



Methods of Preparation of **Carbonyl Compounds**



1. The major products of the following reaction are:

[Sep. 06, 2020 (I)]

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} - \text{CH} - \text{CH} - \text{CH}_{3} & \xrightarrow{(i)\text{KO}^{1}\text{Bu}/\Delta} \\ \text{OSO}_{2}\text{CH}_{3} & \xrightarrow{(ii)\text{O}_{3} \ / \ \text{H}_{2}\text{O}_{2}} \end{array} \rightarrow \\ \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} & \text{O} \end{array}$$

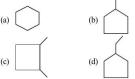
- The correct match between Item I (starting material) and Item - II (reagent) for the preparation of benzaldehyde is:
 - [Sep. 06, 2020 (II)] Item-I Item-II
 - (P) HCl and SnCl₂, H₃O (I) Benzene (II) Benzonitrile (Q) H2, Pd-BaSO4, S and quinoline
 - (III) Benzoyl Chloride (R) CO, HCl and AlCl,
 - (a) (I) (Q), (II) (R) and (III) (P) (b) (I) - (P), (II) - (Q) and (III) - (R)
 - (c) (I) (R), (II) (P) and (III) (Q)
 - (d) (I)-(R), (II)-(Q) and (III)-(P)

In the following reaction A is:

(iii) O₃

wing reaction A is: [Jan. 09, 2020 (II)]

(i)
$$Br_2$$
, hv
(ii) KOH (alc.)
(iii) O_3
(iv) $(CH_3)_2S$



(v) NaOH(aq) + Δ

The major product(s) obtained in the following reaction [April 12, 2019 (I)]

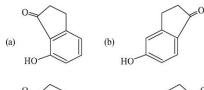
$$\underbrace{\begin{array}{c} (i) \text{ KO}^{l}\text{Bu} \\ \hline (ii) \text{ O}_{3}/\text{Me}_{2}\text{S} \end{array}}_{\text{Br}}$$

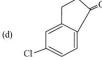
- (c) OHC

The major product of the following reaction is:

[April 12, 2019 (I)]







The major product of the following reaction is:

[April 9, 2019 (I)]

In the following reaction

[April 9, 2019 (II)]

Carbonyl compound + MeOH =

Rate of the reaction is the highest for: (a) Acetone as substrate and methanol in excess.

- (b) Propanal as substrate and methanol in stoichiometric
- amount.
- (c) Propanal as substrate and methanol in excess.
- (d) Acetone as substrate and methanol in stoichiometric amount.
- In the following reaction

[Jan. 12, 2019 (I)]

 $Aldehyde + Alcohol \xrightarrow{HC\ell} Acetal$

Aldehyde Alcohol

НСНО ^tBuOH

CH₂CHO MeOH

The best combination is:

- (a) CH₃CHO and [†]BuOH (b) HCHO and MeOH
- (c) CH3CHO and MeOH (d) HCHO and BuOH
- The major product of the following reaction is:

$$R-C \equiv N \xrightarrow{(i) \text{ AlH } (i-Bu)_2} \xrightarrow{(ii) \text{ H}_2\text{O}}$$

[Jan. 9, 2019 (I)]

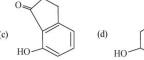
(a) RCOOH (b) RCONH2 (c) RCHO (d) RCH2NH2

10. The major product of the following reaction is:

[Jan. 9, 2019 (I)]

Br
$$\xrightarrow{(1) \text{ KOH (aqueous)}}$$

 $\xrightarrow{(2) \text{ CrO}_3/\text{H}^{\top}}$
 $\xrightarrow{(3) \text{ H}_2\text{SO}_4/\Delta}$



11. The major product of the following reaction is:

$$\overset{O}{\longleftarrow} \overset{OH}{\longleftarrow} \overset{CH_3}{\longleftarrow} \xrightarrow{AlCl_3,\Delta}$$

[Jan. 9, 2019 (II)]

(a)
$$OH$$
 CH_3 OH CH_3

$$H_3C$$
 OH OH CH_3

12. The total number of optically active compounds formed in the following reaction is: [Online April 15, 2018 (II)]

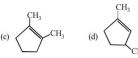
$$\longrightarrow^{O} \longrightarrow^{HBr}$$

(c) Four

(d) Two

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13. Which compound would give 5 - keto - 2 - methylhexanal



- 14. Which of the following on heating with aqueous KOH, [2009] produces acetaldehyde?
 - (a) CH₃CH₂Cl
- (b) CH2ClCH2Cl
- (c) CH₃CHCl₅
- (d) CH₃COCl

TOPIC 2 Properties of Carbonyl Compounds



15. The major product [R] in the following sequence of [Sep. 04, 2020 (II)]

$$\label{eq:hc} \begin{split} HC \equiv CH &\xrightarrow{(i) \text{LiNH}_2/\text{ether}} & [P] \\ &\xrightarrow{(ii) \text{H}_3\text{C}} & \text{CH} - \text{Br} \end{split}$$

$$\xrightarrow{\text{(i) HgSO}_4/\text{H}_2\text{SO}_4} \quad \text{[Q]} \quad \xrightarrow{\text{Conc. H}_2\text{SO}_4} \quad \text{[R]}$$

(a)
$$\begin{array}{c} \text{H}_2\text{C} \\ \text{C} - \text{CH}_2 - \text{CH}_3 \\ \text{CH(CH}_3)_2 \end{array}$$

(b)
$$H_3C$$
 $C = CH - CH_3$ $(CH_3)_2CH$

(c)
$$H_3C$$

 $C = C(CH_3)_2$
 H_3CCH_2

(d)
$$H_3C$$

 $CH - CH = CH_2$
 $(CH_3)_2CH$

The major product [C] of the following reaction sequence

$$CH_2 = CH - CHO \xrightarrow{\text{(i) NaBH}_4} [A] \xrightarrow{\text{O}} [B] \xrightarrow{DBr} [C]$$

$$(a) \bigcirc Br$$

$$(b) \bigcirc D$$

$$Br$$

17. The increasing order of the reactivity of the following compounds in nucleophilic addition reaction is: Propanal, Benzaldehyde, Propanone, Butanone

[Sep. 03, 2020 (II)]

- (a) Benzaldehyde < Butanone < Propanone < Propanal $(b) \ \ Butanone < Propanone < Benzaldehyde < Propanal$
- (c) Propanal < Propanone < Butanone < Benzaldehyde
- (d) Benzaldehyde < Propanal < Propanone < Butanone The compound A in the following reactions is:

[Sep. 03, 2020 (II)]

$$B \xrightarrow{(i) O_3} C + D$$

$$C \xrightarrow{(i) \text{ Conc. KOH}} \bigcirc \bigcirc \longrightarrow \bigcirc COO^{\bigodot}K^+ +$$

$$\bigcirc$$
 CH₂OH

(a)
$$C_6H_5 - C - CH_3$$

(b)
$$C_6H_5 - C - CH < CH_3 \\ CH_3$$

(c)
$$C_6H_5 - CH_2 - C - CH_3$$



19. The increasing order of the following compounds towards HCN addition is : [Sep. 02, 2020 (I)]

$$H_3CO$$
 CHO CHO NO_2 (ii) (iii) CHO O_2N CHO CHO (iii) (iv)

- (a) (i)<(iii)<(iv)<(ii) (b) (iii)<(iv)<(i)<(ii) (c) (iii)<(i)<(iv)<(ii) (d) (iii)<(iv)<(ii)<(i)
- 20. Identify (A) in the following reaction sequence:

