

# **Carbonyl Compounds**and Acid Derivatives

# **Question Bank**

# LEVEL 1

- 1. When phenyl ethanoate is alkylated with chloroethane/AlCl<sub>3</sub>, the para product is the major product. This is because
  - (a) Alkylation usually occurs at the para position.
  - (b) The -Cl group is a weakly deactivating and an ortho/para director.
  - (c) The -OCOMe group is an activator and an ortho/para director.
  - (d) The -Et group is weakly activating and an ortho/para director.
- 2. Terminal alkynes react with 9-borabicyclononane (9-BBN) and then aq. alkaline hydrogen peroxide to give aldehydes because
  - (a) Acid catalysed electrophilic addition of water follows Markovnikov's rule.
  - (b) Acid catalysed electrophilic addition of water is anti-Markovnikov.
  - (c) The radical addition is anti-Markovnikov.
  - (d) Steric and electronic effects cause the boron to the terminal carbon.
- 3. In general, ketones are more reactive towards nucleophiles than esters because
  - (a) The  $\alpha$ -protons of a ketone are more acidic than those of an ester.
  - (b) The alkyl group in a ketone is an electron donating group due to hyperconjugation.
  - (c) Alkoxy (RO-) groups are sterically larger than the related alkyl group.
  - (d) Alkoxy (RO-) groups are stronger electron donating than alkyl groups via resonance.

**4.** When 2-methylcyclohexanone reacts with a base and is then treated with an electrophile such as methyl iodide the product depends on the reaction conditions, see below. At high temperature, the major product is the geminal dimethyl compound. This is because

$$\begin{array}{c|c} O & O^- & O \\ \hline & CH_3I & \hline & Et_3N \\ \hline & heat & \hline & O^\circ C & \hline & CH_3I \\ \hline \end{array}$$

- (a) Alkyl groups are weak electron donors due to inductive effects and hyperconjugation.
- (b) The enolate formed at high temperature is more stable.
- (c) diisopropyl amide (LDA) is a much stronger base than Et<sub>3</sub>N.
- (d) Lithium diisopropyl amide (LDA) promotes an anti-Markovnikov type addition.
- **5.** The reaction of a Grignard reagent with a carboxylic acid does not give a secondary alcohol. This is because
  - (a) Grignard reagents only react with the aldehydes, ketones, esters and epoxides.
  - (b) The carboxylic acid is too sterically hindered to react.
  - (c) The carboxylic acid is not electrophilic enough to react.
  - (d) The Grignard reagent is a base, so an acid-base reaction occurs.
- **6.** When 1-phenylpropyne reacts with H<sub>2</sub>O/HgSO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub>, the major product is propiophenone shown below. This is because

- (a) Alkyl groups are weak electron donors due to inductive effects and hyperconjugation.
- (b) Carbonyl groups are electron withdrawing groups due to resonance.
- (c) Phenyl groups can stabilise positive charge by resonance.
- (d) The reaction is controlled by steric factors.
- 7. When methyl benzoate is nitrated with  $HNO_3/H_2SO_4$ , the meta product is the major product. This is because
  - (a) The -CO<sub>2</sub>CH<sub>3</sub> group is a meta director.
  - (b) The -OCH<sub>3</sub> is a meta director.
  - (c) The -NO<sub>2</sub> group is deactivating and a meta director.
  - (d) Nitration usually occurs at the meta position.
- **8.** A chemist attempted to reduce the compound shown below with NaBH<sub>4</sub>, but could not isolate the desired product 4-hydroxybutanoic acid. This is because

- (a) NaBH<sub>4</sub> reduced both the carboxylic acid and the aldehyde.
- (b) NaBH<sub>4</sub> is not reactive enough to reduce the carboxylic acid or the aldehyde.
- (c) An intermediate was formed that reacted to give a cyclic acetal.
- (d) An intermediate was formed that reacted to give a cyclic ester.

