >C=NH_2 \xrightarrow[\text{heat}]{KOH/\text{ethylene glycol}} >CH_2 + N_2$$

[1]

(ii) **Etard reaction** is a reaction in which chromyl chloride oxidises methyl group to a chromium complex which gives benzaldehyde upon hydrolysis.



[1]

Commonly Made Error

- Sometimes, student get confused between Wolff-Kishner reduction and Clemmensen reduction and write Clemmensen reduction in place of Wolff-Kishner reduction.

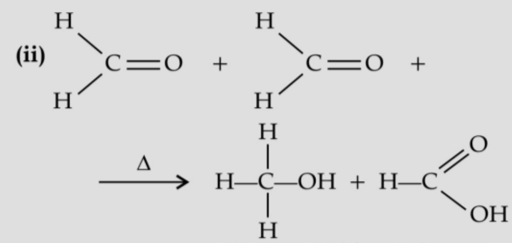
Answering Tip

- Learn and understand the above reduction reactions.

Q.4 **Write the reactions involved in the following reaction :**
(i) Clemmensen reduction
(ii) Cannizzaro reaction

R **[CBSE, Delhi Set 3, 2017]**

Ans. (i) $$>C=O \xrightarrow[HCl]{Zn-Hg} >CH_2 + H_2O$$ **[1]**



[1]

[CBSE Marking Scheme, 2017]

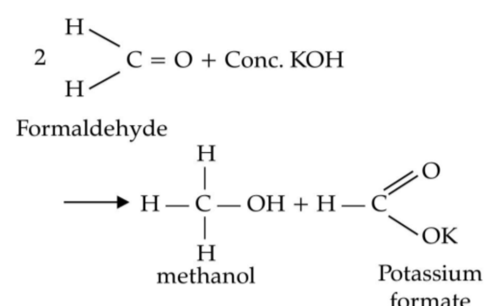
Detailed Answer :

(i) **Clemmensen reduction** is the process by which the carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc-amalgam and concentrated hydrochloric acid. The reaction involved in the process is :

$$>C=O \xrightarrow[HCl]{Zn-Hg} >CH_2 + H_2O$$

[1]

(ii) **Cannizzaro reaction** is one in which aldehydes which do not have an α-hydrogen atom, undergo self-oxidation and reduction (disproportionation) reaction on treatment with a concentrated alkali.

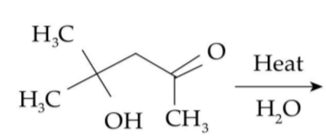


[1]

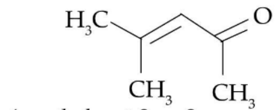
Q.5. **Write chemical equations for the following reactions :**
(i) Propanone is treated with dilute $Ba(OH)_2$.
(ii) Acetophenone is treated with Zn(Hg)/ Conc. HCl. R

Ans. (i)

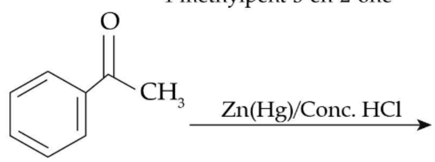
$$2CH_3-CO-CH_3 \overset{Ba(OH)_2}{\rightleftharpoons}$$



4-hydroxy-4-methylpentan-2-one

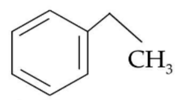


4-methylpent-3-en-2-one **[1]**

(ii) 

[1]

1-phenylethen-1-one



ethyl benzene

Q.6. **(i) What type of aldehydes undergo Cannizzaro reaction ?**

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

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

(b) $Cl-CH_2-COOH$, $F-CH_2-COOH$, CH_3-COOH (acidic character) R + A

Ans. (i) Having no α - hydrogen **[1]**

(ii) (a) $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$ **[½]**

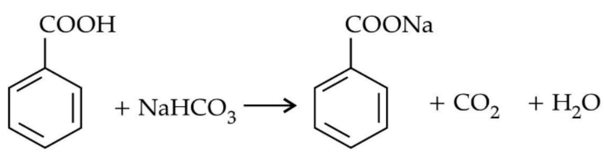
(b) $CH_3COOH < Cl-CH_2-COOH < F-CH_2-COOH$ **[½]**

Q.7. **Give simple chemical tests to distinguish between the following pairs of compounds :**

(a) Benzaldehyde and Benzoic acid

(b) Propanal and Propanone R

Ans. (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 Tollens' reagent to gives silver mirror but propanone being a ketone does not.

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

Q.8. **How will you convert the following :**

(a) Propanone to propan-2-ol

(b) Ethanal to 2-hydroxy propanoic acid R

Ans. (a)

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

(b)

$$\underset{\text{Ethanal}}{(H_3C)(H)C=O} + HCN \longrightarrow (H_3C)(H)C(OH)(CN) \xrightarrow[HCl]{H_2O} \underset{\text{2-Hydroxy propanoic acid}}{(CH_3)(H)C(OH)(COOH)}$$
[1]

Q.9. **Ketones are less reactive than aldehydes Why?** A

Ans. Ketones are less reactive than aldehydes due to following facts :

(i) Electron releasing effect

In ketones, the carbonyl carbon is attached to alkyl groups image from MS which are electron releasing in nature. These alkyl groups push electrons towards carbonyl carbon and therefore, decrease the magnitude of positive charge on it and make it less reactive toward nucleophilic attack. **[1]**

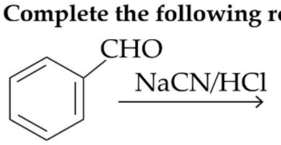
(ii) Steric effect

In ketones, the bulk of two alkyl groups also hinders the approach of the nucleophile to the carbonyl carbon. **[1]**

Short Answer Type Questions-II

(3 marks each)

AI **Q. 1. Complete the following reactions :**

(i) 

(ii) $(C_6H_5CH_2)_2Cd + 2CH_3COCl$

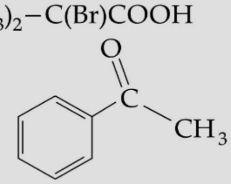
(iii) $CH_3-\overset{CH_3}{\overset{|}{CH}}-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(I) } Br_2/\text{Red P}}$

U **[CBSE Delhi Set-1, 2019]**

Ans. (i) $C_6H_5-CH(OH)-CN$ **[1]**

(ii) $2\,CH_3COCH_2C_6H_5 + CdCl_2$ **[1]**

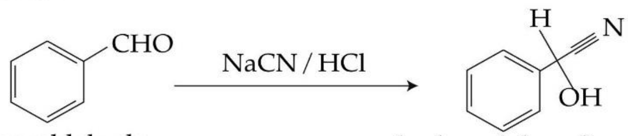
(iii) $(CH_3)_2-C(Br)COOH$ **[1]**



[CBSE Marking Scheme, 2019]

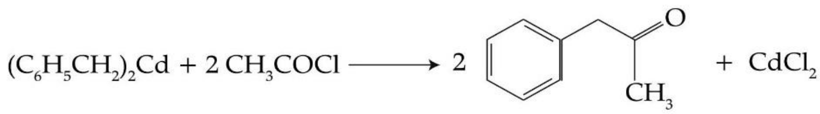
Detailed Answer :

(i)



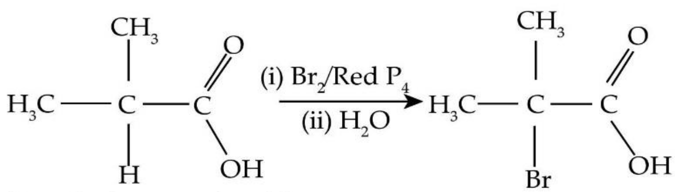
Benzaldehyde → hydroxy(phenyl)acetonitrile

(ii)



1-phenylpropan-2-one

(iii)



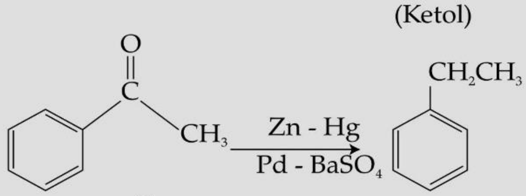
2-methylpropanoic acid → 2-bromo-2-methylpropanoic acid **[3]**

[AI] Q.2. Write chemical equations for the following reactions :
(i) Propanone is treated with dilute $Ba(OH)_2$.
(ii) Acetophenone is treated with Zn(Hg)/ Conc. HCl
(iii) Benzoyl chloride is hydrogenated in presence of $Pd/BaSO_4$. **[R] [CBSE Delhi Set-1, 2019]**

Ans. **(i)** $2CH_3-CO-CH_3 \underset{}{\overset{Ba(OH)}{\rightleftharpoons}} CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2CO-CH_3$ **[2]**

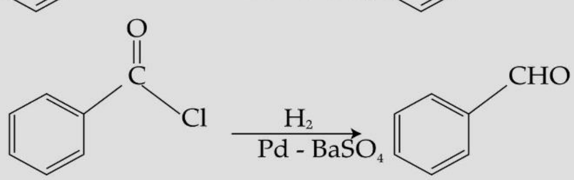
Propanone (Ketol)

(ii)



[1]

(iii)

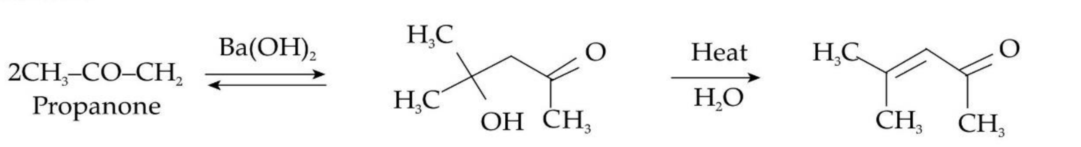


[1]

[CBSE Marking Scheme, 2019]

Detailed Answer :

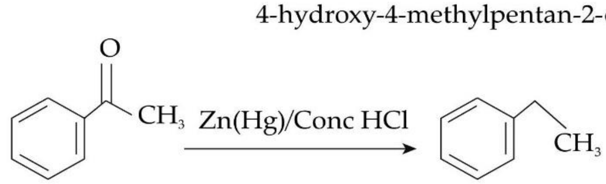
(i)



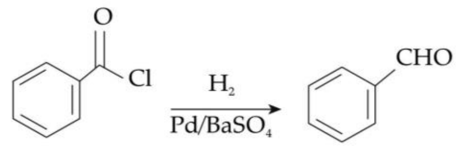
4-methylpent-3-en-2-one

4-hydroxy-4-methylpentan-2-one

(ii)



Acetophenone → Ethylbenzene

(iii) 

Benzoyl chloride → (H_2, Pd/$BaSO_4$) → Benzaldehyde

AI Q. 3. (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 ?

U + A [CBSE Delhi/Outside Delhi, 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 **[CBSE Marking Scheme, 2018] 1**

Detailed Answer :

(a) The possible non-cyclic functional isomers of a carbonyl compound having molecular formula. C_4H_8O are —

$CH_3-CH_2-CH_2-CHO$ (I)

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

$CH-CH(CH_3)-CHO$ (III)

Since isomer (B) does not give Tollen's test, it must be a ketone but it gives positive iodofo on test, so it must be methyl ketone. Hence, structure of (B) is (II).

The isomers (A) and (C) give positive Tollen's test so both the isomers are aldehydes. Since isomers (A) and (B) on reduction with Zn/Hg/ conc. HCl give the some product (D).

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

∴ Structure of (A) is (I) and

Structure of (C) is (III).

Hence, A ⇒ $CH_3-CH_2-CH_2-CHO$

B ⇒ $CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3$

C ⇒ $CH_3-\underset{\underset{CH_3}{|}}{CH}-CHO$

D ⇒ $CH_3-CH_2-CH_2-CH_3$

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

OR

The possible isomers of a carbonyl compound with molecular formula C_4H_8O are —

I: $CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3$ II: $CH_3-CH_2-CH_2-CHO$ III: $CH_3-\underset{}{\overset{\overset{CH_3}{|}}{CH}}-CHO$

Since isomer (B) does not give Tollens test. It must be a Ketone and it gives iodoform test, so it is a methyl Ketone ∴ structure of B is I.

(A) and (C) give positive Tollens test, so both are aldehydes. Since (A) and (B) give same product on reduction with Zn(Hg)/conc. HCl

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

∴ Structure of (A) is II
∴ Structure of (C) is III

(a) (A) → $CH_3-CH_2-CH_2-CHO$
Butanal

(B) → $CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3$
Butan-2-one

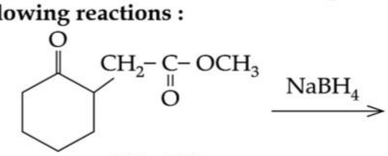
(C) → $_3CH_3-{_2}\underset{CH_3}{\underset{|}{CH}}-{_1}CHO$
2-methyl propanal

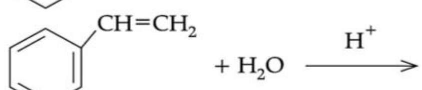
(D) → $CH_3-CH_2-CH_2-CH_3$
Butane

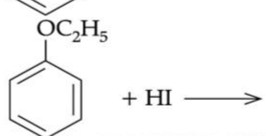
(b) (B) → $CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3$ is least reactive towards HCN addition.