[Jan. 09, 2020 (I)]

$$\begin{array}{ccc} \text{(A)} & \xrightarrow{\text{(i)} & \text{CH}_3 \text{MgBr}} & \text{(B)} & \xrightarrow{\text{O}_3 / \text{Zn}, \text{H}_2 \text{O}} & \text{O} \\ & & \text{(ii)} & \text{H}', \text{H}_2 \text{O} & \text{II} \\ & & \text{positive} & \text{(ii)} & \text{Conc.} & \text{H}_2 \text{SO}_4 / \Delta \\ & & \text{test} & & & \text{C} - \text{O} \\ & & & & \text{C} + \text{II} \\ & & & & & \text{C} - \text{O} \\ & & & & & \text{C} + \text{II} \\ & & & & & & \text{C} - \text{O} \\ & & & & & & \text{C} + \text{II} \\ & & & & & & & \text{C} + \text{II} \\ & & & & & & & \text{C} + \text{II} \\ & & & & & & & \text{C} + \text{II} \\ & & & & & & & \text{C} + \text{II} \\ & & & & & & & & \text{C} + \text{II} \\ & & & & & & & & \text{C} + \text{II} \\ & & & & & & & & & \text{C} + \text{II} \\ & & & & & & & & & \text{C} + \text{II} \\ & & & & & & & & & & \text{C} + \text{II} \\ & & & & & & & & & & & \text{C} + \text{II} \\ & & & & & & & & & & & & & & & & \\ & & & & & & & & & & & & & \\ & & & & & & & & & & & & & \\ & & & & & & & & & & & & \\ & & & & & & & & & & & & \\ & & & & & & & & & & & \\ & & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ &$$

(a)
$$CH_3$$
 (b) CH_3 CH_3

(c)
$$CH_3$$
 CH_3 CH_3 CH_3

- 21. Consider the following reactions
 - $A \xrightarrow{\quad (i)CH_3MgBr \quad} B \xrightarrow{\quad Cu \quad} \text{2-methyl-2-butene}$

The mass percentage of carbon in A is $_$. [NV, Jan. 09, 2020 (II)]

[144, Jan. 05, 2020

22. The major product in the following reaction is: [Jan. 08, 2020 (II)]

23. What is the product of following reaction?

$$\text{Hex-3-ynal} \xrightarrow{\text{(ii) NaBH}_4} ?$$

[Jan. 07, 2020 (I)]

- (a) COOH
- (b) COOH
- (c) < < < COOH
- (d) _= _ C00H
- 24. Major products of the following reaction are:

[April 10, 2019 (I)]

(a)
$$CH_2OH$$
 and $COOF$

(d) CH₃OH and HCO₂H

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25. Compound $A(C_9H_{10}O)$ shows positive iodoform test. Oxidation of A with KMnO₄/KOH gives acid B(C₈H₆O₄). Anhydride of B is used for the preparation of phenolphthalein. Compound A is: [April 10, 2019 (II)]

(a)
$$CH_3$$
 (b) CH_2 CH_3 (c) CH_3 (d) CH_3 CH_3

26. p-Hydroxybenzophenone upon reaction with bromine in [April 9, 2019 (II)] carbon tetrachloride gives:

- ${f 27.}$ The major product of the following reaction is:

An organic compound neither reacts with neutral ferric chloride solution nor with Fehling solution. It however, reacts with Grignard reagent and gives positive iodoform test. The compound is: [April 8, 2019 (I)]

(a)
$$CH_3$$
 (b) CH_3 OH OH CH_3 (c) CH_3 (d) CH_3 CH_3 CH_3

29. The major product obtained in the following reaction is: [April 8, 2019 (II)]

[April 8, 2019 (I)] 30. In the following reactions, products A and B are:

$$I_3C$$
 H_3C CH_3 H $dil NaOH$ A

$$[A] \xrightarrow{H_3O^+} [B]$$

(a)
$$A = \begin{pmatrix} CH_3 \\ CH_2 \end{pmatrix}$$
; $B = \begin{pmatrix} CH_2 \\ CH_2 \end{pmatrix}$



(b)
$$A = \begin{pmatrix} CH_3 \\ HO \end{pmatrix}$$
 CH_3 ; $B = \begin{pmatrix} CH_3 \\ CH_3 \end{pmatrix}$ CH_3 CH

31. The major product of the following reaction is:

[Jan. 12, 2019 (II)]

32. The aldehydes which will not form Grignard product with one equivalent Grignard reagents are: [Jan. 12, 2019 (II)]

(D)
$$_{\mathrm{HOH_{2}C}}^{\mathrm{CHO}}$$

(b) (B),(C)

(c) (B),(C),(D) (d) (C),(D)

33. The major product formed in the following reaction is:

[Jan. 9, 2019 (II)]

$$H_3C$$
 H + C CH_3 CH_3 CH_3

$$(d) \begin{array}{c} O \\ H_3C \end{array}$$

34. The major product B formed in the following reaction [Online April 16, 2018]

$$\begin{array}{c}
\text{CHO} & \xrightarrow{\text{(i) } C_2H_5MgBr} \\
\text{(ii) } H_2O
\end{array}
A \xrightarrow{\text{HCl}} B$$

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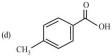
35. Which of the following compounds will most readily be dehydrated to give alkene under acidic condition?

[Online April 16, 2018]

- (a) 4-Hydroxypentan-2-one
- (b) 3-Hydroxypentan-2-one
- (c) 1-Pentanol
- (d) 2-Hydroxycyclopentanone
- 36. The correct sequence of reagents for the following conversion will be:

$$\bigcup_{\text{CHO}}^{\text{O}} \longrightarrow \bigcup_{\text{HO}+\text{CH}_3}^{\text{HO}} \cup \bigcup_{\text{CH}_3}^{\text{CH}_3}$$

- (a) $[Ag(NH_3)_2]^+OH^-, H^+/CH_3OH, CH_3MgBr$
- (b) CH₃MgBr, H⁺/CH₃OH, [Ag(NH₃)₂]⁺OH⁻
- (c) CH₃MgBr, [Ag(NH₃)₂]+OH-, H+/CH₃OH
- (d) $[Ag(NH_3)_2]^+OH^-, CH_3MgBr, H^+/CH_3OH$
- 37. A compound of molecular formula $C_8H_8O_2$ reacts with acetophenone to form a single cross-aldol product in the presence of base. The same compound on reaction with conc. NaOH forms benzyl alcohol as one of the products. The structure of the compound is: [Online April 9, 2017]



The correct statement about the synthesis of erythritol (C(CH2OH)4) used in the preparation of PETN is:

[Online April 10, 2016]

- Thy synthesis requires three aldol condensations and one Cannizzaro reaction.

 (b) Alpha hydrogens of ethanol and methanol are
- involved in this reaction.
- (c) The synthesis requires two aldol condensations and two Cannizzaro reactions.
- (d) The synthesis requires four aldol condensations between methanol and ethanol.
- 39. In the reaction sequence [Online April 11, 2015]

2CH₃CHO
$$\xrightarrow{OH^-}$$
A $\xrightarrow{\Delta}$ B; the product B is :

- (a) CH₃-CH₂-CH₂-CH₂-OH (b) CH₃-CH=CH-CHO
- (c) CH₃-CH₂-CH₂-CH₃
- (d) CH₃ C CH₃
- Which one of the following reactions will not result in the formation of carbon-carbon bond?

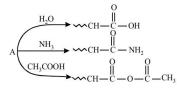
[Online April 9, 2014]

- (a) Reimer-Tieman reaction (b) Friedel Craft's acylation
- (c) Wurtz reaction (d) Cannizzaro reaction
- 41. Which is major product formed when acetone is heated with iodine and potassium hydroxide?

[Online April 9, 2014]

- (a) Iodoacetone
- (b) Acetic acid (d) Acetophenone
- (c) Iodoform An organic compound A, C₅H₈O; reacts with H₂O, NH₃ and CH3COOH as described below:

[Online April 11, 2014]





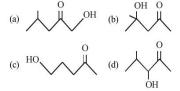
(c)
$$CH_3 - CH_2 - C = C = C$$

 CH_3

- 43. Tischenko reaction is a modification of:
 - (a) Aldol condensation

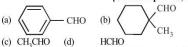
[Online April 11, 2014]

- (b) Claisen condensation
- (c) Cannizzaro reaction
- (d) Pinacol-pinacolon reaction
- 44. Formaldehyde can be distinguished from acetaldehyde by the use of: [Online April 9, 2013]
 - (a) Schiff's reagent
- (b) Tollen's reagent
- (c) L/Alkali
- (d) Fehling's solution
- 45. Clemmensen reduction of a ketone is carried out in the presence of: [Online April 22, 2013]
 - (b) Zn-Hg with HCl (a) LiAlH,
 - (c) Glycol with KOH
- (d) H, with Pt as catalyst
- Which of the following is the product of aldol [Online April 23, 2013]



Cannizaro's reaction is not given by:

[Online April 25, 2013]



Which of the following reagent(s) is/are used for the conversion? [Online April 25, 2013]

$$\stackrel{O}{\longleftarrow}_{CO,Et} \longrightarrow \stackrel{O}{\longleftarrow}_{OH}$$