(a) 
$$Br$$
 (b)  $Br$  (c)  $N^+ \equiv N$  (d)  $N^+ \equiv N$ 

11. ? 
$$\xrightarrow{\text{(i) CH}_3\text{CO}_3\text{H}}$$
  $\xrightarrow{\text{(ii) H}^+, \text{H}_2\text{O}}$   $\xrightarrow{\text{H}_3\text{C}-\text{C}-\text{OH}}$   $\xrightarrow{\text{H}_3\text{C}-\text{C}-\text{OH}}$   $\xrightarrow{\text{H}_3\text{C}-\text{C}-\text{OH}}$   $\xrightarrow{\text{H}_3\text{C}-\text{C}-\text{OH}}$   $\xrightarrow{\text{H}_3\text{C}-\text{C}-\text{OH}}$   $\xrightarrow{\text{Identify reactant}}$   $\xrightarrow{\text{CH}_3}$   $\xrightarrow{\text{CH}_3}$ 

(50:50 of these enantiomers)

13. 
$$? \xrightarrow{(i) \text{ KOH, heat}} OH$$
 Identify reactant  $CH_2CH_3$ 

14. ? 
$$(i) BH_3$$
  $(ii) NaOH, H_2O_2$   $(ii) NaOH, H_2O_2$   $(ii) NaOH, H_2O_2$   $(ii) NaOH, H_2O_2$   $(ii) NaOH, H_2O_2$ 

(50:50 of these enantiomers)

15. Appropriate reagent for the following conversion is

$$\bigcup_{Br} \bigcup_{Br} \bigcup_{Br}$$

- (a) NH<sub>2</sub>NH<sub>2</sub>; EtOH/OH
- (b) Red  $P + I_2$
- (c) Zn-Hg/HCl
- (d) All of them

**16.** In the given reaction

- (a)  $Me_3C-CH_2OH + Ph-COO^-$
- (b) Me<sub>3</sub>C-COO<sup>-</sup> + Ph-CH<sub>2</sub>OH

(d) 
$$Me-CH_2-C-Me+Ph-CH-OH$$

17. Which of the following gives glyoxal as one of the product on ozonolysis

(b) 
$$H_2C=CH$$

(c) H<sub>3</sub>C=CH-CH=CH,

(d) Both (a) and (c)

**18.** The correct statement is

- (a) chloral forms stable hydrate
- (b) methanal is more reactive than ethanal towards nucleophilic addition
- (c) protonated carbonyl group is more reactive towards KCN
- (d) all of them

**19.** In the given reaction sequence, the B is

CHO
$$CH_{2}\text{-OH}$$

$$CH_{3} \xrightarrow{CH_{2}\text{-OH}} A \xrightarrow{(i) H_{2}N-NH_{2}} B$$

$$(ii) KOH/C_{2}H_{5}OH$$

$$(iii) H_{3}O^{\oplus}$$

$$(c) \xrightarrow{CH_{3}} CHO$$

$$(d) \text{ none of these}$$

**20.** The maximum reactive towards the nucleophilic attack is

21. Match column I (reaction) with column II (name of the reaction) and select the correct answer using the codes given.

#### Column I

# Column II

- (a) 2C<sub>6</sub>H<sub>5</sub>CHO (i) Benzoin condensation
- (b)  $C_6H_5CHO + HCHO \xrightarrow{20\% \text{ NaOH}}$ (ii) Self-Cannizzaro reaction
- (c) 2C<sub>6</sub>H<sub>5</sub>CHO KCN/(alc.) (iii) Cross Cannizzaro reaction
- (d)  $C_6^{"}H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa}_{\Delta}$ (iv) Perkin reaction
- (a) a i, b ii, c iii, d iv (b) a - ii, b - iii, c - i, d - iv
- (c) a i, b iii, c iv, d ii (d) a - ii, b - iii, c - iv, d - i