[Topper's Answer 2018] [3]

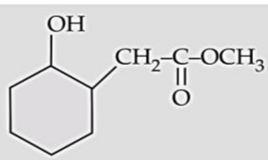
Q.4. Write the structures of the main products in the following reactions : **3**

(i) 

(ii) 

(iii) 

U + A [CBSE Delhi/Outside Delhi, 2018]

Ans. (i)  [1]

(ii) $C_6H_5CH(OH)CH_3$ [1]

(iii) $C_2H_5I + C_6H_5OH$ (No splitting of marks) [1]

[CBSE Marking Scheme, 2018]

AI Q.5. Predict the products of the following reactions :

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

(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]

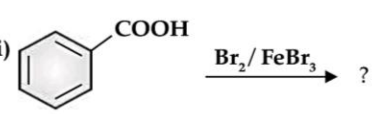
(iii) CH_4 [1]

[CBSE Marking Scheme 2015]

Q. 6. Predict the products of the following reactions :

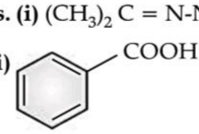
(i) $CH_3-\underset{CH_3}{\underset{|}{C}}=O \xrightarrow{H_2N-NH_2}$?

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

(iii) 

A [CBSE OD 2015]

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

(ii)  [1]

Benzoic acid

(iii)  [1]

m-Bromobenzoic acid

AI Q. 7. How will you bring about the following conversions :

(i) Propanone to propane

(ii) Benzoyl chloride to benzaldehyde.

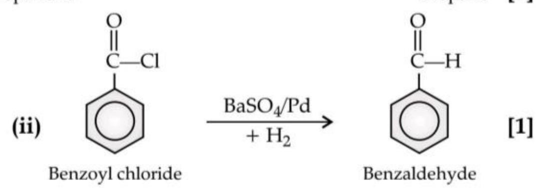
(iii) Ethanal to but-2-enal. A

Ans. (i)

$$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3 \xrightarrow[\text{Zn(Hg) + HCl (Conc.)}]{\text{Clemmensen Reduction}} CH_3-CH_2-CH_3$$

Propanone → Propane **[1]**

(ii)



[1]

(iii)

$$2CH_3-CHO \xrightarrow[\text{Aldol Condensation}]{\text{Dil.NaOH}} CH_3-\overset{\overset{\large OH}{|}}{CH}-CH_2-CHO$$

Ethanal → 3-hydroxybutanal

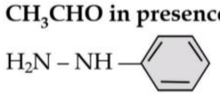
$$\xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

But-2-enal **[1]**

Long Answer Type Questions (5 marks each)

Q. 1. (a) Write the products formed when benzaldehyde reacts with the following reagents :

(i) CH_3CHO in presence of dilute NaOH

(ii) 

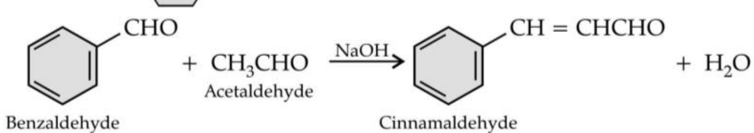
(iii) Conc. NaOH

(b) Distinguish between following:

(i) $CH_3-CH=CH-CO-CH_3$ and $CH_3-CH_2-CO-CH=CH_2$

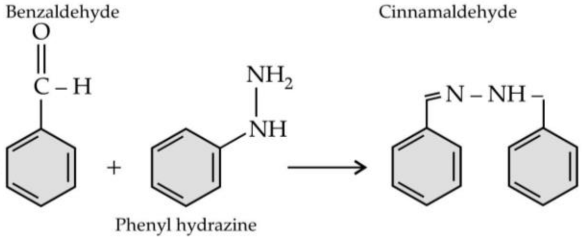
(ii) Benzaldehyde and Benzoic acid

Ans. (a) (i)



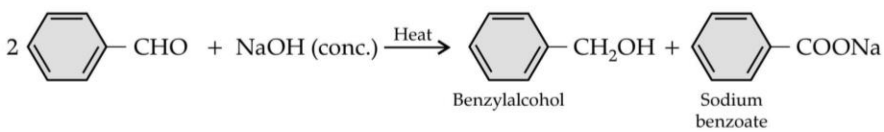
[1]

(ii)



[1]

(iii)



[1]

(b) (i) $CH_3-CH=CH-CO-CH_3$ gives iodoform test while $CH_3-CH_2-CO-CH=CH_2$ does not give.

$$CH_3-CH=CH-\underset{\underset{\large O}{\|}}{C}-CH_3+3NaOI \longrightarrow \underset{\text{Yellow ppt.}}{CH_3I}+2NaOH+CH_3-CH=CHCOONa$$ **[1]**

$CH_3CHCOCH=CH_2 + 3NaOI \rightarrow$ No ppt

(ii) (1) Benzaldehyde reacts with tollen's reagent to form silver mirror. Benzoic acid does not give this reaction.

(2) With $NaHCO_3$ benzaldehyde does not react while benzoic acid produces brisk effervescence. **[1]**

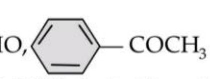
Q. 2. (a) Write the final products in the following :

(i) $$\overset{CH_3}{\underset{CH_3}{>}}C=O \xrightarrow[\text{Conc. HCl}]{\text{Zn / Hg}}$$

(ii) 

(iii) $$CH_2=CH-CH_2-CN \xrightarrow[\text{(b) } H_3O^+]{\text{(a) DIBAL–H}}$$

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

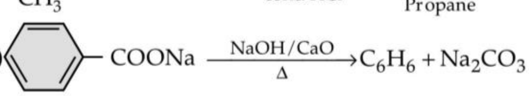
CH_3COCH_3, HCHO, CH_3CHO, 

(c) Draw the structure of 2, 4 DNP derivative of acetaldehyde. U + R **[CBSE Delhi Set-1, 2020]**

Ans. (a) (i)

$$\overset{CH_3}{\underset{CH_3}{>}}C=O + 4[H] \xrightarrow[\text{conc. HCl}]{\text{Zn/Hg}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O$$ **[1]**

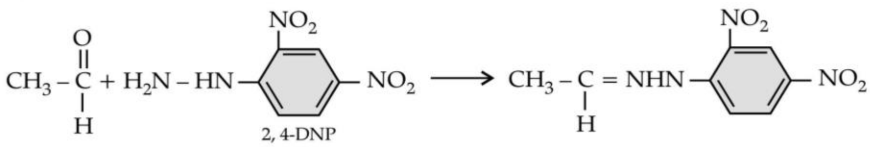
(ii)



[1]

(iii) $CH_2=CH-CH_2-CN \xrightarrow[(b)H_3O^+]{(a)DIBAL-H} CH_2=CH-CH_2-\overset{\overset{\large O}{||}}{C}-H$ **[1]**

(b)  $COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$ **[1]**

(c)  **[1]**

Commonly Made Error
• Some students get confused for arranging aldehydes and ketones in increasing order of their reactivity towards nucleophilic addition reaction.

Answering Tip
• Learn and understand the factors affecting reactivity (i.e. electron releasing effect and steric effect) of aldehydes and ketones towards nucleophilic addition reaction.

AI Q.3. (a) An organic compound (A) having molecular formula C_4H_8O gives orange red precipitate with 2, 4-DNP reagent. It does not reduce Tollens' reagent but gives yellow precipitate of iodoform on heating with NaOH and I_2. Compound (A) on reduction with $NaBH_4$ gives compound (B) which undergoes dehydration reaction on heating with conc. H_2SO_4 to form compound (C). Compound (C) on ozonolysis gives two molecules of ethanal.

Identify (A), (B) and (C) and write their structures. Write the reactions of compound (A) with (i) NaOH/I_2 and (ii) $NaBH_4$.

(b) Give reasons :

(i) Oxidation of propanal is easier than propanone.

(ii) α-hydrogen of aldehydes and ketones is acidic in nature.

Ans. (a) Compound A (C_4H_8O) gives positive, 2, 4-DNP test, it must be carbonyl compound. It gives iodoform test.

$$\underset{\text{(A) Butanone}}{CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3} \xrightarrow{NaBH_4} \underset{\text{(B) Butan-2-ol}}{CH_3-\overset{OH}{\underset{H}{C}}-CH_2-CH_3} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{(C) But-2-ene}}{CH_3CH=CHCH_3} \xrightarrow{\text{Ozonolysis}} \underset{\text{Ethanal}}{2CH_3CHO}$$ **[1]**

(i) $\underset{(A)}{CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3} \xrightarrow{NaOH/I_2} C_2H_5COOH + \underset{\text{Iodoform}}{CHI_3}$ **[1]**

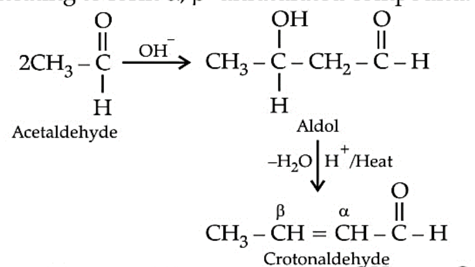
(ii) $\underset{(A)}{CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3} \xrightarrow{NaBH_4} \underset{\text{Butan-2-ol}}{CH_3-\overset{OH}{\underset{H}{C}}-CH_2-CH_3}$ **[1]**

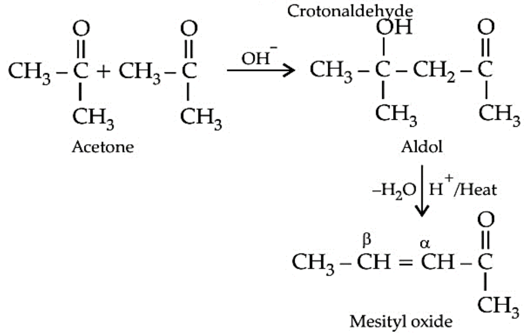
(b) (i) Oxidation of propanal is easier than propanone because aldehydes have one hydrogen atom attached to the carbonyl group while ketones have two alkyl or aryl groups attached to the carbonyl group. Propanal easily oxidised to form acid with same number of carbon atoms whereas propanone is difficult to be oxidise and form acids with less number of carbon atoms.

$$\underset{\text{Propanone}}{CH_3-\underset{\underset{O}{||}}{C}-CH_3} \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3-\overset{OH}{C}=CH_2 \xrightarrow{\text{Oxidation}} \underset{\text{Ethanoic acid}}{CH_3COOH} + CO_2 + H_2O$$ **[1]**

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H \xrightarrow{[O]} CH_3CH_2COOH$$

(ii) α-hydrogen of aldehydes and ketones is acidic in nature. They can be easily abstracted by suitable bases. Two molecules condense to form a β-hydroxyaldehyde or β-hydroxyketone which gets dehydrated in presence of acid upon heating to form α, β -unsaturated compound.





[1]

Q. 4. (a) Draw structures of the following derivatives :

(i) Cyanohydrin of cyclobutanone

(ii) Hemiacetal of ethanal

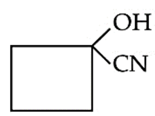
(b) Write the major product(s) in the following :

(i) $CH_3-CH=CH-CH_2-CN \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) DIBAL–H}}$

(ii) $CH_3-CH_2-OH \xrightarrow{CrO_3}$

(c) How can you distinguish between propanal and propanone? U + R **[CBSE Delhi Set-1, 2020]**

Ans. (a) (i) Cyanohydrin of cyclobutanone

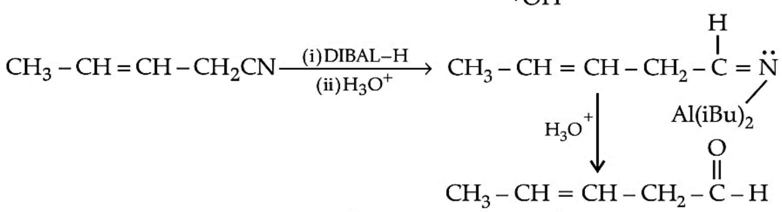


[1]

(ii) Hemiacetal of ethanol

$$CH_3-CH\begin{matrix} OR \\ OH \end{matrix}$$ **[1]**

(b) (i)



[1]

(ii) $CH_3-CH_2-OH \xrightarrow{CrO_3} [CH_3-\overset{\overset{O}{\|}}{C}-H] \longrightarrow [CH_3-\overset{\overset{O}{\|}}{C}-OH]$ **[1]**

(c) By iodoform test : Propanone on treatment with I_2/NaOH undergoes iodoform test to give a yellow ppt. of iodoform.

$$CH_3COCH_3 + 3NaOI \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3} + CH_3COONa + 2NaOH$$ **[1]**

Propanal does not give this test.

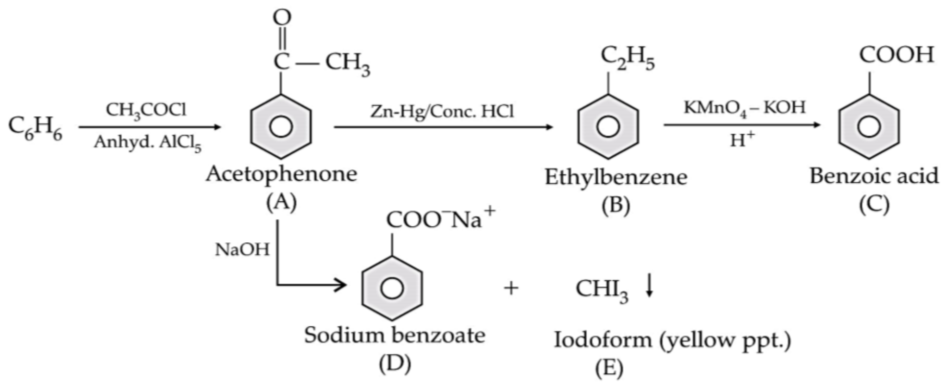
AI Q. 5. Write the structures of A, B, C, D and E in the following reactions :

$$C_6H_6 \xrightarrow[\text{Anhyd.AlCl}_3]{CH_3COCl} A \xrightarrow{\text{Zn–Hg/Conc.HCl}} B \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } KMnO_4-KOH,\Delta} C$$

$$A \xrightarrow{NaOH} D + E$$

Ans. A-$C_6H_5COCH_3$ **[1]**
B-$C_6H_5CH_2CH_3$ **[1]**
C-C_6H_5COOH **[1]**
D ,E -C_6H_5COONa, CHI_3 **[1+1]**
[CBSE Marking Scheme, 2016]

Detailed Answer :



Q. 6. (a) Write the chemical equation for the reaction involved in Cannizzaro reaction.

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

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

(d) Write the product in the following reaction

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

(e) How can you distinguish between propanal and propanone ?