- (a) glycol/LiAlH₄/H₃O⁺
- (b) glycol/NaH/H₃O⁺
- (c) LiA1H₄
- Iodoform can be prepared from all except: [2012] (a) Ethyl methyl ketone (b) Isopropyl alcohol
 - (c) 3-Methyl 2-butanone (d) Isobutyl alcohol
- In the given transformation, which of the following is the [2012] most appropriate reagent?

$$CH$$
= CH - $COCH_3$ $Reagent$
 CH = CH - CH_2 - CH

- (a) NH₂NH₂, OH
- (b) Zn-Hg/HCl
- (c) Na, Liq NH₃
- (d) NaBH₄
- Among the following the order of reactivity towards nucleophilic addition is [Online May 7, 2012]
 - (a) CH3CHO>CH3COCH3>HCHO
 - (b) HCHO>CH,CHO>CH,COCH,
 - (c) CH,CHO>HCHO>CH,COCH,
 - (d) CH₃COCH₃ > CH₃CHO > HCHO
 - [Online May 12, 2012] The reaction,
 - CH₃CHO Zn(Hg)/Conc. HCl[H] → CH₃CH₃ is
 - (a) Cannizzaro's reaction (b) Rosenmund reduction
 - (c) Wolf-Kishner reduction (d) Clemmenson reduction
- Tollen's reagent and Fehling solutions are used to distinguish between [Online May 26, 2012]
 - (a) acids and alcohols
 - (b) alkanes and alcohols
 - (c) ketones and aldehydes
 - (d) n-alkaens and branched alkanes
- In Cannizzaro reaction given below

$$2PhCHO \xrightarrow{:\overline{O}H} PhCH_2OH + PhC\overline{O}_2$$

the slowest step is: [2009]

- (a) the transfer of hydride to the carbonyl group
- (b) the abstraction of proton from the carboxylic group
- (c) the deprotonation of Ph CH₂OH
- (d) the attack of: OH at the carboxyl group
- The increasing order of the rate of HCN addition to [2006] compound A to D is
 - (A) HCHO
- (B) CH3COCH3
- (C) PhCOCH₃
- (D) PhCOPh
- (a) D < C < B < A
- (b) C < D < B < A
- (c) A < B < C < D
- (d) $D \le B \le C \le A$
- Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as [2005]
 - (a) an amine
- (b) an imine
- (c) an enamine
- (d) a Schiff's base
- On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is
 - (a) CH2COCl+C2H2OH+NaOH
 - (b) CH₃COONa+C₂H₅OH
 - (c) CH₃COOC₂H₅+NaCl
 - (d) CH₃Cl+C₂H₅COONa
- Acetyl bromide reacts with excess of CH₃MgI followed by treatment with a saturated solution of NH₄Cl gives [2004]
 - (a) 2-methyl-2-propanol (b) acetamide
 - (c) acetone
- (d) acetyl iodide





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59. Which one of the following is reduced with zinc amalgam and hydrochloric acid to give the corresponding hydrocarbon?

- (a) Acetamide
- (b) Acetic acid
- (c) Ethyl acetate
- (d) Butan-2-one

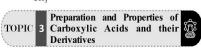
 $\textbf{60.} \quad \text{Which one of the following undergoes reaction with } 50\%$ sodium hyroxide solution to give the corresponding alcohol and acid?

- (a) Butanal
- (b) Benzaldehyde
- (c) Phenol
- (d) Benzoic acid
- 61. On vigorous oxidation by permanganate solution.

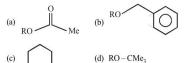
[2002]

 $(CH_3)_2C = CH - CH_2 - CHO$ gives он он (a) $CH_3 - \overset{|}{C} - CH - CH_2CHO$

- (c) CH_3 $C = O + OHCCH_2COOH$
- (d) CH_3 $C = O + OHCCH_2CHO$



62. Which of the following derivatives of alcohols is unstable [Sep. 05, 2020 (I)]



63. The increasing order of the acidity of the α -hydrogen of the following compounds is: [Sep. 05, 2020 (I)]

- (a) (D) < (C) < (A) < (B) (b) (B) < (C) < (A) < (D)
- (c) (A) < (C) < (D) < (B) (d) (C) < (A) < (B) < (D)

64. In the following reaction sequence the major products A

$$\underbrace{ \begin{array}{c} O \\ \\ O \end{array}} \underbrace{ \begin{array}{c} \text{anhydrous} \\ \text{AICI}_3 \end{array}} A \underbrace{ \begin{array}{c} 1. \text{Zn-Hg/HCI} \\ 2. \text{H}_3 \text{PO}_4 \end{array}} B$$

(b)
$$A = \bigcup_{CO_2H} O$$
; $B = \bigcup_{CO_2H} O$

(c)
$$A = \bigcup_{CO_2H} O$$
; $B = \bigcup_{CO_2H} O$

(d)
$$A = \bigcup_{CO_2H} G$$
; $B = \bigcup_{CO_2H} G$

An organic compound (A) (molecular formula C₆H₁₂O₂) was hydrolysed with dil. H₂SO₄ to give a carboxylic acid (B) and an alochol (C). 'C' gives white turbidity immediately when treated with anhydrous ZnCl2 and conc. HCl. The organic compound (A) is: [Sep. 04, 2020 (I)]

$$(c)$$
 \bigcirc \bigcirc \bigcirc

 $\begin{tabular}{ll} \bf 66. & [P] on treatment with $Br_2/FeBr_3$ in CCl_4 produced a single isomer $C_8H_2O_2Br$ while heating $[P]$ with sodalime gave toluene. The compound $[P]$ is: $$ [Sep. 04, 2020 (I)]$ \end{tabular}$





67. An organic compound [A], molecular formula C₁₀H₂₀O₂ was hydrolyzed with dilute sulphuric acid to give a carboxylic acid [B] and an alcohol [C]. Oxidation of [C] with CrO₃-H₂SO₄ produced [B]. Which of the following structures are not possible for [A]? [Sep. 03, 2020 (I)]

(a)
$$CH_3 - CH_2 - CH - OCOCH_2CH - CH_2CH_2$$

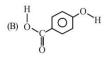
 CH_3

(b)
$$CH_3 - CH_2 - CH - COOCH_2 - CH - CH_2CH_3$$

 $CH_3 - CH_2 - CH - COOCH_2 - CH - CH_2CH_3$

- (c) CH₃CH₅CH₅COOCH₅CH₅CH₅CH₅CH₅
- (d) (CH₃)₃-C-COOCH₂C(CH₃)₃
- 68. Consider the following molecules and statements related to them: [Sep. 03, 2020 (II)]





- (1) (B) is more likely to be crystalline than (A)
- (2) (B) has higher boiling point than (A)
- (3) (B) dissolves more readily than (A) in water Identify the **correct** option from below:

[Sep. 03, 2020 (II)]

- (a) (1) and (2) are true
- (b) (1) and (3) are true
- (c) only (1) is true
- (d) (2) and (3) are true

69. Arrange the following labelled hydrogens in decreasing order of acidity: [Sep. 02, 2020 (II)]

- (a) (ii)>(i)>(iii)>(iv)
- (b) (iii)>(ii)>(iv)>(i)
- (c) (ii)>(iii)>(iv)>(i)
- (d) (iii)>(ii)>(i)>(iv)
- 70. The most suitable reagent for the given conversion is:

[Jan. 08, 2020 (I)]

71. An unsaturated hydrocarbon X absorbs two hydrogen molecules on catalytic hydrogenation, and also gives following reaction:

$$X \xrightarrow{O_3} A \xrightarrow{[Ag(NH_3)_2]^+}$$

B(3-oxo-hexanedicarboxylic acid)

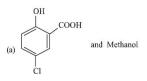
X will be:

[Jan. 08, 2020 (II)]

72. The major products of the following reaction are:

[April 12, 2019 (I)]

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73. The major product of the following reaction is:

74. The major product of the following reaction is:

[April 9, 2019 (I)]

$$\underbrace{\text{CH}_2\text{CH}_3}_{\text{(ii) alkaline KMnO}_4} \xrightarrow{\text{(ii) H}_3\text{O}^+}$$

75. The major product of the following reaction is:

[April 9, 2019 (II)]