22. In the reaction

$$CH_3-C-CH_3^+$$
  $C_2H_5ONa$  Product

the product is

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

**23.** The product of the given reaction is

$$CH_{3}-CH-CI \xrightarrow{(i) Ph_{3}P} [X]$$

$$CH_{3}-CH-CI \xrightarrow{(ii) BuLi} OCH_{3}$$

$$(iii) O= CH_{3}$$

$$CH_{3}-CH_{3}$$

$$CH_{3}-CH_{3}$$

$$CH_{3}-CH_{3}$$

$$CH_{3}-CH_{3}$$

$$CH_{3}-CH_{3}$$

$$CH_{3}-CH_{3}$$

$$CH_{3}-CH_{3}$$

(c) 
$$CH_3$$
- $CH_3$ 
 $CH_3$ 
 $CH_3$ 

- 24. Which of the following gives positive Fehling's solution test
  - (a) Ph-CHO
- (b) CH<sub>3</sub>CHO
- (c) CCl<sub>3</sub>CHO
- (d) All of them

25. In the given reaction

$$\begin{array}{ccc} & \text{H}_{3}\text{C} & \text{O} \\ \text{CH}_{3}\text{-C-C-CHO} & \xrightarrow{\text{(i) Conc. NaOH}} & \text{Product is} \\ & \text{CH}_{3} & & \text{(ii) H}_{3}\text{O}^{\oplus} & \end{array}$$

$$\begin{array}{c} H_3C \quad O \\ (d) \quad CH_3-C -C -C +C + OH \\ CH_3 \end{array}$$

**26.** In the given reaction, (P) will be

$$\begin{array}{c}
O \\
\hline
(i) (CH_3)_2CuLi \\
(ii) H_3O^{\oplus}
\end{array}$$
(P)

(a) 
$$H_3C$$
—

CH<sub>3</sub>

OH

$$(d) \bigcirc CH_3$$

27. In the given reaction

$$\begin{array}{c}
O \\
(i) C_2H_5ONa/C_2H_5OH \\
\hline
(ii) R
\end{array}$$
CHO

- (R) would be
- (a) HCHO
- (b) CH<sub>3</sub>CHO
- (c) HCOOC<sub>2</sub>H<sub>5</sub>
- (d)  $(COOC_2H_5)$ ,
- 28. Aldehydes and ketones react with  $\alpha$ -bromo esters and zinc in ether or benzene medium to yield
  - (a) α-keto ester
- (b)  $\beta$ -hydroxy ester (c)  $\gamma$ -keto acids
- (d) β-keto ester
- 29. In the given reaction sequence, compound (B) is

$$(i) \overset{\odot}{OH} (A) \xrightarrow{NH_2NH_2/OH} (B)$$

(a) 
$$\bigcirc$$
 =CH-C<sub>6</sub>H<sub>5</sub>

(c) 
$$CH_2-C_6H_5$$
 (d)  $CH_2-C_6H_5$ 

30. In the given reaction sequence

$$(i) O_3 \longrightarrow (A) \xrightarrow{\bigcirc OH/\Delta} (B)$$

compound (B) is

- 31. Two isomeric ketones, 3-pentanone and 2-pentanone can be distinguished by
  - (a) I<sub>2</sub>/NaOH
- (b) NaHSO<sub>3</sub>
- (c) NaCN/HCl

 $\ddot{\text{CH}}$ – $\text{C}_6\text{H}_5$ 

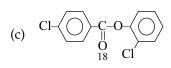
- (d) 2,4-DNP
- 32. Silver mirror test with Tollen's reagent is given by
  - (a) C<sub>6</sub>H<sub>5</sub>CHO
- (b) Ph-OH
- (c)  $C_6H_5$ – $CH_2$ –C– $CH_2OH$
- (d) CH<sub>3</sub>CHO

**33.** Which of the following is a correct conversion?

(b) 
$$\frac{\text{(i) Mg, ether}}{\text{(ii) C}_2\text{H}_5\text{OH}}$$
 OC<sub>2</sub>H<sub>5</sub>