U + R **[CBSE Delhi 2016]**

Ans. (a) $HCHO + HCHO \xrightarrow{conc.NaOH} HCOONa + CH_3OH$
(or any other example) **[1]**

(b) $CH_3CH=N–NHCONH_2$ **[1]**

(c) Stronger -I effect of fluorine, stronger acid less pk_a / strong electron withdrawing power of fluorine. **[1]**

(d) $CH_3CH=CHCH_2\ CHO$ **[1]**

(e) Silver mirror formed on adding ammonical silver nitrate to propanal and not with propanone. **[1]**
(or any other correct test)
[CBSE Marking Scheme, 2016]

Detailed Answer :

(a) $2HCHO \xrightarrow{50\%NaOH} CH_3OH + HCOONa$

(b) $CH_3-CH=N-NH-CO-NH_2$

(c) In FCH_2-COOH, fluorine is more electron withdrawing than chlorine in $ClCH_2-COOH$, so FCH_2-COOH, flurine is more acidic than $ClCH_2COOH$ hence its pK_a value is lesser than $ClCH_2COOH$.

(c) $CH_3-CH=CH-CH_2-CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL–H}} CH_3-CH=CH-CH_2-CHO$

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

(e) Propanal and propanone can be differentiated by Tollens' reagent i.e., propanal will give silver mirror but propanone will not.

$$CH_3-CH_2-CHO + 2[Ag(NH_3)_2]^+ \rightarrow CH_3-CH_2-COO^- + 2Ag\downarrow + H_2O + 4NH_3$$ **[1×5]**

Silver mirror

Q. 7. (a) Write the structures of A and B in the following reactions :

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

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

(b) Distinguish between :

(i) $C_6H_5-COCH_3$ **and** C_6H_5-CHO,

(ii) CH_3COOH **and** $HCOOH$.

(c) Arrange the following in the increasing order of their boiling points :
CH_3CHO, CH_3COOH, CH_3CH_2OH.

Ans. (a) (i) A : CH_3CHO, B : $CH_3CH{=}N{-}OH$ [½ + ½]
(ii) A : CH_3COOH , B : CH_3COCl [½ + ½]
(b) (i) Heat both compounds with NaOH and I_2, $C_6H_5COCH_3$ forms yellow ppt. of CHI_3 whereas C_6H_5CHO does not. [1]
(ii) Add ammonical solution of silver nitrate (Tollens' reagent) to both the compounds, HCOOH gives silver mirror but CH_3COOH does not.
(or any other suitable test) [1]
(c) $CH_3CHO < CH_3CH_2OH < CH_3COOH$ [1]
[CBSE Marking Scheme, 2016]

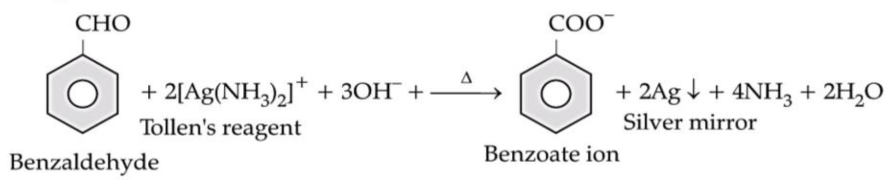
Detailed Answer :

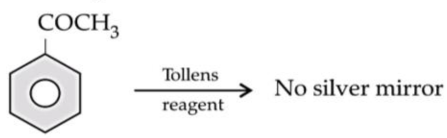
(a) (i) $CH_3COCl \xrightarrow{H_2, Pd-BaSO_4} CH_3CHO \xrightarrow[-H_2O]{H_2N-OH} CH_3{-}CH = N - OH$

[A] Acetaldehyde   [B] Acetaldoxime

(ii) $CH_3MgBr \xrightarrow[2H_3O^4]{1.\ CO_2} CH_3COOH \xrightarrow{PCl_5} CH_3COCl + HCl + POCl_3$

(b) (i) C_6H_5 CHO being an aldehyde reduces Tollens' reagent to shining silver mirror whereas $C_6H_5COCH_3$ being a ketone does not.





(ii) HCOOH gives silver mirror test with Tollens' reagent whereas ethanoic acid does not.

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

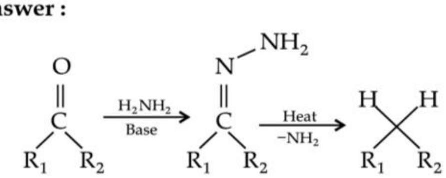
$CH_3COOH \xrightarrow[\text{reagent}]{\text{Tollens'}}$ No silver mirror

Q. 8. (a) Write the chemical reaction involved in Wolff-Kishner reduction.
(b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction :
$C_6H_5COCH_3$, CH_3-CHO, CH_3COCH_3
(c) Why carboxylic acid does not give reactions of carbonyl group ?
(d) Write the product in the following reaction.
$CH_3CH_2CH = CH - CH_2CN \xrightarrow[2.\ H_2O]{1.\ (i-Bu)_2AlH}$?
(e) 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.

U + R **[CBSE Delhi 2016]**

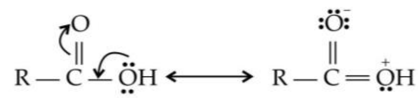
Ans. (a) $>C = O \xrightarrow[-H_2O]{NH_2NH_2} >C = NNH_2 \xrightarrow[\text{heat}]{\text{KOH/ethylene glycol}} >CH_2 + N_2$ [1]
(b) $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$ [1]
(c) Because of resonance in carboxylic group, the carbonyl group, loses a double bond character. [1]
(d) $CH_3CH_2CH{=}CH{-}CH_2CHO$ [1]
(e) A : CH_3CH_2CHO [½]
B : CH_3COCH_3 [½]
[CBSE Marking Scheme, 2016]

Detailed Answer :

(a) 

(b) $C_6H_5COCH_3 < CH_3{-}COCH_3 < CH_3{-}CHO$ [1]

(c) Carboxylicacids do not give reactions of carbonyl groups as it enters into resonance with lone pair of –COOH groups thereby making the carbon atoms less electrophilic. **[1]**



(d) $CH_3CH_2CH = CH — CH_2CN \xrightarrow[2.H_2O]{1.(i\text{-}Bu)_2AlH} CH_3CH_2CH = CH – CH_2 — \overset{O}{\overset{||}{C}} —H$

Hex-3-ene nitrile Hex-3-enal **[1]**

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

Propanal

[A] **[½]**

$CH_3 — \overset{O}{\overset{||}{C}} — CH_3 + 3\,NaOH + 4I_2 \xrightarrow{\Delta} CHI_3 + 3NaI + CH_3COONa + 3H_2O$

Acetone Iodoform

[B] (Yellow precipitate) **[½]**

Commonly Made Error

- Students forget to mention the observation in the answers.

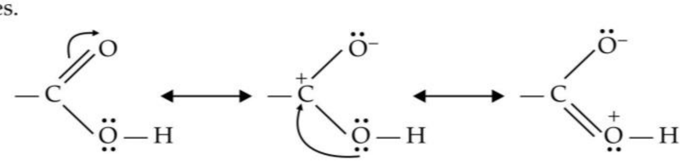
Answering Tips

- 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.

TOPIC-2
Carboxylic Acids

Revision Notes

- Carboxylic acids are those compounds which have $—\overset{O}{\overset{||}{C}}—OH$ 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 structures.

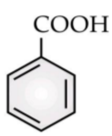
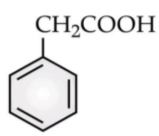
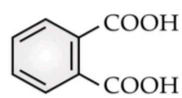
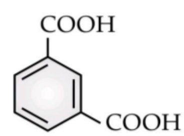
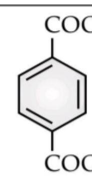


- **Nomenclature of carboxylic acids :** Derived by replacing terminal 'e' of the alkane with 'oic acid'.

Carboxylic acids **Structural formula**	**General formula :** $R—\overset{O}{\overset{||}{C}}—OH$, where $R = C_nH_{2n+1}$		
	Condensed formula	**Common name**	**IUPAC name**
$R—\overset{O}{\overset{||}{C}}—OH$	HCOOH	Formic acid	Methanoic acid
$CH_3—\overset{O}{\overset{||}{C}}—OH$	CH_3COOH	Acetic acid	Ethanoic acid

$CH_3CH_2—\overset{O}{\overset{\|\|}{C}}—OH$	CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2—\overset{O}{\overset{\|\|}{C}}—OH$	$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$CH_3—\underset{CH_3}{\underset{\|}{CH}}—\overset{O}{\overset{\|\|}{C}}—OH$	$(CH_3)_2CHCOOH$	Isobutyric acid	2-Methylpropanoic acid

Dicarboxylic Acids

COOH–COOH (Oxalic acid) Ethane-1, 2-dioic acid	$CH_2(COOH)_2$ (Malonic acid) Propane-1, 3-dioic acid	CH_2COOH–CH_2COOH Butane-1, 4-dioic acid	$CH_2(CH_2COOH)_2$ (Glutaric acid) Pentane-1, 5-dioic acid
CH_2CH_2COOH–CH_2CH_2COOH (Adipic acid) Hexane-1, 6-dioic acid	$CH_2—COOH$ $\|$ $CH—COOH$ $\|$ $CH_2—COOH$ Propane-1, 2- 3-tricarboxylic acid	$CH_3—CH = CH—COOH$ (Crotonic acid) But-2-enoic acid	$CH_3—\overset{OH}{\overset{\|}{CH}}—COOH$ (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 :

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

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

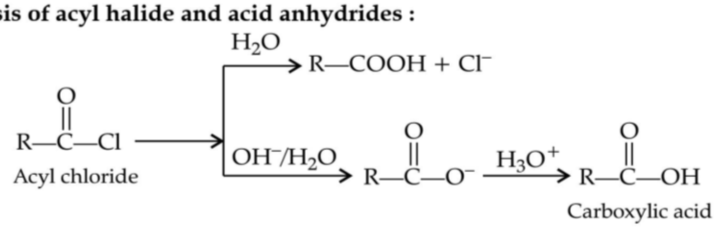
(ii) From nitriles and amides :

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

(iii) From Grignard reagent :

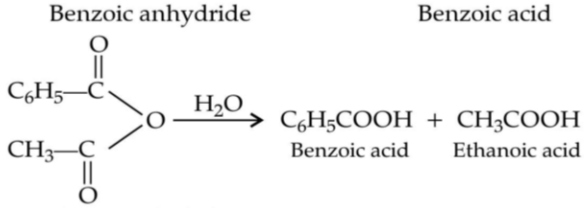
$$\overset{\delta^-}{R}—\overset{\delta^+}{Mg}—X + \overset{O}{\overset{\|\|}{C}} = O \xrightarrow[\text{Ether (dry ice)}]{\text{Dry}} R—\overset{O}{\overset{\|\|}{C}}—OMgX \xrightarrow{H_3O^+} \underset{\text{Carboxylic acid}}{R—\overset{O}{\overset{\|\|}{C}}—OH}$$

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



$$(C_6H_5CO)_2O \xrightarrow{H_2O} 2C_6H_5 — COOH$$

Benzoic anhydride   Benzoic acid



(v) By hydrolysis of esters :

$$CH_3—CH_2—CH_2—COOCH_2—CH_3 \underset{}{\overset{NaOH}{\rightleftharpoons}} CH_3—CH_2—CH_2—COONa + CH_3CH_2OH \xrightarrow{H_3O^+} CH_3CH_2CH_2COOH$$

Ethyl butanoate   Butanoic acid

➢ **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 metals and alkalies.