OH

CH₂OH

CH₂OH

CHCl₃

OH

OH

OH

OEt

76. The major product of the following reaction is:

[April 8, 2019 (II)]

$$(a) \qquad \begin{array}{c} CH_3 \\ \hline \\ CI \\ CI \\ \end{array}$$

$$(b) \qquad \begin{array}{c} CO_2H \\ \hline \\ CI \\ \end{array}$$

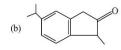
$$(c) \qquad \begin{array}{c} CH_2OH \\ \hline \\ CI \\ \end{array}$$

$$(d) \qquad \begin{array}{c} CHCl_2 \\ \hline \\ CI \\ \end{array}$$

77. The major product of the following reaction is:

[April 8, 2019 (II)]

$$\begin{array}{c} & & & \\ & &$$



78. The major product of the following reaction is:

[Jan. 12, 2019 (I)]

$$\overset{\text{(i) DIBAL-H}}{\bigoplus} \overset{\text{(ii) H}_3O^{7}}{\bigoplus}$$

(a)
$$\begin{array}{c} \text{CHO} \\ \text{O} \\ \text{O} \end{array}$$
 (b) $\begin{array}{c} \text{CH = NH} \\ \text{OH} \\ \end{array}$

Among the following four aromatic compounds ,which one will have the lowest melting point? [Jan. 12, 2019 (I)]

(a)
$$OH$$
 (b) CH_3

80. The major product of the following reaction is:

$$\begin{array}{c} CH_2CH_3 \\ \\ H_3C \blacktriangleright C - CI \xrightarrow{NaOEt} \Delta \end{array} \qquad \qquad \text{[Jan. 12, 2019 (II)]} \\ COOCH_2CH_3 \end{array}$$

(a)
$$CH_3CH_2C = CH_2$$

 $CO_2CH_2CH_3$

(b)
$$CO_2CH_2CH_3$$

 $CH_3 - C = CH CH_3$

(c)
$$H_3C$$
 \leftarrow C \leftarrow CH_2CH_3 \leftarrow CCH_2CH_3 \leftarrow $COOCH_2CH_3$

81. The major product of the following reaction is:

$$\begin{array}{c} \text{OEt} & \text{(i) Ni/H}_2\\ \text{CN} & \text{(ii) DIBAL-H} \end{array}$$

[Jan. 11, 2019 (I)]

82. The major product of the following reaction is:

$$\begin{array}{c|c} COCH_{3} & \xrightarrow{(i) \ KMnO_{4}/KOH/\Delta} \\ \hline (ii) \ H_{2}SO_{4}(dii) & \\ \hline \textbf{[Jan. 11, 2019 (I)]} \end{array}$$

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83. The major product obtained in the following reaction is:

[Jan. 11, 2019 (II)]

84. Which of the following compounds reacts with ethylmagnesium bromide and also decolourizes bromine water solution? [Jan. 11, 2019 (II)]

85. The major product obtained in the following conversion is: [Jan. 11, 2019 (II)]

$$\begin{array}{c} \text{CH}_3 \\ \\ \\ \\ \\ \\ \end{array} \xrightarrow{\text{Br}_2(1 \text{ eq.})} \\ \xrightarrow{\text{MeOH}} \end{array}$$

(c)
$$_{\mathrm{Br}}$$
 (d) $_{\mathrm{Br}}$ (e) $_{\mathrm{CH_{3}}}$

86. Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride?

[Jan. 10, 2019 (I)]

(a)
$$CH_2$$
 OH CH_2 OH (b) CH_2 OH CH_2 OH CH_2 OH CH_2 OH $COOH$

87. The decreasing order of ease of alkaline hydrolysis for the following esters is [Jan. 10, 2019 (I)]



- (a) III > II > IV > I
- (b) III>II>IV
- (c) IV > II > III > I
- (d) II>III>I>IV
- An aromatic compound 'A' having molecular formula C₂H₆O₂ on treating with aqueous ammonia and heating forms compound 'B'. The compound 'B' on reaction with molecular bromine and potassium hydroxide provides compound 'C' having molecular formula C6H7N. The structure of 'A' is: [Jan. 10, 2019 (II)]

89. The major product obtained in the following reaction is:

$$CO_2Et$$
 $NaOEt/\Delta$

[Jan. 10, 2019 (II)]

(d)
$$CO_2Et$$

- 90. The correct decreasing order for acid strength is:
 - [Jan. 9, 2019 (I)]
 - (a) NO₂CH₂COOH> FCH₂COOH> CNCH,COOH>CICH,COOH
 - (b) FCH,COOH>CNCH,COOH> NO,ČH,COOH > CICH,COOH

- (c) CNCH2COOH>NO2CH2COOH> FCH,COOH>CICH,COOH
- (d) NO₂CH₂COOH> CNCH₂COOH> FCH2COOH>ClCH2COOH
- 91. The major product of the given reaction is:

[Online April 16, 2018]

$$(a) \qquad (b) \qquad (b) \qquad (c) \qquad (d) \qquad (d)$$

92. The major product formed in the following reaction is:

$$\begin{array}{c} \text{OCOCH}_3 & \text{PCC} \\ \text{(Pyridinium chlorochromate)} \\ \text{OH} & \text{CHCl}_3 \end{array}$$

[Online April 15, 2018 (II)]





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93. The increasing order of the acidity of the following carboxylic acids is: [Online April 15, 2018 (II)]

$$\bigcap_{NO_2}^{CO_2H} \bigcap_{II}^{CO_2H} \bigcap_{II}^{CO_2H} \bigcap_{II}^{CO_2H}$$

- (a) III < II < IV < I (c) IV < II < III < I
- (b) I < III < II < IV (d) II < IV < III < I
- 94. The major product of the following reaction is

[Online April 15, 2018 (I)]



 $\textbf{95.} \quad \text{The reagent(s) required for the following conversion are:} \\$

$$EtO_2C$$
 CO_2H
 HO_2C
 CHO

[Online April 15, 2018 (I)]

- (a) (i) NaBH₄, (ii) Raney Ni/H₂, (iii) H₃O⁺
- (b) (i) LiAlH₄, (ii) H₃O⁺
- (c) (i) B_2H_6 , (ii) DIBAL-H, (iii) H_3O^+
- (d) (i) B_2H_6 , (ii) $SnCl_2/HCl$, (iii) H_3O^4
- **96.** The main reduction product of the following compound with NaBH₄ in methanol is:

(e)
$$NMe_2$$
 (d) NMe_2

- 97. Sodium salt of an organic acid 'X' produces effervescences with conc. H₂SO₄, 'X' reacts with the acidified aqueous CaCl₂ solution to give a white precipitate which decolourises acidic solution of KMnO₄, 'X' is: [2017]
 - (a) C₆H₅COONa
- (b) HCOONa
- (c) CH₃COONa
- (d) Na₂C₂O₄
- 98. The major product obtained in the following reaction is:

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9. The major product expected from the following reaction is:

[Online April 8, 2017]

$$\begin{array}{c} \text{CH}_2\text{OH O} \\ \text{OH} \end{array} \\ \begin{array}{c} \text{NH}_2 \xrightarrow{\text{HCI(g)}/\text{CCI}_4} \end{array} \\ \end{array}$$

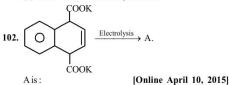
(c)
$$O \longrightarrow O \longrightarrow NH_2$$

$$(d) HO_2C \longrightarrow O$$

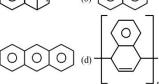
- 100. Bouveault-Blanc reduction reaction involves:
 - [Online April 9, 2016]
 - (a) Reduction of an acyl halide with H₂/Pd
 - (b) Reduction of an anhydride with LiAlH₄
 - (c) Reduction of an ester with Na/C2H5OH
 - (d) Reduction of a carbonyl compound with Na/Hg and HCl.
- 101. In the presence of a small amount of phosphorous, aliphatic carboxylic acids react with chlorine or bromine to yield a compound in which α-hydrogen has been replaced by halogen. This reaction is known as:

[Online April 10, 2015]

- (a) Wolff Kishner reaction
- (b) Rosenmund reaction
- (c) Etard reaction
- (d) Hell Volhard Zelinsky reaction



A is:
(a) (b)