(c) 
$$(i)$$
  $(i)$   $(i)$ 

**34.** For the given reaction, the product is



- 35. Which one of the following does not respond positive to iodoform test even on heating?
  - (a)  $CH_3$ –C– $CH_2$ –C–OPh (b)  $CH_3$ –C– $CH_3$  (c)  $CH_3NO_2$
- (d) Both (a) and (b)
- **36.** The rate of reduction of the following carbonyl compounds by NaBH<sub>4</sub>

(iii) 
$$H_3C$$
  $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

(iv)  $O_2N$ 

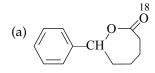
(a) iv > i > ii > iii

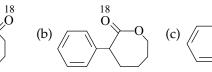
(b) i > ii > iv > iii

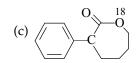
(c) iii > ii > i > iv

(d) ii > i > iii > iv

37. 
$$CF_3CO_3H$$
 A; product (A) is







(d) None of these

Alc. KCN (ii)  $H_2O$  Products

The number of possible stereoisomers in the product mixture is

- (a) 1
- (b) 2

- (c) 3
- (d) 4

- **40.** The incorrect statement amongest the following is
  - (a) The order of reduction reaction by  $LiAlH_4$  and that of the reduction by  $NaBH_4$  each is two
  - (b) Al–H bond is more ionic than B–H bond and hence LiAlH<sub>4</sub> can produce larger concentration of hydride ion than that of NaBH<sub>4</sub>
  - (c) LiAlH<sub>4</sub> cannot reduce –NO<sub>2</sub> group
  - (d) Inspite of very small rate constant of reduction of any carbonyl function other than aldehydes and ketones, the rate of reduction with LiAlH<sub>4</sub> becomes appreciable due to large concentration of hydride ion
- 41. Which of the following ketones has the largest equilibrium constant for addition of water?







O 42. Ethyl acetoacetate react with CH<sub>3</sub>–C–H in the presence of base/Δ followed by acidic hydrolysis and subjected to heat, product formed is

(a) 
$$O = \begin{array}{c} H_3C & O \\ & \parallel \\ -C - OH \end{array}$$

(b) 
$$O = \begin{array}{c} H_3C & O \\ -C-OH \\ CH_3 \end{array}$$

(c) 
$$O = \left(\begin{array}{c} O \\ -C - OH \end{array}\right)$$

**43.** Identify the product (C) of the given sequence of reaction

Ph AlCl<sub>3</sub> (A) 
$$\xrightarrow{\text{Ph}}$$
 (B)  $\xrightarrow{\text{KOH}/\Delta}$  (C)

- **44.** Which of the following gives positive Fehling's solution test
  - (a) HCOOH
- (b) HOOC-CHO
- (d) HC-CH O O
- **45.** Which of the following geminal diol is most unstable?
  - (a)  $F_3C$  C OH OH

(b)  $H_3C$  C OH OH

(c) 
$$\begin{array}{c} \text{CICH}_2 \\ \text{CICH}_2 \end{array}$$
 C  $\begin{array}{c} \text{OH} \\ \text{OH} \end{array}$  (d)  $\begin{array}{c} \text{Cl}_3\text{C} \\ \text{OH} \end{array}$ 

**46.** In the given reactions, sequence

$$\begin{array}{c}
O \\
HCN \\
+A \\
\hline{(ii) H_2O}
\end{array} \rightarrow B \xrightarrow{H_2SO_4 + NaNO_2} C$$

The compound C is

(a) 
$$H_3C$$
 (b)  $H_3C$   $NH_2$  (c)  $H_3C$  (d)  $H_3C$ 

- 47. What will be the pH of an acetate-acetic acid solution when the ratio of [CH<sub>3</sub>CO<sub>2</sub>]/[CH<sub>3</sub>CO<sub>2</sub>H] is 10? (A table of pK<sub>3</sub> data is given below.)
  - (a) 5.76
  - (b) 4.76
  - (c) 3.76
  - (d) 1.76