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

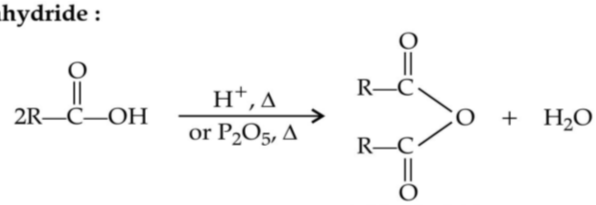
Sodium carboxylate

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

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

(ii) Reactions involving cleavage of C — OH Bond :

(a) Formation of anhydride :



(b) Esterification :

$$R — COOH + R' — OH \overset{H^+}{\rightleftharpoons} R — COOR' + H_2O$$

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

$$R — COOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$$

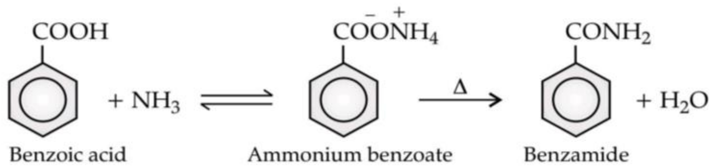
acyl chloride

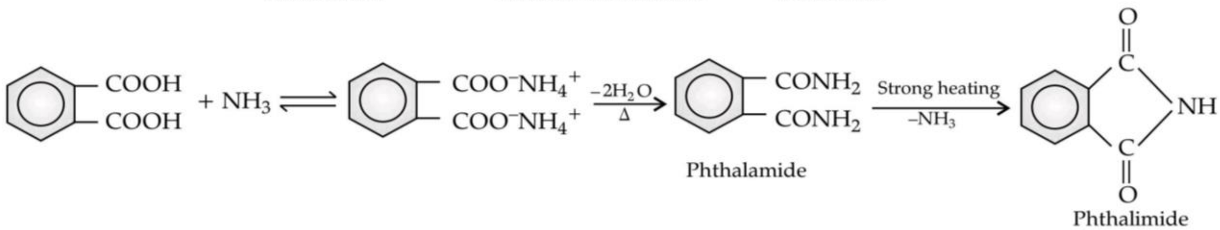
$$R — COOH + SOCl_2 \rightarrow RCOCl + SO_2\uparrow + HCl\uparrow$$

(d) Reaction with ammonia :

$$R — COOH + NH_3 \rightleftharpoons R — COO – NH_4 \xrightarrow[-H_2O]{\Delta} R — CONH_2$$

Carboxylic acid   Amide





(iii) Reduction involving –COOH group :

(a) Reduction :

$$R-COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4 \text{ / Ether or } B_2H_6} R-CH_2-OH$$

1° – Alcohol

(b) Decarboxylation :

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

Sodium carboxylate

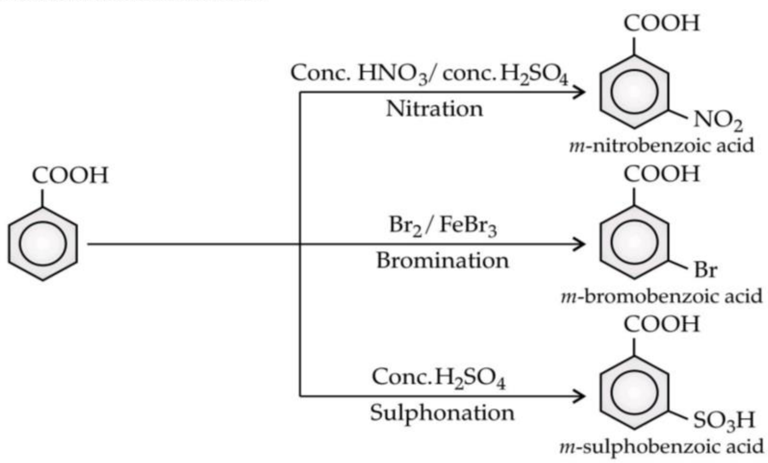
(c) Halogenation :

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

α-halo acid
(X = Cl, Br)

This reaction is known as Hell-Volhard-Zelinsky(HVZ) reaction.

(iv) Electrophilic Substitution Reaction :



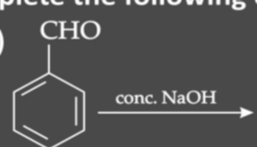
Mnemonics

- **Concept:** To memorise regents used for converting -C=O- to alkanes in Clemmenson and Wolf Reaction
- **Mnemonic: Can Zebra WOo Nightingale**
- **Interpretation:** To memorise regents used for converting –C=O– to alkanes
  C and **Z**- Clemmenson reduction ⟶ **Zn**-Hg/HCl
  W and **N**- Wolff- Kishner reduction ⟶ N_2NH_2/OH^-

How is it done on the GREENBOARD?

Q. Complete the following equations :

(a)



(b) $CH_3COCH_3 \xrightarrow{LiAlH_4}$

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

Solution: STEP I: (a)

STEP II: (b) $CH_3COCH_3 + 2[H] \xrightarrow{LiAlH_4} CH_3CH(OH)CH_3$

STEP III: (c) $CH_3\text{—}COOH \xrightarrow[(ii)\ H_2O]{(i) Cl_2/Red phosphorus} CH_2(Cl)\text{—}COOH$

Objective Type Questions

(1 mark each)

[A] MULTIPLE CHOICE QUESTIONS :

Q.1. Common name of Ethane-1,2-dioic acid is known as

(a) Oxalic acid **(b)** Phthalic acid
(c) Adipic acid **(d)** Acetic acid [R]

Ans. Correct option : (a)

Explanation : Structural formula of Ether-1,2-dioc acid is

COOH
|
COOH

∴ It is oxalic acid.

Q.2. The carboxylic acid that does not undergo HVZ reaction is

(a) CH_3COOH **(b)** $(CH_3)_2COOH$
(c) $CH_3CH_2CH_2CH_2COOH$ **(d)** $(CH_3)_3CCOOH$ [A]

Ans. Correct Option : (d)

Explanation : The carboxylic acids having α-hydrogen atom undergo HVZ reaction. Since $(CH_3)_3C.\ COOH$ doesnot contain α-H-atm; so, it doesnot undergo HVZ reaction.

Q.3. Which of the following acids does not form anhydride ?

(a) Formic acid **(b) Acetic acid**
(c) Propionic acid **(d) n-butyric acid** [A]

Ans. Correct Option : (a)

Explanation : Formic acid(HCOOH) does not form anhydride because it does not contain α-C-atom.

Q.4. Which of the following is the strongest acid?

(a) Acetic acid **(b) Phenol**
(c) Methyl alcohol **(d) Water** [U]

Ans. Correct Option : (a)

Explanation : Acetic acid is the strongest acid because it loses H^+ ion to form carboxylic ion (CH_3COO^-) which gets stabilised by resonance.

Q.5. The reaction in which the aqueous solution of sodium salt of carboxylic acids on electrolysis give alkanes :

(a) Soda lime decarboxylation
(b) Kolbe's electrolysis decarboxylation
(c) Dry distillation of calcium formate
(d) Reduction of carboxylic acid. [R]

Ans. Correct Option : (b)

Explanation : It is Kolbe's electrolytic decarboxylation.

$RCOONa(aq) \rightarrow RCOO^- + Na^+$

At anode, $2RCOO^- \rightarrow \underset{\text{Alkane}}{R\text{–}R} + 2CO_2 + 2e^-$

At cathode, $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

[B] ASSERTIONS AND REASONS

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

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

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

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

[AI] **Q. 1. Assertion (A) : Benzoic acid does not undergo Friedel-craft's reaction.**

Reaction (R) : The carboxyl group is activating and undergo electrophilic substitution reaction.
[CBSE, Outside Delhi Set 1, 2020]

Ans. Correct Option : (c)

Explanation : The carboxyl group (-COOH) is deactivating group because it is electron with drawing group. It decreases the electron density at benzene ring, hence deactivates it towards electrophilic substitution reactions.

Q. 2. Assertion (A): Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids.

Reason (R): Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.

Ans. Correct option : (b)

Explanation: Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids.

Q. 3. Assertion (A): Aromatic carboxylic groups do not undergo Friedel- Crafts reaction.

Reason (R): Carboxyl group is deactivating and the catalyst aluminium chloride gets bonded to the carboxyl group.

Ans. Correct option : (a)

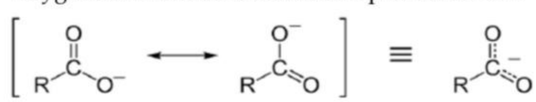
Explanation: Aromatic carboxylic groups do not undergo Friedel-Crafts reaction because Carboxyl group is deactivating and the catalyst aluminium chloride gets bonded to the carboxyl group.

Q. 4. Assertion (A) : Carboxylic acids are more acidic than phenols.

Reason (R) : Phenols are ortho and para directing.
[CBSE, SQP, 2020-21]

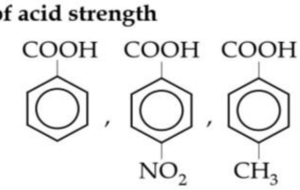
Ans. (b) [CBSE SQP Marking Scheme 2020]

Explanation: Carboxylic acids are more acidic than phenols as the carboxylate ion, the conjugate base of carboxylic acid is stabilized by two equivalent resonance structures. Thus, the negative charge is delocalized effectively. However, in phenols, negative charge is less effectively delocalized over oxygen atom and carbon atoms in phenoxide ion.



[C] VERY SHORT ANSWER TYPE QUESTIONS

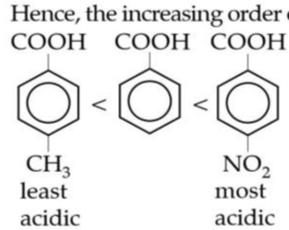
Q.1. Arrange the following compounds in increasing order of acid strength



[A]

Ans. The electron with drawing group (–NO_2) increases the acid strength of aromatic acids while electron releasing group (–CH_3) decreases the acid strength of aromatic acids.

Hence, the increasing order of acid strength is given as



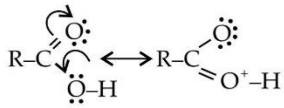
Q.2. Draw the resonating structures of carboxylic acid. [R]

Ans. $R\text{–}\overset{O}{\overset{\|}{C}}\text{–}\ddot{O}\text{–}H \rightleftharpoons R\text{–}\overset{O}{\overset{\|}{C}}\text{–}\ddot{O}^{-} + H^+$

Carboxyl acid   Carboxylateion

Q.3. Carboxylic acids behave as fairly strong acids. Comment. U

Ans. Carboxylic acids are quite strong acids due to the presence of pdar O–H group. They ionize to give H^+ ions and therefore, behave as acids



Carboxylic acids as well as carboxylate ion both are stabilised by resonance.

Q.4. Complete the following reaction –

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

Ans. $CH_3COONa + NaOH \xrightarrow{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$

Q.5. Which bond C–OH or CO–H of carboxylic acid is broken when

(i) Acid reacts with alcohol

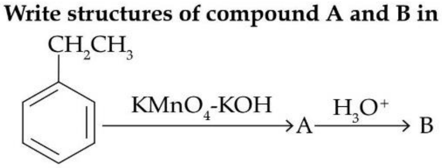
(ii) Acid reacts with Sodium R

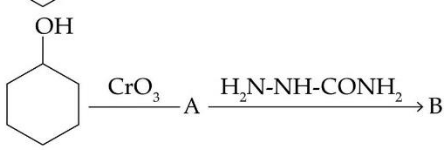
Ans. (i) C–OH [½]

(ii) CO–H [½]

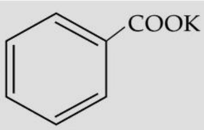
Short Answer Type Questions-I (2 marks each)

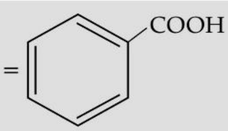
AI **Q. 1. Write structures of compound A and B in each of the following reactions:**

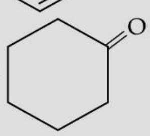
(i) 

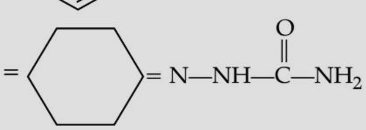
(ii) 

A&E **[CBSE Delhi Set-1 2019]**

Ans. (i) A = 

B = 

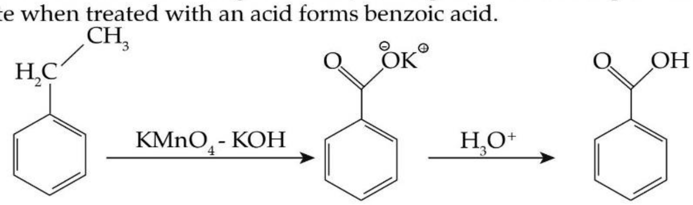
(ii) A = 

B = 

[CBSE Marking Scheme, 2019] [½ × 4]

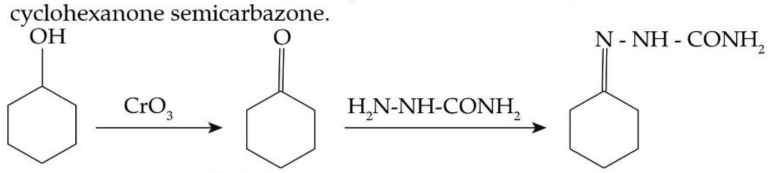
Detailed Answer :

(i) Ethyl benzene when treated with $KMnO_4$ and KOH, undergoes oxidation to produce potassium benzoate. This potassium benzoate when treated with an acid forms benzoic acid.



Potassium benzoate (A) | Benzoic acid (B)

(ii) Cyclohexanol is oxidized by CrO_3 to cyclohexanone. Cyclohexanone when treated with semicarbazide produces cyclohexanone semicarbazone.



Cyclohexanone (A) | Cyclohexanone semicarbazone (B)

Commonly Made Error

- Some students are unable to find correct product in case of organic reaction.

Answering Tips

- Do practice for organic reactions and be precise in your answer.