103. COOH is used as : [Online April 10, 2015]

- (a) Analgesic
- (b) Insecticide
- (c) Antacid
- (d) Antihistamine

104. In the reaction,

 $\begin{array}{c} CH_{3}COOH \xrightarrow{LiAlH_{4}} A & \xrightarrow{PCl_{5}} B \xrightarrow{Alc.KOH} C, \\ \text{the product C is:} & \textbf{[2014]} \end{array}$

- (a) Acetaldehyde
- (b) Acetylene
- (c) Ethylene
- (d) Acetyl chloride
- 105. Phthalic acid reacts with resorcinol in the presence of concentrated H₂SO₄ to give: [Online April 12, 2014]
 - (a) Phenolphthalein (b) Alizarin
 - (c) Coumarin (d) Fluorescein
- 106. An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br₂ to give $CH_3CH_2NH_2$. A is : [2013]
 - (a) CH₂COOH (b)
 - (b) CH₃CH₂CH₂COOH

107. Monocarboxylic acids are functional isomers of:

[Online April 23, 2013]

- (a) Ethers
- (b) Amines
- (c) Esters
- (d) Alcohols
- 108. A liquid was mixed with ethanol and a drop of concentrated $\rm H_2SO_4$ was added. A compound with a fruity smell was formed. The liquid was : [2009]
 - (a) HCHO
- (b) CH₃COCH₃
- (c) CH₃COOH
- (d) CH₃OH
- 109. The correct order of increasing acid strength of the compounds [2006]
 - (A) CH₃CO₂H
- (B) MeOCH₂CO₂H
- (C) CF₃CO₂H
- (D) $\stackrel{\text{Me}}{\longrightarrow}$ CO_2H
- is
- (a) D < A < B < C
- (b) A < D < B < C
- (c) B<D<A<C
- (d) D<A<C<B
- 110. Among the following acids which has the lowest pK_0 value? [2005]
 - (a) CH₃CH₂COOH
- (b) (CH₃)₂CH COOH
- (c) HCOOH
- (d) CH₃COOH
- 111. When CH₂ = CH COOH is reduced with LiAlH₄, the compound obtained will be [2003]
 - (a) CH₂=CH—CH₂OH (b) CH₃—CH₂—CH₂OH
- (c) $CH_3 CH_2 CHO$ (d) $CH_3 CH_2 COOH$ 112. $CH_3CH_2COOH - \frac{Cl_2}{red P} A - \frac{alc. KOH}{A} B$, What is B? [2002]
 - (a) CH₃CH₂COCl
- (b) CH₃CH₂CHO
- (c) CH₂=CHCOOH
- (d) ClCH,CH,COOH.



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Hints & Solutions



Chemistry

(II)
$$\bigcirc \bigcap_{\substack{S \text{RCL}_2 + \text{H}_3 \text{O}^* \\ \text{HCI} \\ \text{(Stephens)}}} \bigcirc \bigcap_{\substack{C \text{HO} \\ \text{(Stephens)}}} \bigcirc \bigcap_{\substack{C \text{CHO} \\ \text{(Stephens)}}} \bigcirc \bigcap_{\substack{C \text{CHO} \\ \text{(MS)} \\ \text{(Rosenmund)}}} \bigcirc \bigcap_{\substack{C \text{HO} \\ \text{(Rosenmund)}}} \bigcap_{\substack{C$$

3. (a) Br₂, hv alc KOH
$$\Delta$$

$$O_{Me_2S}$$

$$O_{H}$$

$$O_{H}$$

$$O_{M}$$

$$O_{H}$$

4. (a)
$$\xrightarrow{^{1}BuO^{-}}$$
 $\xrightarrow{^{1}BuO^{-}}$ $\xrightarrow{^{1}BuO^{-}}$

(b)
$$OH \xrightarrow{CiO_3} HO$$
 OH $SOCI_2$

(c)
$$PBr_3 \rightarrow PRr_4$$
 $Alc. OH$ $Alc.$

Generally, aldehydes are more reactive than ketones in nucleophilic addition reactions. $\therefore \mbox{ Rate of reaction with alcohol to form acetal and ketal is}$

(b) Best combination is HCHO (more reactive alde-

$$\begin{array}{c} O \\ H-C-H+CH_3OH \xrightarrow{\hspace{1cm} HCl} & HC \\ \end{array} \xrightarrow[Acetal]{} \begin{array}{c} OMe \\ HCOMe \\ \end{array}$$



 $\begin{array}{ll} \textbf{9.} & \textbf{(c)} & R-C \equiv N - \stackrel{(i)}{=} A | H(i-Bu)_2} \rightarrow R-CHO \\ & \text{The reduction of nitriles to aldehydes can be done using } D|BAL-H[A]H(i-Bu)_s]. \\ \\ \textbf{10.} & \textbf{(a)} & \text{For the given reaction condition, the major product is:} \end{array}$

11. (c) Reaction involved:

12. (c) The total number of optically active compounds formed is four. The product has two chiral C atoms. Thus, it has $2^n = 2^n = 4$ stereoisomers.

13. (d)
$$(CH_3) = (CH_3) + (C$$

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15. (c)

$$CH \equiv CH \xrightarrow{\text{LiNH}_2/\text{ether}} CH \xrightarrow{\text{CH}} CH \xrightarrow{\text{CH}_3} CH \xrightarrow{\text{CH}_3} CH - CH(CH_3)_2$$

$$CH_3 - CH - CH(CH_3)_2 \xleftarrow{\text{HgSO}_4} (H_2SO_4) CH_3 - CH - CH(CH_3)_2$$

$$CH_3 \qquad CH \qquad CH \qquad CH_{12} CH_{12} CH_{13} CH_{14} CH_{15} CH_{$$

16. (a)

$$CH_{2} = CH - CHO \xrightarrow{(i) \text{ NaBH}_{4}} H_{2}C = CH - CH_{2}OH$$

$$H_{2}C = CH - CH_{2} - CI$$

$$[A]$$

$$H_{2}C = CH - CH_{2}CI \xrightarrow{Anhy} DBr$$

$$G[B]$$

$$DBr$$

$$G[C]$$

$$G[C]$$

17. (b) Rate of Nucleophillic addition reaction is directly proportional to the –I and –M effect of the substituents present in the substrate. Ketones are less susceptible to the nucleophillic addition, due to the presence of alkyl (R) group which has +I effect. Thus reactivity order is

$$CH = O$$

$$(ii)$$

$$(ii) > (iv) > (iii)$$

$$(iii)$$

$$(iv)$$

$$(iv)$$

18. (c) $O \xrightarrow{CH_2-C-CH_3} \xrightarrow{(i)CH_3MgBr/H_2O}$

$$\overbrace{ \text{OY} \atop \text{CH}_2\text{-C-CH}_3 \atop \text{CH}_3} \xrightarrow{\text{(ii) conc. H}_2\text{SO}_4}$$

$$CH = C \xrightarrow{CH_3} \xrightarrow{(i) O_2} O \xrightarrow{CHO} CHO$$

$$CH_3 \xrightarrow{(ii) Zn/H_3O} O \xrightarrow{CHO} + CH_3 - C - CH_3$$

$$(C) \qquad CH_2OH \qquad CO\bar{O}K^+ \\ Conc. KOH \qquad O \qquad + O \qquad CH_3-C-CH_3 \\ CH_3-C-CH_3 \qquad Ba(OH)_2/\Delta \\ (D) \qquad CH_3 \qquad CH$$

 (c) —I effect of NO₂ increases reactivity towards nucleophilic addition reaction with HCN. – OCH₃ group is electron donating due to resonance effect which decreases the reactivity towards nucleophillic addition.

20. (b)
$$(i) CH_3MgBr \\ (ii) H_3O^7 \\ (ii) H_3O^7 \\ CH=O \\ O \\ CD_3 \\ CH_3 \\ (B)$$



Compound A is CH₃—C—CH₂—CH₃(C₄H₈O)

Mass percentage of carbon

$$= \left(\frac{12 \times 4}{48 + 16 + 8} \times 100\right) = 66.67$$

22. (d)
$$\overset{\text{if}}{\bigcirc} \overset{\text{if}}{\longrightarrow} \overset{\text{OH}}{\longrightarrow} \overset{\text{OH}}$$

23. (d)

25. (d) (i) Since compound $A(C_9H_{10}O)$ contains relatively very low H as compared to C, so it must contain a benzene ring.