- **48.** If the internal pH of a muscle cell is 6.8. Which one of the following statements about the concentrations of PO<sub>4</sub> <sup>3-</sup>, HPO<sub>4</sub> <sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub> <sup>1-</sup>, and H<sub>3</sub>PO<sub>4</sub> is true? (Hint: use the table of pK<sub>3</sub>s given in the previous question.)
  - (a) The species with the highest concentration is H<sub>3</sub>PO<sub>4</sub>.
  - (b) The species with the highest concentration is  $H_2PO_4^{\ 1^-}$ .
  - (c) The species with the highest concentration is  $PO_4^{3-}$ .
  - (d) The species with the highest concentration is  $HPO_4^{2^-}$ .
- **49.** Choose the incorrect statement about the following acid/base reactions involving propyne and its anion propynide.

$$\begin{array}{ccc} & & pK_{a} \\ H_{2}O & & 16 \\ H_{3}C-C \equiv CH & & 25 \\ NH_{3} & & 34 \end{array}$$

(i) 
$$H_3C - C \equiv CH + OH^{\ominus} \rightleftharpoons H_3C - C \equiv C^{\ominus} + H_2O$$

(ii) 
$$H_3C - C \equiv CH + NH_2^{\odot} \Longrightarrow H_3C - C \equiv C^{\odot} + NH_3$$

- (a) The equilibrium in equation (i) lies to the left.
- (b) The equilibrium in equation (ii) lies to the right.
- (c) In reaction (ii) ammonia, NH<sub>3</sub>, acts as a base.
- (d) Propyne,  $CH_3C \equiv CH$ , is a stronger acid than ammonia,  $NH_3$ .

- **50.** Choose among the following reactions those that will give a racemic mixture of two enantiomers as the products.
  - (i) OOCH<sub>3</sub> O(ii) OH O(iii) OH O(iii) O(iii) OH O(iii) O(iii) O(iii) O(iii) O(iv) O(iv
  - (iii)  $\begin{array}{c} O \\ \hline (ii) \text{ NaBH}_4 \\ \hline (ii) \text{ H}_2 O \end{array}$
  - (a) i (b) ii
- (c) iii (d) ii + iii
- **51.** Choose the order that has the following carbonyl groups correctly arranged with respect to increasing reactivity with NaBH<sub>4</sub>.

  - increasing increasing increasing increasing acidity acidity acidity
- **52.** Which of the following is the correct order for hydrate formation of the given compounds?

(i) 
$$\bigcirc$$
 (ii)  $\bigcirc$  (iii)  $\bigcirc$  (iv)  $\bigcirc$  HO

(a) i > ii > iii > iv

(b) iv > i > ii > iii

(c) iii > ii > i > iv

(d) iii > i > iv > ii

53. 
$$\xrightarrow{\text{OH}} \xrightarrow{\text{H}_2\text{SO}_4} [X] \xrightarrow{\text{(i) O}_3} [Y] \xrightarrow{\text{(i) dil. OH}^{\odot}/\Delta} [Z]$$

$$(iii) \text{ H}_2\text{O} \xrightarrow{\text{(iii) H}_2\text{O}} [Z]$$

In the above sequence, compoud [Z] is

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

$$O = \underbrace{\begin{array}{c} OH & PCC \\ \hline \\ NaOH \end{array}} P_1 \xrightarrow{I_2} P_2 + P_3 \text{ (Yellow ppt.)}$$

54. 
$$P_2 \xrightarrow{\text{(i) NaBH}_4} P_4$$

Final compound P<sub>4</sub> is

(a) 
$$O$$
 (b)  $O$  (c)  $O$  (d)  $O$  (d)  $O$  (e)  $O$  (d)  $O$  (e)  $O$  (for  $O$  (d)  $O$  (for  $O$  (e)  $O$  (for  $O$  (for  $O$  (for  $O$  (for  $O$  ))  $O$  (for  $O$  )  $O$ 