AI Q. 2. Write structures of main compounds A and B in each of the following reactions :

(a) $C_6H_5COOH \xrightarrow{PCl_5} A \xrightarrow{H_2/Pd-BaSO_4} B$

(b) $CH_3CN \xrightarrow[(ii)H_3O^+]{(i)CH_3MgBr} A \xrightarrow{Zn(Hg)/conc.\ HCl} B$ A [CBSE OD Set-2 2019]

Ans. (i) A = C_6H_5COCl, B = C_6H_5CHO [½ + ½]

(ii) A= CH_3COCH_3, B = $CH_3CH_2CH_3$ **[CBSE Marking Scheme, 2019] [½ + ½]**

Detailed Answer :

(a) $C_6H_5COOH \xrightarrow{PCl_5} \underset{\text{Benzoyl chloride}}{\underset{[A]}{C_6H_5COCl}} \xrightarrow{H_2/Pd-BaSO_4} \underset{\text{Benzaldehyde}}{\underset{[B]}{C_6H_5CHO}}$

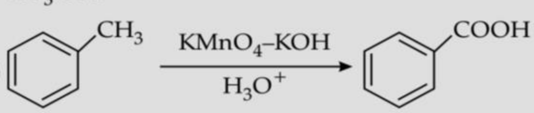
(b) $CH_3CN \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} \underset{\text{Acetone}}{\underset{[A]}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}} \xrightarrow{Zn(Hg)/conc.HCl} \underset{\text{Propane}}{\underset{[B]}{CH_3CH_2CH_3}} + H_2O$

AI Q. 3. How do you convert the following ?

(a) Ethanal to Propanone

(b) Toluene to Benzoic acid A

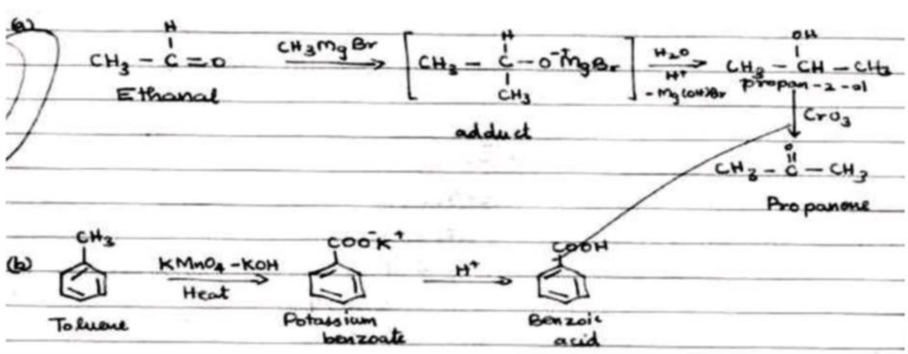
Ans. (a) $CH_3CHO \xrightarrow{\text{(i) } CH_3MgBr\text{, Dry ether (ii) } H_2O/H^+} CH_3CH(OH)CH_3 \xrightarrow{CrO_3} CH_3COCH_3$ **[1]**

(b) 

[1]

[CBSE Marking Scheme 2018]

Detailed Answer:



[Topper's Answer 2018]

Q. 4. 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) 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 stabilizes 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.

(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.

AI Q. 5. Write the reactions involved in the following :

(i) Hell-Volhard-Zelinsky reaction

(ii) Decarboxylation reaction

R **[CBSE, Delhi Set 2, 2020]**

Ans. (i)

$$R-CH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{RedP}} R-\underset{\underset{X}{|}}{CH}-COOH$$

X = Cl, Br **[1]**

(ii) $R-COONa \xrightarrow[\text{Heat}]{\text{NaoH \& CaO}} R-H + Na_2CO_3$ **[1]**

[CBSE Marking Scheme, 2017]

Detailed Answer :

(i) In **Hell-Volhard-Zelinsky (HVZ) reaction,** carboxylic acid having an α-hydrogen is halogenated at α-position on treatment with chlorine or bromine in the presence of red phosphorus to give α-halogenated carboxylic acid.

$$RCH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red P}} R\underset{\underset{X}{|}}{CH}COOH$$ **[1]**

(ii) In **Decarboxylation reaction,** carboxylic acid loses CO_2 to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO) in the ratio 3 : 1.

$$RCOONa \xrightarrow[\Delta]{\text{NaOH and CaO}} RH + Na_2CO_3$$ **[1]**

Commonly Made Error

- Students often do not write all reagents or the reaction conditions.

Answering Tip

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

Q. 6. 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]**

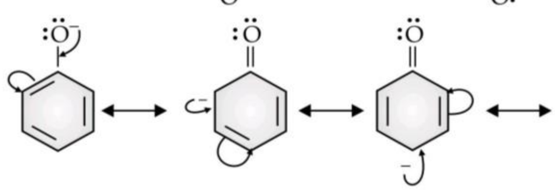
(ii) $CH_3CH_2COOH \xrightarrow{Br_2/\text{Red P}} CH_3CH(Br)COOH \xrightarrow[\text{(ii) } H^+]{\text{(i) aq KOH or NaOH}} CH_3CH(OH)COOH$ **[1]**

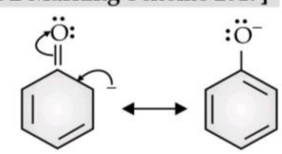
(or any other suitable method)

[CBSE Marking Scheme 2017]

Q. 7. 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

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**

Commonly Made Error

- Students often only write the reason and do not draw the resonance structures.

Answering Tip

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

Short Answer Type Questions-II (3 marks each)

AI Q. 1. (a) Give reasons :

(i) Benzoic acid is a stronger acid than acetic acid.

(ii) Methanal is more reactive towards nucleophilic addition reaction than ethanal.

(b) Give a simple chemical test to distinguish between propanal and propanone.

A + R [CBSE, Outside Delhi set 2, 2019]

Ans. (a) (i) Due to greater electronegativity of sp^2 hybridised carbon to which carboxyl carbon is attached / Due to greater resonance stabilization of carboxylate ion with the benzene ring.

(ii) Because carbonyl carbon of methanal is more electrophilic than that of ethonol / due to + I effect of methyl group in ethanal, reactivity decreases. **[1 + 1]**

(b) On heating with Tollens' reagent / $[Ag(NH_3)_2]^+$, propanal forms silver mirror whereas propanone does not. **(or any other suitable chemical test)**

[CBSE Marking Scheme, 2019] 1

Detailed Answer :

(a) (i) Strength of acid depends on the ease of release of H^+ ions. Benzoic acid contains benzene ring which is electron withdrawing where as acetic acid contains methyl group which is electron releasing. The benzoate ion resulted from dissociation of benzoic acid stabilized by resonance where as the acetate ion resulted from dissociation of acetic acid is not stabilized. Therefore, benzonic acid easily releases H^+ ion than acetic acid.

(ii) In methanal, presence of comparatively bulky group than ethanal attached to carbonyl group hinders the attack of nucleophile. Also $\mathbf{CH_3}$ group present in ethanal decreases the positive charge on carbonyl carbon by +I effect which is not possible in methanal. As Nu attack is favourable with more positive charge and less hindrance at carbonyl carbon, therefore methanal is more reactive than ethanal.

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

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3COO^- + \underset{\text{silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

[3]

AI Q.2. Write structures of compounds A, B and C in each of the following reaction :

$$\textbf{(i)}\quad C_6H_5Br \xrightarrow{\text{Mg/dry ether}} A \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } CO_2(g)} B \xrightarrow{PCl_3} C$$

$$\textbf{(ii)}\quad CH_3CN \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } SnCl_2/HCl} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta} C$$

Ans. (i)	A : 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]**

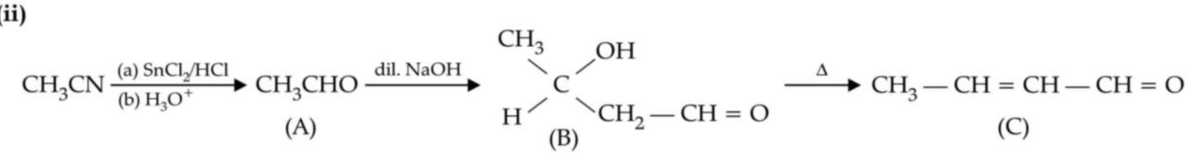
[CBSE Marking Scheme, 2017]

Detailed Answer :

(i)

$$C_6H_5Br \xrightarrow[\text{dry ether}]{\text{Mg/}} \underset{(A)}{C_6H_5MgBr} \xrightarrow{\text{(a) } CO_2(g)} C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{\ominus\ \oplus}{O}MgBr \xrightarrow[H^{\oplus}]{\text{(b) } H_3O^+} \underset{(B)}{C_6H_5COOH} \xrightarrow{PCl_5} \underset{(C)}{C_6H_5-\overset{O}{\overset{\|}{C}}-Cl}$$ **[1½]**

(ii)



[1½]

Q. 3. 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 U + R [CBSE, Outside Delhi set 1, 2017]

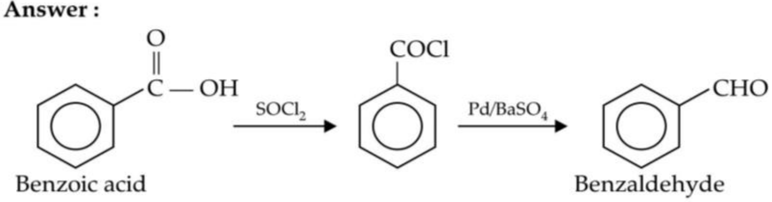
Ans. (i) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow{H_2,\ Pd - BaSO_4} C_6H_5CHO$ [1]

(ii) $C_6H_5C_2H_5 \xrightarrow{H_2Cr_2O_7/H^+} C_6H_5COOH$ [1]

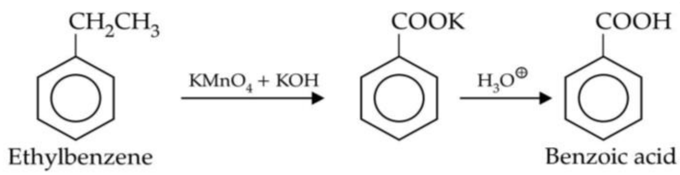
(iii) $CH_3COCH_3 \xrightarrow{NaBH_4} CH_3CH(OH)CH_3 \xrightarrow{conc.\ H_2SO_4} CH_3CH{=}CH_2$ [1]

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

Detailed Answer :

(i) 

[1]

(ii) 

[1]

(iii) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{LiAlH_4} CH_3\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow{H_2SO_4} CH_3CH=CH_2$ [1]
Propanone → Propene

AI **Q. 4. 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

Ans. A : $CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-OH$ [1]

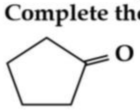
B : $CH_3-\overset{CH_3}{\overset{|}{C}H}-COOH$ [½]

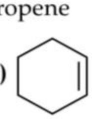
C : $CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2\,CH_3$ [½]

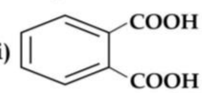
D : $CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$ [½]

A and D are position isomers. [½]

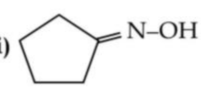
Q. 5. Complete the following reactions :

(i)  + $H_2N—OH \longrightarrow$

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

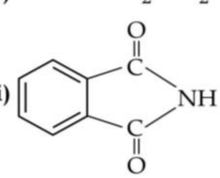
(iii) 

+ $NH_3 \xrightarrow{\text{Strong heating}}$ A

Ans. (i) 

[1]

(ii) $HOOC–CH_2–CH_2–CH_2–CH_2–COOH$ [1]

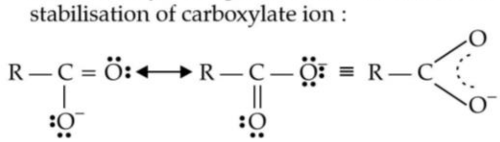
(iii) 

[1]

Q. 6. (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 :
Rosenmund reduction.
A&E + R

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) Rosenmund reaction :

$$\underset{\text{Acyl chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + H_2 \xrightarrow[\Delta]{Pd/BaSO_4} \underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + HCl$$

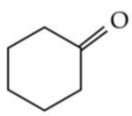
$$\underset{\text{Acetyl chloride}}{CH_3-\overset{O}{\overset{\|}{C}}-Cl} + H_2 \xrightarrow[\Delta]{Pd/BaSO_4} \underset{\text{Acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + HCl$$

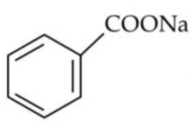
[1]

Long Answer Type Questions

(5 marks each)

AI Q. 1. (a) Write the product(s) in the following reactions :

(i)  **+ HCN → ?**

(ii)  **+ NaOH $\xrightarrow[\Delta]{CaO}$?**

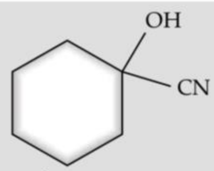
(iii) $CH_3-CH=CH-CN \xrightarrow[(b)\ H_2O]{(a)\ DIBAL\text{-}H}$ **?**

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

(i) Butanal and Butan-2-one

(ii) Benzoic acid and Phenol

R + A **[CBSE Outside Delhi Set-1, 2017]**

Ans. (a) (i) 