(ii) Further the oxidation product $B(C_8H_0O_4)$ of A is a dicarboxylic acid which forms anhydride on heating, hence the acid is phthalic acid which is further comfirmed by the fact that it is used in the preparation of phenolphthalein when condensed with phenol in presence of cone. H_3SO_4 . So the given compound A corresponds to option (4).

$$(A) \xrightarrow{CH_3} \xrightarrow{I_2+NaOH} \xrightarrow{CO^-Na^+} CH_3$$

$$\begin{array}{c} & & & \\$$



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28. (d)

$$\begin{array}{c} OH \\ CH-CH_3 \\ COC_2H_5 \end{array} \xrightarrow{I_2/NaOH} \begin{array}{c} O \\ C-O^- \\ COC_2H_3 \end{array} + CHI_3$$

Reaction with +ve Electrophilic centre or Grignard reagent acidic hydrogen is present

Fehling solution test -ve CHO group is absent

Neutral FeCl₃ test —ve phenolic group is absent

Iodoform test +ve -COCH₃ or -CH(OH)-

keto group (C = O) into -OH group.

(a) Grignard reagent will not react with aldehydes if it has a functional group which contains acidic hydrogen.
 Thus options (B) and (D) have —COOH and —CH₂OH respectively which contain acidic H-atom. Therefore, acid

$$HO_2C$$
 CHO
 $RMgX$
 $XMgO_2C$
 $+R-H$
 $+R-H$
 $XMgO_3C$
 $+R-H$

(3) Reaction mechanism involved:

34. (d)
$$C - H \xrightarrow{(i) C_2 H_5 MgBr} MeO$$

give unsaturated ketone
$$\longrightarrow \alpha$$
, β -Unsaturated ketono

$$\begin{array}{c} OH \\ \hline \\ MeO \end{array} \begin{array}{c} OH \\ \hline \\ \hline \\ MeO \end{array} \begin{array}{c} CI \\ \hline \\ MeO \end{array}$$

6. (a)
$$\bigcap_{\text{CHO}} \frac{[\text{Ag(NH}_3)_2]\text{OH}}{\text{Tollens reagent}} \longrightarrow \bigcap_{\text{CO}_2\text{H}}$$

35. (a)

$$\xrightarrow{\text{H}^+/\text{CH}_3\text{OH}} \xrightarrow{\text{O}} \xrightarrow{\text{C}} \xrightarrow{\text{CH}_3\text{MgBr}} \xrightarrow{\text{CH}_3\text{MgBr}} \xrightarrow{\text{C}} \xrightarrow$$

37. (a) CHO
$$CHO$$
 CHO CHO

38. (a) The pentaerythritol is typically produced via a base-catalyzed reaction of acetaldehyde with excess formaldehyde. The aldol condensation of three moles of formaldehyde with one mole of acetaldehyde is followed by a crossed Cannizzaro reaction between pentaerythritol, the intermediate product, and formladehyde to give the final pentaerythritol product and sodium formate as a byproduct. These reactions are shown below

$$\begin{array}{c} C(CH_2OH)_3CHO {\longrightarrow} C(CH_2OH)_4 + HCOONa \\ (Cannizaro's reaction) \end{array}$$

9. **(b)**
$$CH_3 - C - H \xrightarrow{OH^-}$$

$$\frac{\Delta}{\text{(Aldol condensation)}} CH_3 - CH = CH - C - 1$$

of aldehyde in which one molecule of aldehyde reduces to alcohol whereas other oxidises to salt of carboxylic

 $C_6H_5CHO+KOH \longrightarrow C_6H_5CH_2OH+C_6H_5COOK$

41. (c) $CH_3COCH_3 + 3I_2 + 4KOH \longrightarrow CHI_3 + CH_3COOK + 3HI + 3HI_2O$

42. (c) Given compound A is
$$CH_3 - CH_2 - C = C = O$$

$$CH_3$$

$$CH_3$$

$$CH_3 - CH_2 - C = C = O \xrightarrow{NH_3}$$
 CH_3

$$\begin{bmatrix} H & & & & \\ & & & & & \\ CH_3 - CH_2 - C & C - O \end{bmatrix}$$

$$\downarrow & & & \\ CH_3 - CH_2 - C & C & OH \\ CH_3 & CH_2 - C & C & OH \end{bmatrix}$$

$$CH_3 - CH_2 - CH_2 - C - NI$$

$$CH_3 - CH_2 - C = C = O \xrightarrow{H_2O}$$

$$CH_3 - CH_2 - C = C = O \xrightarrow{H_2O}$$

$$\label{eq:CH3-CH2-CH-COOHCH3} CH_3-CH_2-CH-COOH \\ CH_3$$

$$CH_3-CH_2-C=C=O \xrightarrow{CH_3COOH}$$

40. (d) Cannizzaro's reaction is a disproportionation reaction 43. (c) Tishchenko reaction is a modification of Cannizzaro's reaction. This reaction involves disproportionation of an aldehyde lacking a hydrogen atom in the alpha position in the presence of an alkoxide. The reaction product is an ester. Catalysts are aluminium alkoxide or sodium alkoxide. In Cannizzaro's reaction the base is sodium hydroxide and the oxidation product is a carboxylic acid and the reduction product is an alcohol.

$$\begin{array}{c}
\overrightarrow{O} \\
R - C - H + AI(OEt)_3 \longrightarrow R - \overrightarrow{C}H \\
O \xrightarrow{AI(OEt)_3} \longrightarrow R - \overrightarrow{C}H \\
\xrightarrow{R - CHO} R - \overrightarrow{C} - H \\
O \xrightarrow{C} \overrightarrow{C}HR \longrightarrow R - C - OCH_2R
\end{array}$$

5. **(b)**
$$C = 0 \xrightarrow{Z_1 \cdot H_g/HC_1} CH_2$$

47. (c) Only those aldehydes which do not have α-H atom undergo Cannizaro's reaction. Hence CH₃CHO will not undergo Cannizaro's reaction as it has 2 α H atoms. undergo Cannizaro's reaction as it has 3 $\alpha\,H$ atoms.

$$OC_2H_5 \xrightarrow{HO OH} OC_2H_5$$

$$Liall_4 \longrightarrow OH$$

49. (d) Iodoform test is given by methyl ketones, acetaldehyde and methyl secondary alcohols.

Isobutyl alcohol is a primary alcohol except ethanol, C₂H₅OH, primary alcohols do not give haloform test. Hence does not give positive iodoform test.

- (a) Aldehydes and ketones can be reduced to hydrocarbons by the action (i) of amalgamated zinc and concentrated hydrochloric acid (Clemmenson reduction), or (ii) of hydrazine (NH₂NH₂) and a strong base like NaOH, KOH or potassium *tert*-butoxide in a high-boiling alcohol like ethylene glycol or triethylene glycol (Wolf-Kishner reduction) -OH group is acid-sensitive, so Clemmenson reduction can not be used.
- (b) Presence of alkyl group in carbonyl compounds decreases their reactivity towards nucleophilic addition. Further greater the number of such groups lesser will be the reactivity towards nucleophilic addition, thus correct
- HCHO > CH₃CHO > CH₃COCH₃
- 52. (d) The reaction given is a Clemmenson reduction.
 53. (c) All aldehydes show reaction with Tollen's reagent and Fehling solutions, but ketones do not show this

Note:- Benzaldehyde do not give reaction with Fehling

55. (a) Note: Addition of HCN to carbonyl compounds is nucleophilic addition reaction. The order of reactivity of carbonyl compounds is

Aldehydes (smaller to higher) > Ketones (smaller to higher). Therefore,

higher). Therefore,
HCHO>CH₃COCH₃>PhCOCH₃>PhCOPh
Note: The lower reactivity of ketones is due to presence of
two alkyl group which show +I effect. The reactivity of
ketones decreases as the size of alkyl group increases.