(a) 
$$\bigcirc$$
 CH<sub>2</sub> (b)  $\bigcirc$  CH<sub>2</sub> (c)  $\bigcirc$  CHO (d)  $\bigcirc$  CH<sub>3</sub>

**56.** Product "P" obtained by the reaction

OMe 
$$\xrightarrow{PhMgBr (excess)}$$
 (A)  $\xrightarrow{H_2O}$  (B)  $\xrightarrow{heat}$  Product

Ph
Ph
Ph
(c) Ph
Ph
Ph

57. 
$$CH_2$$
 + Ph - C - H  $\xrightarrow{NaOEt}$  major products  $NO_2$ 

(a) 
$$C = CH - Ph$$
 (b)  $C = C$  OEt NC OH OH O2N Ph (d) None of these O2N

58. Aldehydes and ketones having  $\alpha$ -hydrogen convert into carbanion in the presence of base as follows

$$\begin{array}{ccc}
O & O \\
CH_3 - C - R & \xrightarrow{OH^-} \overline{C}H_2 - C - R
\end{array}$$

This carbanion is stable because of

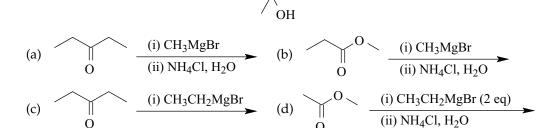
- (a) Presence of -I group (-CO-)
- (b) Delocalisation of negative charge by pi bond
- (c) Presence of +I group (i.e., R) on -CO-
- (d) Both (a) and (b)

COOPh

59. 
$$\xrightarrow{\text{(i) Zn/Et}_2O}$$
 A, A is
$$\xrightarrow{\text{(ii) CH}_2O}$$

$$\xrightarrow{\text{(iii) H}_3O^+;}$$
COOH
COOH
COOH
OH
OH
OH

**60.** Choose the reaction that would not be successful for the preparation of the following alcohol.



**61.** Choose the major product of the following reaction sequence.

(a) (b) 
$$O$$
 (i)  $CH_3CH_2Li$  (excess) (ii)  $NH_4Cl$ ,  $H_2O$  OH (d)  $O$  OH

**62.** The compounds A, B and C in the reaction sequence

$$\begin{array}{c} CH_{3} \\ CH_{3} \end{array} \hspace{-0.5cm} C = \hspace{-0.5cm} \hspace{-0.5c$$

are given by the set

- (a) Iodoform, ethylene, ethyl alcohol
- (b) Iodoform, acetylene, acetaldehyde
- (c) Iodoform, propyne, acetone
- (d) Iodoform, 2-propanol, propanone
- 63. Any one of the product formed is by (CHO OHC OHC II) Conc. NaOH II) CHO OHC OHC III) Conc. NaOH III) CHO OHC

(c) 
$$CH_2OH$$
  $COOH$   $CH_2OH$  (d)  $O$ 

- **64.** A compound "A" formula of  $C_xH_pCl_x$  on reaction with alkali can give "B" of formula  $C_xH_pCl_x$ or "C" of formula C<sub>3</sub>H<sub>4</sub>. "B" on oxidation gave a compound of the formula C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>. "C" with dilute H<sub>2</sub>SO<sub>4</sub> containing Hg<sup>2+</sup> ion gave "D" of formula C<sub>3</sub>H<sub>6</sub>O, which with bromine and alkali gave the sodium salt of C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>. Then "A" is
  - (a) CH<sub>2</sub>CH<sub>2</sub>CHCl<sub>2</sub>
- (b) CH<sub>3</sub>CCl<sub>2</sub>CH<sub>3</sub>
- (c) CH,ClCH,CH,Cl (d) CH,CHClCH,Cl
- **65.** Identify compound [X] in the given reaction

$$Me-C \equiv C-H \xrightarrow{\frac{1\% \text{ HgSO}_4}{\text{dil. H}_2\text{SO}_4}} [P_1] \xleftarrow{\text{P.C.C}} \text{compound [X]}$$