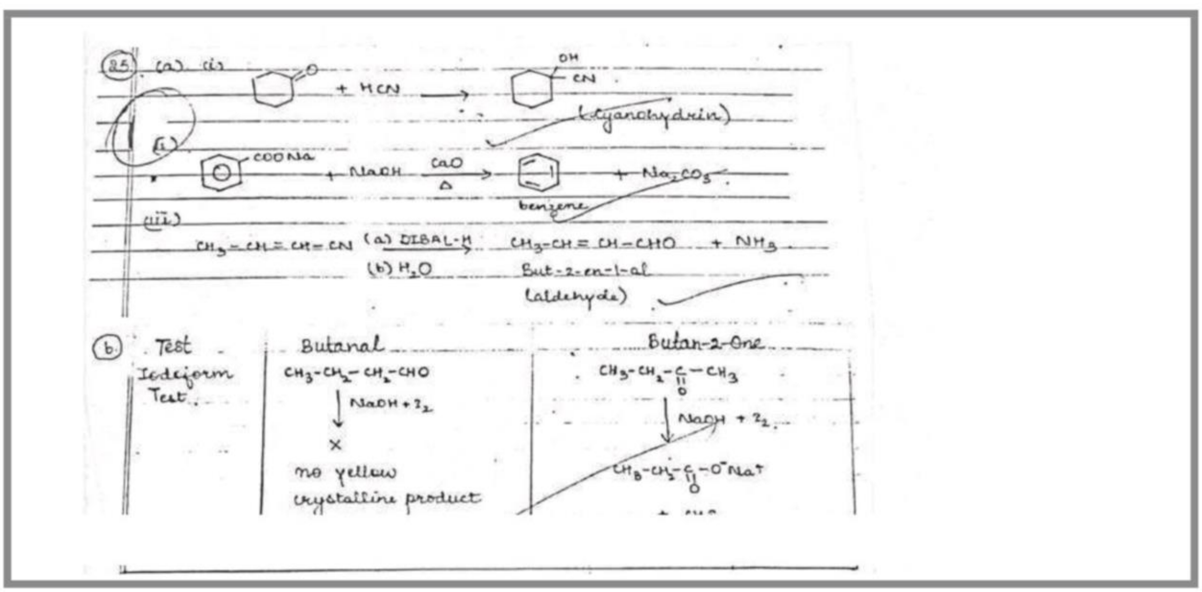
(ii)  **[1 + 1]**

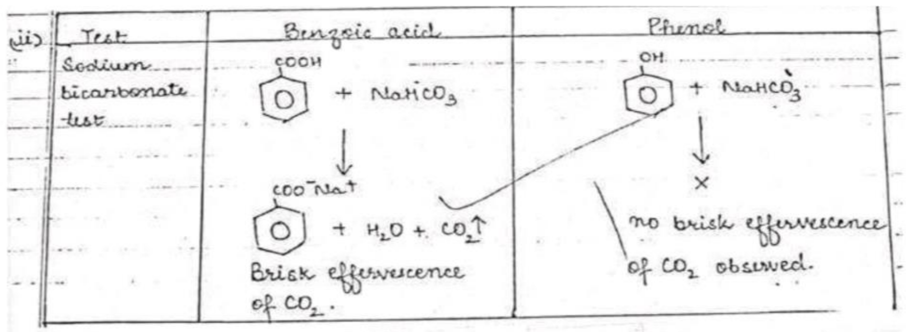
(iii) $CH_3-CH=CH-CHO$ **[1]**

(b) (i) 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]**

(ii) Add neutral $FeCl_3$ in both the solutions, phenol forms violet colour but benzoic acid does not. **(or any other correct test)**

[CBSE Marking Scheme, 2017] [1]


25 (a) (i) + HCN → (cyanohydrin)
(ii) COONa + NaOH $\xrightarrow[\Delta]{CaO}$ benzene + Na_2CO_3
(iii) $CH_3-CH=CH-CN$ (a) DIBAL-H (b) H_2O → $CH_3-CH=CH-CHO$ + NH_3
But-2-en-1-al (aldehyde)
(b) Test: Iodoform Test
Butanal: $CH_3-CH_2-CH_2-CHO$ → NaOH + I_2 → × no yellow crystalline product
Butan-2-one: $CH_3-CH_2-C(=O)-CH_3$ → NaOH + I_2 → $CH_3-CH_2-C(=O)-O^-Na^+$



[5]
[Topper's Answer 2017]

AI Q. 2. (a) Write the reactions involved in the following :

(i) Etard reaction **(ii) Stephen reduction**

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

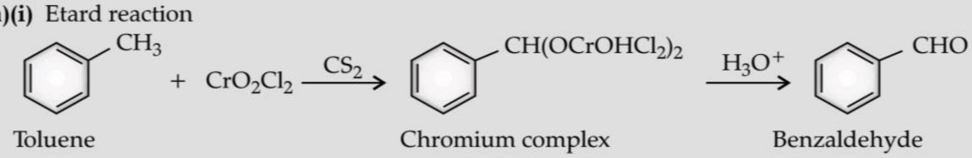
(i) Benzoic acid to benzaldehyde

(ii) Acetophenone to benzoic acid

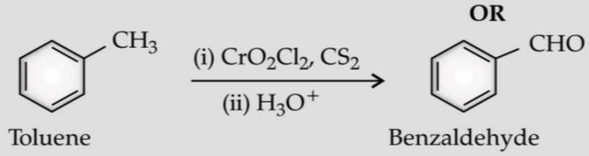
(iii) Ethanoic acid to 2-hydroxyethanoic acid

R + U [CBSE Outside Delhi Set-1, 2017]

Ans. **(a)(i)** Etard reaction



OR



[1]

(ii) Stephen reaction

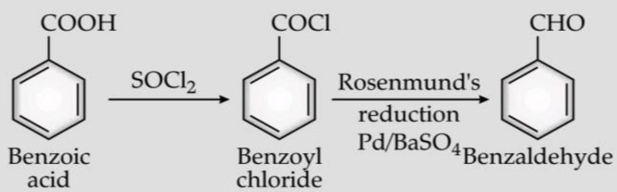
$$RCN + SnCl_2 + HCl \rightarrow RCH = NH \xrightarrow{H_3O^+} RCHO$$

OR

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

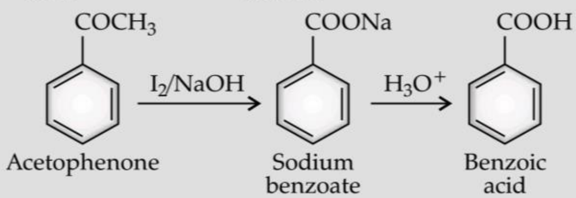
[1]

(b) (i)



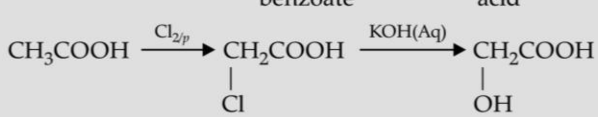
[1]

(ii)



[1]

(iii)

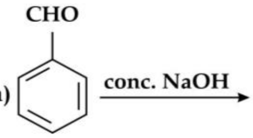


[1]

(or any other correct method)

[CBSE Marking Scheme, 2017]

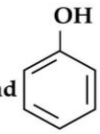
[AI] Q. 3. (i) Complete the following equations :

(a) 

(b) $CH_3COCH_3 \xrightarrow{LiAlH_4}$

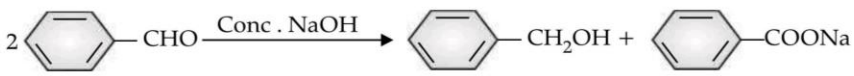
(c) $CH_3-COOH \xrightarrow[(b)\ H_2O]{(a)\ Cl_2/P}$

(ii) Distinguish between :

(a) CH_3COOH **and** 

(b) CH_3-CHO **and** $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

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

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

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

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

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

$$\underset{\text{Carboxylic acid}}{RCOOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium carboxylate}}{RCOONa} + H_2O + CO_2$$ **[1]**

Phenol does not give this test.

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

$$CH_3CHO + \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]^+} + 3\,OH^- \longrightarrow CH_3-COO^- + \underset{\text{(Silver mirror)}}{2\,Ag\downarrow} + 2H_2O + 4NH_3$$

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

[AI] Q. 4. (i) Describe the following giving chemical equations :

(a) Decarboxylation reaction

(b) Friedel-Crafts reaction

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

(a) Benzoic acid to Benzaldehyde

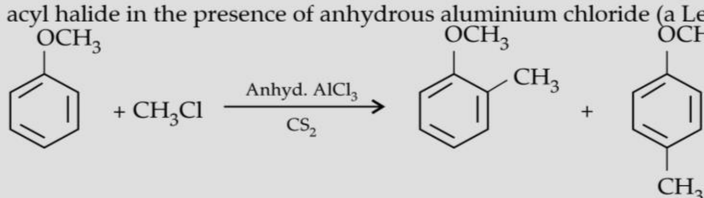
(b) Benzene to m-Nitroacetophenone

(c) Ethanol to 3-Hydroxybutanal

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

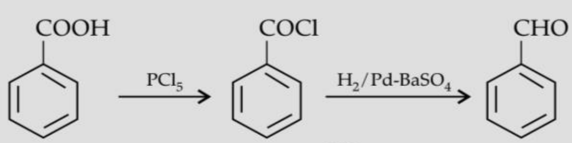
$$R-COONa \xrightarrow[Heat]{NaOH\ \&\ CaO} R-H + Na_2CO_3$$ **[1]**

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

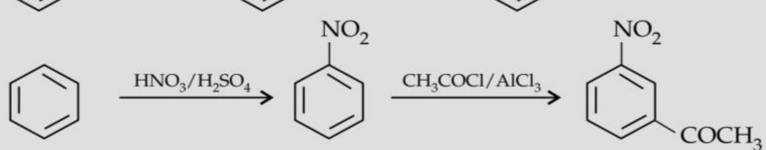


[1]

(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]

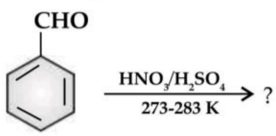
[CBSE Marking Scheme 2015]

Q. 5. (i) Describe the following reactions :

(a) Acetylation (b) Aldol condensation

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

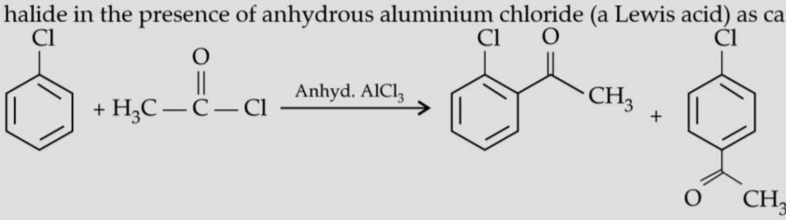
(a) $CH_3-\underset{\underset{O}{||}}{C}-CH_3 \xrightarrow{LiAlH_4} ?$

(b) 

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

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

Ans. (i) (a) The acyl groups are introduced at ortho- and para- positions by reaction of chlorobenzene 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.

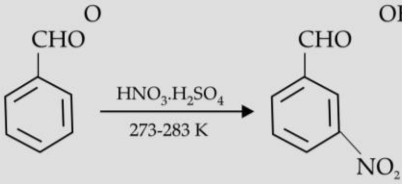
$$2CH_3-CHO \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$$

[1]

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

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

[1]

(b) 

[1]

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

[CBSE Marking Scheme 2015]

Q. 6. (i) Draw the structures of the following :

(a) p-Methylbenzaldehyde,

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

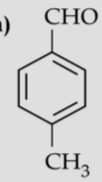
(ii) Give chemical tests to distinguish between the following pairs of compounds :

(a) Benzoic acid and Ethyl benzoate,

(b) Benzaldehyde and Acetophenone

(c) Phenol and Benzoic acid.

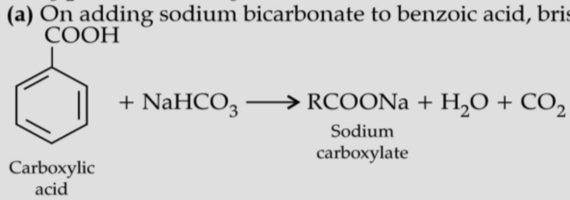
Ans. (i) (a)



[1]

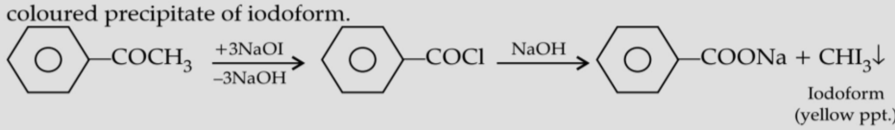
(b) $(CH_3)_2C = CHCOCH_3$ **[1]**

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



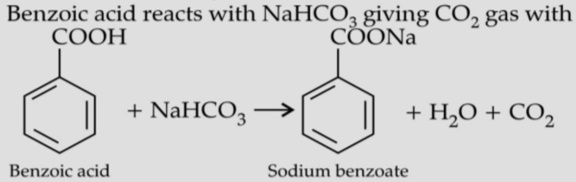
Whereas ethylbenzoate does not. **[1]**

(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]

[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. 7. (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) $CH_3 — \underset{|}{\overset{}{CH}}(OH) — CH_2 — CHO$

(c) CH_3CH_2OH

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

Ans. (i) (a) $(CH_3)_2C = N — OH$ **[1]**

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

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

(b) $2CH_3 — CHO \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} CH_3 — CH(OH) — CH_2 — CHO$ **[1]**

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

[CBSE Marking Scheme 2015]

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

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) $C_6H_6 \xrightarrow{(CH_3CO)O/Anhy\ AlCl_3} PhCOCH_3 \xrightarrow[\text{or } CH_3COCl/AlCl_3]{conc.\ H_2SO_4 + conc.\ HNO_3} m–NO_2C_6H_4COCH_3$

[1]