56. (e)
$$O + HN(CH_3)_2 \longrightarrow OHN(CH_3)_2 \xrightarrow{-H_2O} N(CH_3)_2$$

(c) There is no reaction hence the resultant mixture contains CH₃COOC₂H₅+NaCl.

$$\begin{array}{c} O \\ 0 \\ \parallel \\ C-Br \\ \hline (ii) Saturated \ MH_4CI \\ \hline CH_3 \\ C-OH \\ C-OH \\ CH_3 \\ C-OH \\ C$$

59. (d) It is Clemmensen's reduction

$$\begin{array}{c} O \\ CH_3 - C - CH_2 - CH_3 & \xrightarrow{Zn-Hg} CH_3CH_2 - CH_2CH_3 \\ Butane-2-one & \\ Butane \end{array}$$

(b) This reaction is known as cannizzaro's reaction. In this reaction benzaldehyde in presence of 50%. NaOH undergoes disproportionation reaction and form one mol of benzyl alcohol (reduced product) and one mole of sod. benzoate (oxidation product)

$$\xrightarrow{\text{CHO}} \xrightarrow{\text{50\% NaOH}} \xrightarrow{\text{CH}_2\text{OH}} \xrightarrow{\text{COO}^-\text{Na}^+}$$

- 61. (b) Double bond is leaved and oxidised to -COOH, -CHO is also oxidised to -COOH $(CH_3)_2C = CHCH_2CHO \xrightarrow{KMnO_4}$
 - ${\rm (CH_3)_2CO+HOOCCH_2COOH}$
- 62. (a) Esters are hydrolysed in basic medium (saponification), so it is unstable in aqueous base.
 63. (a) Acidity ∞ stability of conjugate base

) Actially
$$\infty$$
 stability of conjugate base $P_{h} = P_{h} = P$

(C) (D) Thus increasing order of acidity is D \leq C \leq A \leq B.

$$Z_{\text{n-Hg}} \xrightarrow[\text{HCI}]{Z_{\text{n-Hg}}} 0 \xrightarrow[\text{J}]{A_{\text{pO}_4}} 0 \xrightarrow[\text{B}]{A_{\text{pO}_4}} 0$$



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65. (a)
$$O \leftarrow \xrightarrow{H_3O^+} O \rightarrow O + HO \leftarrow 3^\circ$$
 Alcohol (Give Lucas tes immediately

66. (a) COOH COOH

$$CH_3 \longrightarrow CH_3$$

$$NaOH/CaO,\Delta$$

$$CH_3 \longrightarrow CH_3$$

67. (a)
$$CH_3 - CH_2 - CH - OCOCH_2 - CH - CH_2CH_3 \xrightarrow{H_3SO_4(dil.)}$$

$$CH_3 - CH_2 - CH - OH + HOOC - CH_2 - CH - CH_2 - CH_3$$

$$CH_3 - CH_2 - CH - OH + HOOC - CH_2 - CH - CH_2 - CH_3$$

$$(C) - CH_3$$

$$(C) - CH_3 - CH_2 - C = O$$

$$CH_3 - CH_3 - CH_2 - C = O$$

$$CH_3 - CH_3 - CH_3$$

- 68. (a, b, d) Molecule (A) shows intramolecular H-bonding while molecule (B) shows intermolecular H-bonding. Due to presence of intermolecular H-bonding it has more b, p.t. than molecule (A). Molecule (B) also shows intermolecule Hbonding with water which makes it more soluble than A. (B) is crystalline solid while (A) is liquid at room temperature because of weaker intramolecular hydrogen bonding.
- because of weaker intramolecular hydrogen bonding.

 69. (c) Acidic strength & Stability of conjugate base
 General order of acidic strength is

 GOODMER OF ACIDICAL PROCESS.
 - $R-COOH>Ph-OH>R-C\equiv CH$ In between (iii) and (iv), (iii) is more acidic due to -M effect of -NO $_2$.
- Thus, decreasing order of acidity is (ii) > (iii) > (iv) > (i).

 70. (a) B₂H₆ is a very selective reducing agent and usually used to reduce acid to alcohol.

71. (c) O_3 O_{CHO} O_{CHO}

(A)
$$\xrightarrow{[Ag(NH_3)_2]^+}$$
 0 $\xrightarrow{3}$ 2 1 COOH $\overset{4}{_{5}}$ 6 COOH

72. (d)

$$\bigcap_{\text{CI}} \underbrace{\xrightarrow{\text{CHCI}_3}}_{\text{NsOH}} \xrightarrow{\text{CI}} \underbrace{\xrightarrow{\text{CHO}}}_{\text{CI}} \xrightarrow{\text{HCHO, conc. NaOH}}$$

- 73. **(b)** LiAlH₄ reduces esters to alcohols but does not reduce C = C.
 - $CH_3CH = CH CO_2Me \xrightarrow{LiAlH_4} CH_3CH = CHCH_2OH$
- 74. (a) Alkaline KMnO₄ converts \(\subseteq \text{P} \) \(\text{with a benzylich hydrogen into benzoic acid.} \)

$$\underbrace{\text{CH}_2\text{CH}_3}_{\text{(i) alkaline KMnO}_4} \xrightarrow{\text{COOH}}$$



76. (a)
$$CH_3$$
 $CHCl_2$ Cl_2 Cl_3 $CHCl_2$ Cl_3 Cl_4 $CHCl_2$ Cl_4 $CHCl_2$ Cl_5 $CHCl_2$ Cl_5 $CHCl_2$ Cl_5 $CHCl_2$ Cl_5 $CHCl_2$ Cl_5 $CHCl_2$ $CHCl_2$

78. (c) Dissobutyl aluminium hydride, commonly abbreviated as DIBAL-H is a reducing agent for some specific functional groups. It reduces − C = N to − CH = NH (amines) which are easily hydrolysed to − CHO. It also reduces lactones to aldehydes.

$$(i) \xrightarrow{(i) \text{DIBAL-H}} OH$$

$$(ii) \text{Hi,0*} OH$$

$$H$$

79. (d) The force of attraction between the molecules affects the melting point of a compound. Polarity increases the intermolecular force of attraction and as a result increases the melting point.

80. (b) Heating of the given compound in presence of strong base is favoured for elimination reaction resulting in more stable alkene.

81. (d)

$$\begin{array}{c|c} & & & H \\ \hline DIBAL-H \\ \text{(reduces)} \\ \text{cster to} \\ - CHO gp.) \end{array}$$

82. (c) Alkaline $KMnO_4$ is a strong oxidising agent and oxidises – CH_3 as well as – CO group to – COOH.

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$$\begin{array}{c} \text{COCH}_{3} \\ \xrightarrow{\text{(i) KMnO}_{4}/\text{KOH}/\Delta} \\ \xrightarrow{\text{(ii) H}_{2}\text{SO}_{4}\text{(dil)}} \end{array}$$

83. (c)

 $\label{eq:LiAlH4} \begin{tabular}{ll} LiAlH_4 is a nucleophilic reducing agent, hence it will reduce-COOH to CH_2OH, -CO to-CHOH and-NO_2 to NH_2 but does not reduce C=C linkage. \end{tabular}$

84. (d

85. (a)
$$Br^+(1 \text{ eqv.})$$
 $Br^-(1 \text{ eqv.})$ $Br^-(1 \text{ eqv.})$ $Br^-(1 \text{ eqv.})$

86. (a)

$$\begin{array}{ccc} \text{CH}_2 & \text{COOH} & \text{dehydrating agent} \\ \text{CH}_2 & \text{COOH} \\ \text{CH}_2 & \text{COOH} \\ \text{Adipic acid} \end{array} + \text{CO}_2 + \text{H}_2\text{O}$$

Adipic acid does not form anhydride.

87. (b) Rate of reaction ∝ Electrophillicity of carbonyl carbon, so E.W.G. increases the rate, while E.R.G. decreases the rate

$$O_2N - \underbrace{\bigcirc \bigcirc }_{III} C - OC_2H_5 > CI - \underbrace{\bigcirc \bigcirc }_{II} - COOC_2H_5$$

$$\begin{array}{c}
\bigcirc \\
\Gamma
\end{array}
-COOC_2H_5 > MeO - \begin{array}{c}
\bigcirc \\
\Gamma
\end{array}
-COOC_2H_5$$

88. (a)
$$A \xrightarrow{\text{(C_2H_2O_2)}} A \xrightarrow{\text{(i) Aq. NH}_3} B \xrightarrow{Br_2/\text{KOH}} C \xrightarrow{\text{(C_2H_2N)}}$$

going backward, compound C is obtained from B by Br $_2$ and KOH (Hoffmann bromamide reaction), so B must be an amide (– CONH $_2$) and C an amine – NH $_2$ or C $_6$ H $_5$ – NH $_2$. Thus A should be benzoic acid, C $_6$ H $_5$ – COOH or C $_7$ H $_6$ O $_2$.