(b) 
$$OH$$
 (c)  $OH$ 

**66.** What is the major product obtained from the following reaction

(a) 
$$OH$$
  $O-CH_2-CH_2-OH$ 

(b) 
$$\bigcirc$$

$$(d) \bigcirc O-CH=CH_2$$

67. Give the product from the following reaction sequence

$$(a) \begin{array}{c} O \\ O \\ OH \end{array} \begin{array}{c} Ethyleneglycol \\ OH \end{array} \begin{array}{c} Collin's \\ Feagent \end{array} \begin{array}{c} EtMgBr \\ H_2O \end{array} \begin{array}{c} H^{\oplus} \\ H_2O \end{array}$$

68. Predict the major organic product from the following reaction

$$H_3C$$
 $O$ 
 $NaBH_4$ 
 $A$ 
 $LiAlH_4$ 

69. 
$$\stackrel{\text{O}}{\longrightarrow} \stackrel{\text{O}}{\longrightarrow} \stackrel{\text{$$

The product (Z) is

**70.** The final product (Y) of the following reaction sequence is

$$O + HN \stackrel{CH_3}{\longleftarrow} \frac{\text{dil. H}^{\oplus}}{\text{C}_2H_5} \times \frac{\text{(i) CH}_3\text{Br}}{\text{(ii) H}_3\text{O}^+} Y + Z$$

 $Z + Hinsberg reagent \longrightarrow KOH \rightarrow (No dissolution/solid residue)$ 

(a) 
$$CHO$$
 (b)  $CH_3$  (c)  $C_2H_5$  (d)  $CH_3$ 

71. In the given reaction

A and B are

(a) 
$$HCOO^{-} + Me-$$
 CH<sub>2</sub>OH (b)  $CH_{3}OH + Me-$  COO<sup>©</sup> (c)  $HCOO^{-} + Me-$  COO<sup>©</sup> (d)  $CH_{3}OH + Me-$  CH<sub>2</sub>OH

(c) 
$$HCOO^- + Me - COO^{\odot}$$
 (d)  $CH_3OH + Me - CH_2OH$ 

**72.** Choose the major product of the following reaction.

(a) 
$$CH_3$$

$$(i) \text{ LiAlD}_4$$

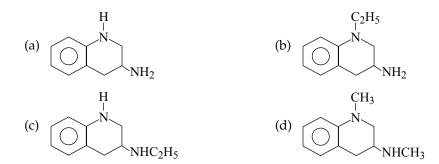
$$(ii) \text{ H}_3\text{O}^{\oplus}$$
(b)  $CH_3$ 

$$(ii) \text{ LiAlD}_4$$

$$(ii) \text{ H}_3\text{O}^{\oplus}$$
(c)  $CH_3$ 

$$(ii) \text{ LiAlD}_4$$

$$(ii) \text{ H}_3\text{O}^{\oplus}$$



- 74. An organic compound  $A(C_6H_{12}O)$  neither decolourise bromine water nor changes the colour of acidic dichromate solution. A on heating with H<sub>2</sub>SO<sub>4</sub> produces an alkene which on oxidative ozonolysis gives B(C<sub>6</sub>H<sub>10</sub>O<sub>3</sub>), which gives an yellow precipitate with NaOH/I<sub>3</sub>. The most probable structure of A is
  - (b) OH (c) OH (d)
- $\begin{array}{c|c}
  \text{H } H \\
  \text{H } H
  \end{array}
  \xrightarrow{\text{HIO}_4.2\text{H}_2\text{O}} A \xrightarrow{\text{NaOH}/\Delta} B \xrightarrow{\text{(i) Me}_2\text{CuLi}} (C).$ HO OH