Q. 9. (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

Ans. (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]**

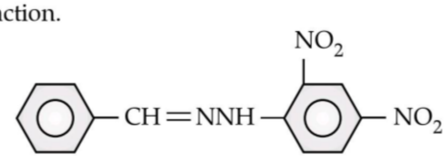
$CH_3CHO + 4NaOI \xrightarrow{NaOH/I_2} CHI_3 + HCOONa + 2NaOH$

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

α-Halo carboxylic acid

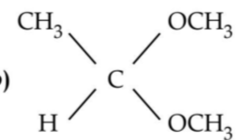
The name of the reaction is Hell-Volhard-Zelinsky reaction. **[½]**

(iii) (a)



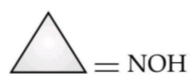
[1]

(b)



1

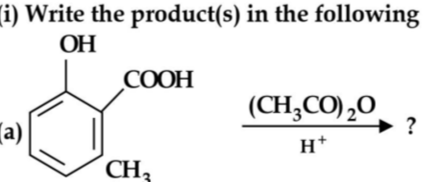
(c)



1

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

(a)



(b) $CH_3-CH(CH_3)-O-CH_2-CH_3 \xrightarrow{HI} ?+?$

(c) $CH_3-CH=CH-CH_2-OH \xrightarrow{PCC} ?+?$

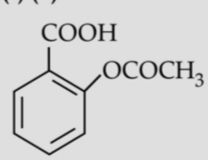
(ii) Give simple chemical tests to distinguish between the following pairs of compounds:

(a) Ethanol and Phenol

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

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

Ans. (i) (a)



[1]

(b) $(CH_3)_2CHOH$ and CH_3CH_2I **[1]**

(c) $CH_3CH=CHCHO$ **[1]**

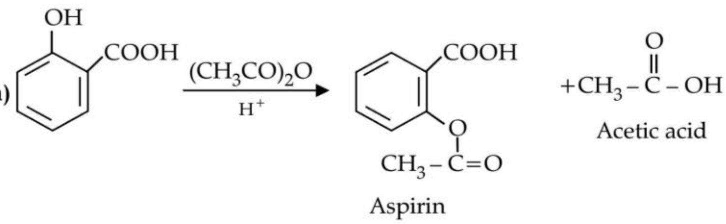
(ii) (a) Add neutral $FeCl_3$ to both the compounds, phenol gives violet complex. **[1]**

(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) 

[1]

(b) $CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}H-O-CH_2-CH_3 \xrightarrow{HI} CH_3-\overset{CH_3}{\overset{|}{C}}H-I + C_2H_5OH$ **[1]**

2-Iodopropene Ethanol

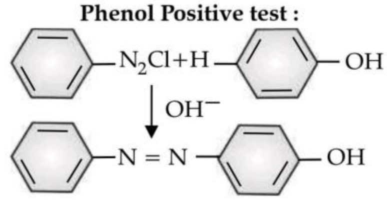
(c) $CH_3-CH=CH-CH_2-OH \xrightarrow{PCC} CH_3-CH=CH-CHO$ **[1]**

But – 2 – enal

(ii) (a) Test : Coupling

Ethanol Negative test :

Phenol Positive test :



Orange $+Cl^-+H_2O$

(b) By Lucas test

$CH_3CH_2CH_2OH \xrightarrow[ZnCl_2]{conc.\ HCl}$ Turbidity appears from heating after longtime

Propanol

$CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow[ZnCl_2]{conc.\ HCl}$ Turbidity appears very quickly

2- Methylpropan-2-ol

[2]

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

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]**

[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 aldehydes 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.

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

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

$$CH_3COCl \xrightarrow{H_2/Pd\text{-}BaSO_4} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta}$$
$$A \xrightarrow{CH_3MgBr/H_3O^+} D$$

(ii) Arrange the following compounds in the increasing order of their boiling points :
CH_3CHO, CH_3CH_2OH, CH_3OCH_3, CH_3COOH

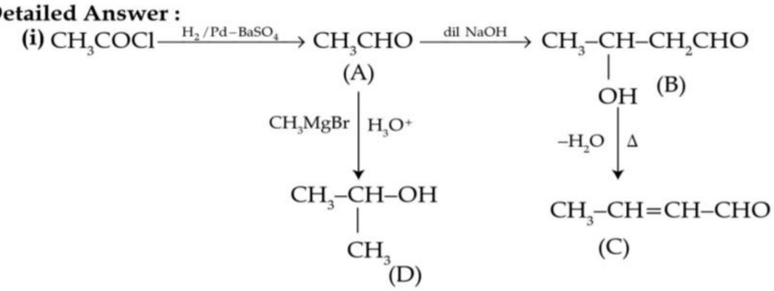
A + U **[CBSE Comptt. OD Set-1, 2, 3 2017]**

Ans. (i) A: CH_3CHO; B: $CH_3\text{-}CH(OH)\text{-}CH_2\text{-}CHO$;
C: $CH_3\text{-}CH{=}CH\text{-}CHO$; D: $CH_3\text{-}CH(CH_3)\text{-}OH$ 1x4

(ii) $CH_3\text{-}O\text{-}CH_3 < CH_3CHO < CH_3\text{-}CH_2\text{-}OH < CH_3\text{-}COOH$ **[1]**

[CBSE Marking Scheme 2017]

Detailed Answer :

(i)


(ii) Acetic acid possess higher boiling point then ethanol due to more extensive association of acetic acid molecules through intermolecular hydrogen bonding. So, acetic acid has higher boiling point than ethanol. Moreover, the polar C=O double bond causes acetaldehyde to have higher boiling point than dimethyl ether.

Hence, the increasing order of the boiling points is:
$CH_3OCH_3 < CH_3CHO < CH_3CH_2OH < CH_3COOH$ **[1]**

Commonly Made Error

- Sometimes, students do not write correct test to distinguish organic compounds.

Answering Tips

- Learn and understand chemical tests to distinguish aldehydes, ketones and carboxylic acids.

Q. 13. (i) How will you convert:

(a) Benzene to acetophenone

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

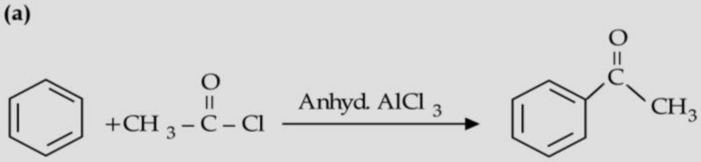
(ii) Give reasons:

(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

Ans (i) (a)



(b) $$CH_3COCH_3 + CH_3MgBr \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OMgBr \xrightarrow{H_2O} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$ **[2]**

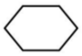
(ii) (a) Because it is a deactivating group/due to electron withdrawing carboxylic group resulting in decreased electron density at o- and p- position. **[1]**

(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]**

[CBSE Marking Scheme 2017]

Q. 14. (i) Write the products of the following reaction:

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

(b)

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

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

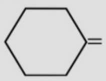
(ii) Write simple chemical tests to distinguish between the following pairs of compounds ?

(a) Propanal and propanone

(b) Benzaldehyde and Benzoic acid

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

Ans. (i) (a)

 = N-NH-CO-NH_2

(b) CH_3 COOH

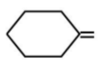
(c)CH_3 — CH(Br)— COOH **[1+1+1]**

(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]

Q. 15. (i) Write the products of the following reactions :

(a)  $= O + H_2N-OH \xrightarrow{H^+}$

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

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

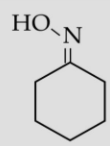
(ii) Give simple chemical tests to distinguish between the following pairs of compounds:

(a) Benzaldehyde and Benzoic acid

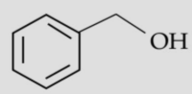
(b) Propanal and Propanone

A **[CBSE Delhi 2014, SQP 2017; DDE]**

Ans (a)



[1]

(b) 

[½+½]

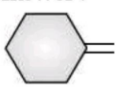
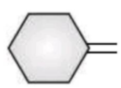
(c) Cl–CH_2–COOH **[1]**

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

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

[CBSE Marking Scheme 2017]

Detailed Answer :

(i) **(a)**  $= O + H_2N-OH \xrightarrow{H^+}$  $= N-OH + H_2O$

Cyclohexanone oxime

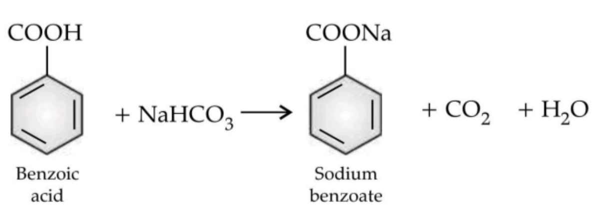
(b) $2C_6H_5OH$ + Conc. NaOH $\longrightarrow$ $C_6H_5CH_2OH$ + C_6H_5COONa

Benzyl alcohol   Sodium benzoate

(c) $CH_3COOH \xrightarrow{Cl_2/P} Cl-CH_2-COOH + HCl$

2–Chloro-ethanoic acid

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



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

$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow CH_3CH_2COO^- + 2Ag\downarrow + 4NH_3 + 2H_2O$

Silver mirror

AI Q. 16. (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

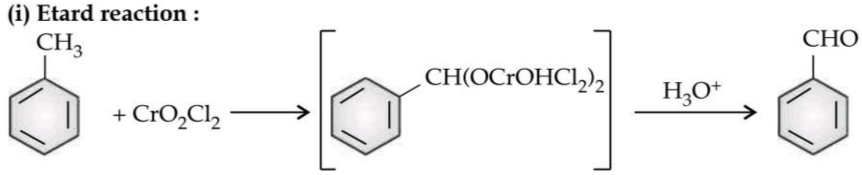
(iii) Why pKa of $Cl-CH_2-COOH$ is lower than the pKa of CH_3COOH?

(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. **(i) Etard reaction :**



(ii) $C_6H_5COCH_3 < CH_3CHO < HCHO$

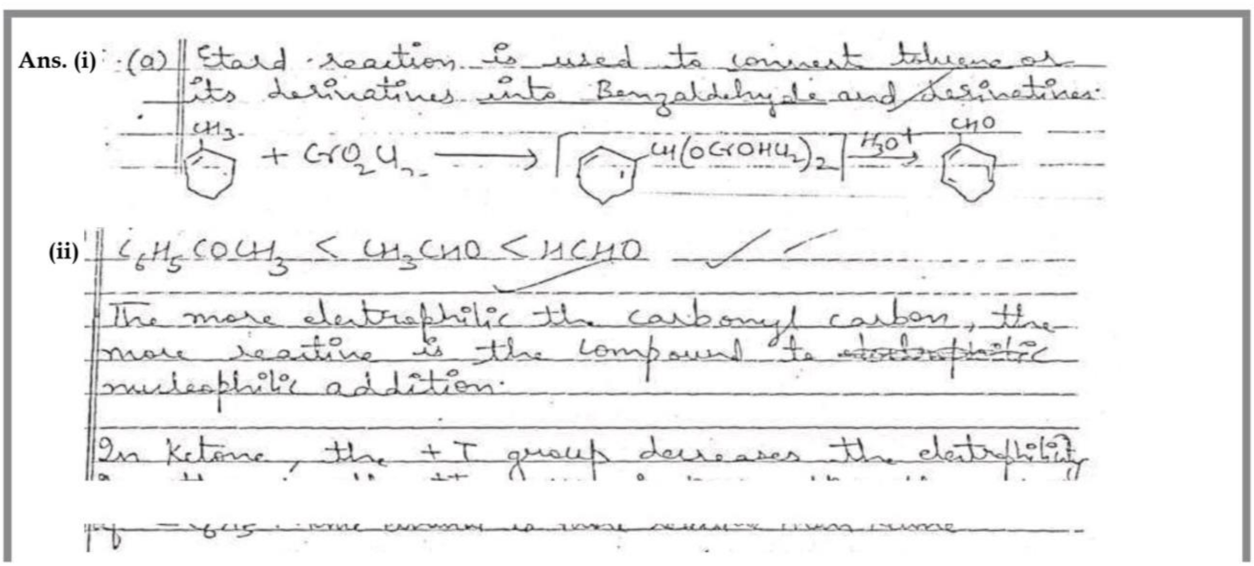
The reactivity of the compound towards nucleophilic addition reaction is directly proportional to electrophilic character of carbonyl carbon. In ketone, the +I group lowers the electrophilicity. Whereas, +I of methyl group in ethanal is less than of $-C_6H_5$. Hence, ethanal is most reactive than acetophenone.

(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.

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

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

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


Ans. (i) (a) Etard reaction is used to convert toluene or its derivatives into Benzaldehyde and derivatives.

(ii) $C_6H_5COCH_3 < CH_3CHO < HCHO$

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

In Ketone, the +I group decreases the electrophilicity

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

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

(v) From the ~~emp~~ structural formula, we can say that C_3H_6O is a compound with one carbonyl group. Hence the compounds are aldehyde ~~or~~ and Ketone.

Ketone will be propanone − $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$
Aldehyde will be propanal − CH_3-CH_2-CHO

Propanone has a $-\overset{O}{\overset{\|}{C}}-CH_3$ group. Hence it will give positive iodoform test. The ~~po~~ aldehyde will not form any ppt.

Since compound A forms yellow ppt, hence

A − propanone (Ketone)
B − ~~pro~~ propanal (aldehyde)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + NaOH + I_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O^-Na^+ + \underset{\text{yellow ppt}}{CHI_3}$

$C_2H_5-CHO + NaOH + I_2 \longrightarrow$ No ppt.