Reaction involved:

$$(A) \qquad (B) \qquad (B) \qquad (C_7H_6O_3) \qquad (B) \qquad (C_7H_6O_3) \qquad (C_7$$

89. (d) Reaction involved:

- 90. (d) The acidic strength of a compound or an acid depends on the inductive effect (-I). Higher the (-I) effect of a substituent higher will be acidic strength. Now, the decreasing order of (-I) effect of the given substituents is NO₂>CN>F>Cl.
 - ∴ The correct decreasing order of acidic strength amongst the given carboxylic acids is:
 - $NO_2CH_2COOH > CNCH_2COOH > FCH_2COOH > CICH_2COOH$
- (b) Acid chloride is more reactive than aldehyde. Hence, phenolic – OH will react with –COCl group first to form ester. This is followed by cyclisation in presence of conc. sulfuric acid.





$$\begin{array}{c} \text{MeO} & \xrightarrow{(i) \text{ OHC CH}_2\text{COCl}} \\ \text{OH} & \xrightarrow{(ii) \text{H}_2\text{SO}_{\Phi}, \text{ heat}} \\ \end{array} \\ \xrightarrow{\text{MeO}} \begin{array}{c} \text{OHC} \\ \text{O$$

92. (b) PCC oxidizes primary alcohols to aldehydes and secondary alcohols to ketones.

In the above reaction, —OCOCH₃ group is hydrolyzed to secondary alcohol which is then oxidised (with PCC) to ketone.

- 93. (a) The increasing order of the acidity of the carboxylic acids is III < II < IV < I. In aromatic acids, electron withdrawing groups like -CI, -CN, -NO, increases the acidity, whereas electron releasing groups like -CH₃, -OH, -OCH₃, -NH₂ decreases the acidity.
- 94. (c) Since acid chloride is more reactive than alkyl halide, so COCl group will react first.

In the second step, Friedel Craft's alkylation occurs in a position that is ortho to alkoxy group and para to methoxy group. Both methoxy and alkoxy groups are ortho para directing groups.

95. (c)
$$EIO_{2}C \longleftrightarrow COOH \xrightarrow{B_{2}H_{6}} EIO_{2}C \longleftrightarrow CH_{2}OH$$

$$SBC_{1}HC_{1}EIO_{2}C \longleftrightarrow CH_{2}OH \qquad HOOC \longleftrightarrow CH_{2}OH$$

- CHO 96. (a) Sodium borohydride reduces ketonic group to alcohol,
- but not the amide group and C = C double bond. 97. (d) $Na_2C_2O_4 + H_2SO_4 \rightarrow Na_2SO_4 + CO\uparrow + CO_2\uparrow + H_2O$

$$\begin{aligned} &\text{Na}_3 \text{C}_2 \text{O}_4 + \text{CaCl}_2 \rightarrow \text{CaC}_2 \text{O}_4 \downarrow + 2 \text{NaCl} \\ &\text{'X'} \qquad \text{(white ppt.)} \end{aligned}$$

$$& 5 \text{CaC}_2 \text{O}_4 \downarrow + 2 \text{KMnO}_4 + 8 \text{H}_2 \text{SO}_4 \longrightarrow \\ &\text{(purple)} \end{aligned}$$

$$& \text{K}_2 \text{SO}_4 + 5 \text{CaSO}_4 + 2 \text{MnSO}_4 + 10 \text{CO}_2 + 8 \text{H}_2 \text{O} \\ &\text{(colourless)} \end{aligned}$$

(b) DIBAL-H is a reducing agent. It reduces both ester and carboxylic group into an aldehyde at low temperature

$$\underbrace{\text{CO^{\text{H}}}}_{\text{O}} \underbrace{\text{Dibat-H}}_{\text{OH}} \underbrace{\text{OH}}_{\text{O}} \underbrace{\text{CHO}}_{\text{H}}$$

$$\xrightarrow{\text{HCI}(g)/\text{CCI}_4} 0 0 0 \text{NH}_2$$

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$$\begin{array}{c} \underset{H_2O}{\longleftarrow} \\ \underset{H_2O}{\longleftarrow} \\ O-H \\ \end{array} \begin{array}{c} O\\ \\ OH \\ \end{array} \begin{array}{c} O\\ \\ NH_2 \\ OH \\ \end{array}$$

100. (c) The Bouveault reduction is a reaction in which an ester is reduced to primary alcohol using absolute ethanol and sodium.

$$\begin{matrix} O \\ R-C-OR \xrightarrow{\quad Na/C_2H_5OH \quad} RCH_2OH+ROH \end{matrix}$$

Bouveault-Blanc reduction.

101. (d) α-Substitution is occaured when a carboxylic acid having \(\alpha\)-hydrogens is treated with chlorine or bromine in presence of small amount of red phosphorous. This reaction is commonly known as HVZ reaction.

$$\begin{array}{ccc} R-CH_2COOH+X_2 & \xrightarrow{P} & \\ & X & \\ & | & \\ R & CH-COOH+HX(X=CI,Br) \end{array}$$

102. (b)
$$\begin{array}{c} O \\ COOK \\ COO$$

103. (a) Drugs which relieve pain are called analgesics drugs. Analgesics are of two types (i) Narcotics and (ii) Non-narcotics. Aspirin (acetylsalicylic acid) is a non-narcotic

104. (c)
$$\begin{array}{cc} \text{CH}_3\text{COOH} & \xrightarrow{\text{LiA1H}_4} \text{CH}_3\text{CH}_2\text{OH} \\ & \xrightarrow{\text{PCI}_5} \text{CH}_3\text{CH}_2\text{Cl} & \xrightarrow{\text{Ale. KOH}} \text{CH}_2 = \text{CH}_2 \\ \text{(B)} & \text{(B)} \end{array}$$

105. (d)
$$+2$$
 OH Conc. H_2SO_4

106. (d)
$$A \xrightarrow{NH_3} B \xrightarrow{\Delta} C \xrightarrow{Br_2} CH_3CH_2NH_2$$

Reaction (III) is a Hofmann bromamide reaction. Hence, C should be $\mathrm{CH_3CH_2CONH_2}$ which can be obtained from

$$\begin{split} & \text{CH}_{3}\text{CH}_{2}\text{COO}^{\frown}\text{NH}_{4}^{+}(B). \\ & \text{Thus (A) should be CH}_{3}\text{CH}_{2}\text{CCOOH} \\ & \text{CH}_{3}\text{CH}_{2}-\text{COOH} \xrightarrow{\text{NH}_{3}}\text{CH}_{3}\text{CH}_{2}\text{CCO}^{\frown}\text{NH}_{4}^{+} \\ & \xrightarrow{\Delta}\text{CH}_{3}\text{CH}_{2}\text{CONH}_{2} \xrightarrow{\text{Br}_{4}}\text{NCH}_{3}\text{CH}_{2}\text{CH}_{2}\\ & \xrightarrow{\text{(C)}} \end{split}$$

107. (c) Mono-carboxylic acids are functional isomers of esters. e.g.,

CH₃COOH HCOOCH₃
Acetic acid Methyl formate

108. (c) Fruity smell is due to ester formation which is formed between ethanol and acid.

 $\text{CH}_{3}\text{COOH} + \text{C}_{2}\text{H}_{5}\text{OH} \xrightarrow{\quad \text{Conc.H}_{2}\text{SO}_{4} \\ \rightarrow \quad}$

 $\mathrm{CH_3COOC_2H_5} + \mathrm{H_2O}$ 109. (a) The correct order of increasing acid strength is $(Me)_2$ CHCOOH < CH $_3$ COOH <

MeOCH,COOH < CF3COOH Note: Electron withdrawing groups increase the acid strength whereas electron donating groups decrease the

acid strength.]

110. (c) $pK_{\alpha} = \log K_{\alpha}$ it COOH is the strongest acid and hence it has the highest K_{α} or lowest pK_{α} value.

111. (a) LiAlH₄ can reduce COOH group but not the double

 $CH_2 = CH - COOH \xrightarrow{LiAlH_4} CH_2 = CH - CH_2OH$

112. (c) $CH_3CH_2COOH \xrightarrow{Cl_2} CH_3CHCICOOH$

-HCI CH2 = CHCOOH