[CBSE, Topper's Answer 2016] 5

Q. 17. (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 and 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

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]**

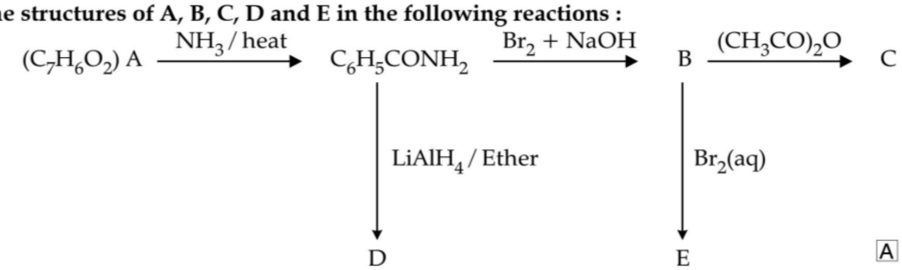
(ii) (a) Add NaOH and I_2 to both the compounds and heat, ethanal gives yellow ppt of iodoform. **[1]**
(b) Add NaOH and I_2 to both the compounds and heat, pentan-2-one gives yellow ppt of iodoform. **[1]**
[CBSE Marking Scheme 2018]

Q. 18. (i) Write structure of the product(s) formed :
(a) $CH_3–CH_2–COOH \xrightarrow{Cl_2,\ \text{red phosphorus}}$
(b) $C_6H_5COCl \xrightarrow{H_2,\ Pd – BaSO_4}$
(c) $2HCHO \xrightarrow{\text{Conc.KOH}}$
(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]**

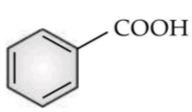
Ans. (i) (a) $CH_3–CH(Cl)–CHO$ **[1]**
(b) C_6H_5CHO **[1]**
(c) $CH_3OH + HCOOK$ **[1]**
(ii) (a) $CH_3COCH_3 \xrightarrow{NaBH_4} CH_3CH(OH)CH_3 \xrightarrow{\text{conc. } H_2SO_4\text{, 443K}} CH_3–CH{=}CH_2$ **[1]**
(b) $C_6H_5CH_2Cl \xrightarrow{KCN} C_6H_5CH_2CN \xrightarrow{H_3O^+} C_6H_5CH_2COOH$ **[1]**
[CBSE Marking Scheme 2018]

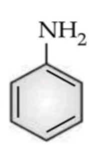
Detailed Answer :
(i) (a) CH_3CHO has a comparatively bulky group attached to carbonyl group than HCHO which hinders the attack of nucleophile to some extent. Also, CH_3 group in CH_3CHO decreases the positive charge on carbonyl carbon by +I effect to some extent which doesn't take place in HCHO. Since,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

AI Q. 19. 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 :

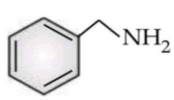


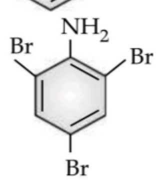
A **[CBSE OD 2015]**

Ans. A = 

B = 

C = $C_6H_5—\ddot{N}(H)—C(=O)—CH_3$ **(1 each)**

D = 

E = 

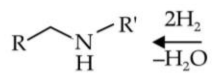
[5]

Visual Case-Based Questions **(4 marks each)**

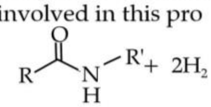
Q. 1. Read the passage given below and answer the following questions : **(1 × 4 = 4)**
Reduction of carboxylic acids and their derivatives plays an important role in organic synthesis, in both laboratory and industrial processes. Traditionally, the reduction is performed using stochiometric amounts of hydride reagents, generating stochiometric amounts of waste. A much more

attractive, atom-economical approach is a catalytic reaction using H2; however, hydrogenation of carboxylic acid derivatives under mild conditions is a very challenging task, with amides presenting the highest challenge among all classes of carbonyl compounds. Very few examples of the important hydrogenation of amides to amines, in which the C-O bond is cleaved with the liberation of water (Scheme 1), were reported. C-O cleavage of amides can also be affected with silanes as reducing agents. received September 5, 2010; E-mail: david. milstein@weizmann
genation of amides to the with cleavage of the C–N products of C–O cleavage the case of anilides). The and neutral, homogeneous

Scheme 1. General Sche
C-O cleavage



We have now prepared the new, dearomatized, bipyridine-based pincer complex 3, catalyst 3 (Here refered as Cat. 3). Remarkably, it efficiently catalyzes the selective hydrogenation of amides to form amines and alcohols (eq 1). The reaction proceeds under mild pressure and neutral conditions, with no additives being required. Since the reaction proceeds well under anhydrous conditions, hydrolytic cleavage of the amide is not involved in this process.
been reported.6 Amines and chemical, pharmaceutical and ch a reaction is conceptually step in amide hydrogenation bonvl group to form a very anhydrous condition
involved in this pro



(Balaraman, E., Gnanaprakasam, B., Shimon, L. J., & Milstein, D. (2010). Direct hydrogenation of amides to alcohols and amines under mild conditions. Journal of the American Chemical Society, 132(47), 16756-16758.)

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

A. Assertion and reason both are correct statements and reason is correct explanation for assertion.

B. Assertion and reason both are correct statements but reason is not correct explanation for assertion.

C. Assertion is correct statement but reason is wrong statement.

D. Assertion is wrong statement but reason is correct statement.

1. **Assertion: The use of catalyst 3 is an efficient method of preparation of primary amines**
   Reason: Use of catalyst 3 is a step down reaction.
2. **Assertion: Use of hydride catalyst or hydrogen brings about cleavage of C-O bond in amides.**
   Reason: Hydride catalyst or hydrogen cause to reduction of amides.
3. **Assertion: N-methyl ethanamide on reaction with catalyst 3 will yield ethanol and methanamine.**
   Reason: Use of Catalyst 3 brings about cleavage of C-N bond of amides
4. **Assertion: Aniline can be prepared from suitable amide using catalyst 3**
   Reason: The use of catalyst 3 is limited to aliphatic amides only.

Ans. **1. B 2. B 3. A 4. C**

Q. 2. Read the passage given below and answer the following questions : **$(1 \times 4 = 4)$**

Aldehydes, ketones and carboxylic acids are few of the major classes of organic compounds containing carbonyl group. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled or selective reduction of acyl halides. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes. Carboxylic acids are prepared by the oxidation of primary alcohols, aldehydes and alkenes by hydrolysis of nitriles and by treatment of Grignard reagents with carbon dioxide.

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

(i) Name a method by which both aldehydes and ketones can be prepared.
(a) Reduction of carboxylic acids
(b) Ozonolysis of alkenes
(c) Oxidation of alcohols
(d) All of the above

(ii) How will you distinguish between aliphatic aldehydes and aromatic aldehydes ?
(a) Fehling's test (b) Benedict's test
(c) Iodoform test (d) Hinsberg reagent

(iii) Name the main compounds A and B formed in the following reaction :

$$CH_3CN \xrightarrow[(ii)H_3O^+]{(i)CH_3MgBr} A \xrightarrow{Zn(Hg)/conc.\ HCl} B$$

(a) CH_3CH_2COOH [A], $CH_3CH_2CH_3$ [B]
(b) CH_3CH_2CHO [A], C_2H_4 [B]
(c) CH_3COCH_3 [A], $CH_3CH_2CH_3$ [B]
(d) CH_3COCH_3 [A], C_2H_6 [B]

(iv) The reagent which does not react with both, acetone and benzaldehyde.
(a) Sodium hydrogensulphite
(b) Phenyl hydrazine
(c) Fehlings' solution
(d) Grignard reagent

OR

Through which of the following reactions number of carbon atoms can be increased in the chain?
(a) Grignard reaction
(b) Cannizzaro reaction
(c) Clemmenson reduction
(d) HVZ reaction

Ans. (i) Correct Option : (d)
Explanation : Both aldehydes and ketones can be prepared by all these methods. **[1]**

(ii) Correct option : (a)
Explanation : On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.

$$R-CHO + 2Cu^{2+} + 5OH^- \longrightarrow R-COO^- + \underset{\text{Reddish brown ppt}}{Cu_2O} + 3H_2O$$ **[1]**

(iii)Correct option : (c)

Explanation :

$$CH_3CN \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr} \underset{\text{Acetone}}{\underset{[A]}{CH_3-\overset{O}{\overset{||}{C}}-CH_3}}$$

$$\xrightarrow{Zn(Hg)/conc.HCl} \underset{\text{Propane}}{\underset{[B]}{CH_3CH_2CH_3}} + H_2O$$ **[1]**

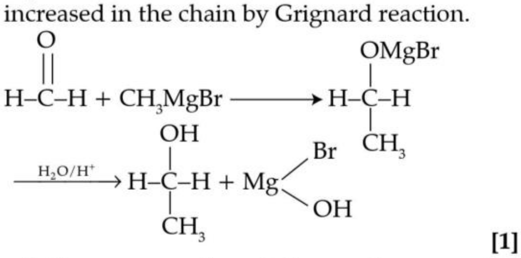
(iv) **Correct option : (c)**

Explanation : Fehling's solution does not react with acetone and benzaldehyde as aromatic aldehydes and ketones do not react with Fehling's solution. **[1]**

OR

Correct option : (a)

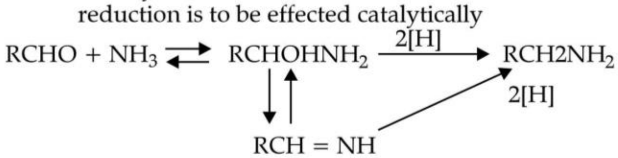
Explanation : The number of C-atoms can be increased in the chain by Grignard reaction.



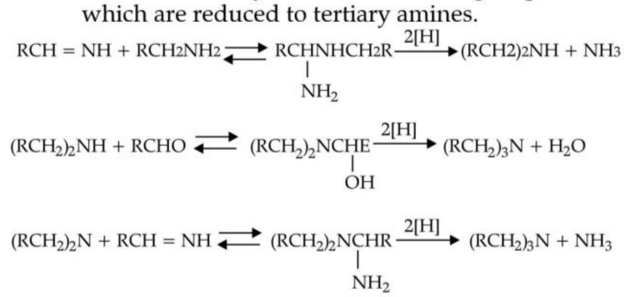
[1]

Q. 3. Read the passage given below and answer the following questions:

Reductive alkylation is the term applied to the process of introducing alkyl groups into ammonia or a primary or secondary amine by means of an aldehyde or ketone in the presence of a reducing agent. The present discussion is limited to those reductive alkylations in which the reducing agent is hydrogen and a catalyst or "nascent" hydrogen, usually from a metalacid combination; most of these reductive alkylations have been carried out with hydrogen and a catalyst. The principal variation excluded is that in which the reducing agent is formic acid or one of its derivatives; this modification is known as the Leuckart reaction. The process of reductive alkylation of ammonia consists in the addition of ammonia to a carbonyl compound and reduction of the addition compound or its dehydration product. The reaction usually is carried out in ethanol solution when the reduction is to be effected catalytically



Since the primary amine is formed in the presence of the aldehyde it may react in the same way as ammonia, yielding an addition compound, a Schiff's base (RCH= NCH2R) and finally, a secondary amine. Similarly, the primary amine may react with the imine, forming an addition product which also is reduced to a secondary amine Finally, the secondary amine may react with either the aldehyde or the imine to give products which are reduced to tertiary amines.



Similar reactions may occur when the carbonyl compound employed is a ketone. (source: Emerson, W. S. (2011). The Preparation of Amines by Reductive Alkylation. Organic Reactions, 174–255. doi:10.1002/0471264180.or004.03)

(i) **Ethanal on reaction with ammonia forms an imine (X) which on reaction with nascent hydrogen gives (Y). Identify 'X' and 'Y'.**
(a) X is $CH_3CH{=}NH$ and Y is CH_3NH_2
(b) X is $CH_3CHOHNH_2$ and Y is $CH_3CH_2NH_2$
(c) X is $CH_3CHOHNH_2$ and Y is CH_3NH_2
(d) X is $CH_3CH{=}NH$ and Y is $CH_3CH_2NH_2$

(ii) **Acetaldehyde is reacted with ammonia followed by reduction in presence of hydrogen as a catalyst. The primary amine so formed further reacts with acetaldehyde. The Schiff's baseformed during the reaction is:**
(a) $CH_3CH{=}NHCH_3$
(b) $CH_3CH{=}NHCH_2CH_3$
(c) $CH_3{=}NHCH_2CH_3$
(d) $CH_3CH_2CH{=}NHCH_3$

(iii) **The reaction of ammonia and its derivatives with aldehydes is called:**
(a) Nucleophilic substitution reaction
(b) Electrophilic substitution reaction
(c) Nucleophilic addition reaction
(d) Electrophilic addition reaction

(iv) **$(CH_3CH_2CH_2)_2NH + CH_3CH_2CHO \rightarrow P \xrightarrow{2[H]} Q$**
The compound Q is:
(a) $(CH_3CH_2CH_2)_3N$
(b) $(CH_3CH_2CH_2)2N(CH_2CH_3)$
(c) $(CH_3CH_2)_3N$
(d) $(CH_3CH_2)2NH$

(v) **Reductive alkylation of ammonia by means of an aldehyde in presence of hydrogen as reducing agents results in formation of:**
(a) Primary amines
(b) Secondary amines
(c) Tertiary amines
(d) Mixture of all three amines

Ans. 1. D 2. B, 3. C 4. A 5. D