Identify "(C)" product

(a) 
$$(b)$$
  $(c)$   $(d)$   $(d)$ 

76. In the given reaction

$$CH_3$$
- $CH_2$ - $COOH \xrightarrow{Br_2/PBr_3} \xrightarrow{NH_3} (A)$ 

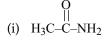
(a) would be

77. 
$$H_3C$$
  $CH_3$   $H_2O/H^{\oplus}$  A (an acid) + B

where A and B are, respectively

| $NH_2$ | ŅH |
|--------|----|
|        |    |

- 78. CH<sub>3</sub>-CH-COOH can be converted into CH<sub>3</sub>-CH-CH<sub>2</sub>OH by the use of
  - (a)  $H_2/Pd$
- (b) LiAIH<sub>4</sub>
- (c) NaBH<sub>4</sub>
- (d) CH<sub>3</sub>MgBr
- 79. Arrange in increasing order of reactivity towards nucleophile



- (ii) CH<sub>3</sub>–C–C
- (iii) CH<sub>3</sub>–C–OAc
- (iv) H<sub>3</sub>C–C–OCH<sub>3</sub>

(a) ii > iv > i > iii

(b) ii > iii > iv > i

(c) iii > ii > i > iv

- (d) iii > iv > ii > i
- **80.** What is the name of the following compound?

- (a) trans-N-ethyl-3-pentenamide
- (b) trans-1-ethyl-3-pentenamide
- (c) trans-N-ethyl-4-pentenamide
- (d) trans-1-ethyl-4-pentenamide
- **81.** What is the name of the following compound?

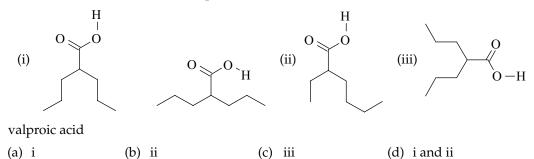
- (a) (R)-3-methylhexaneamine
- (b) (S)-3-methylhexaneamine
- (c) (R)-3-methylhexanenitrile
- (d) (S)-3-methylhexanenitrile
- **82.** What is the name of the following compound?

- (a) (R)-3-hydroxybutanal
- (b) (S)-3-hydroxybutanal
- (c) (R)-3-hydroxybutanol
- (d) (S)-3-hydroxybutanol
- 83. What is not the name of the following compound?



- (a) acetone
- (b) dimethyl ketone
- (c) 2-oxoketone
- (d) propanone
- 84. Which of the following compound has the highest boiling point?
  - (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>
- (b) CH<sub>3</sub>CO<sub>2</sub>H
- (c) CH<sub>3</sub>COCH<sub>3</sub>
- (d) CH<sub>3</sub>CH<sub>2</sub>OH

**85.** Valproic acid found clinical use as an anticonvulsant and mood-stabilizing drug that has proven useful in the treatment of epilepsy, bipolar disorder, and other problems. Choose the constitutional isomer(s) of valproic acid.



**86.** What is the name of the following compound?

- (a) ethyl 4-oxopentanoate
- (b) ethyl ester methyl ketone
- (c) ethyl 4-ketonepentanoate
- (d) ethyl 4-ketone pentyl ester
- 87. What is the structure of 2,4-hexanedione?

(a) 
$$(b)$$
  $(b)$   $(c)$   $(c)$   $(d)$ 

**88.** What is the name of the following compound?

- (a) (R)-2-ketocyclohexane carbaldehyde
- (b) (R)-2-aldehydecyclohexanone
- (c) (S)-2-formylcyclohexanone
- (d) (S)-2-aldehydecyclohexanone
- **89.** If only one equivalent of NH<sub>3</sub> (one mole of NH<sub>3</sub> reacts with one mole of cyclohexyl chloride) was used, the reaction may not go to completion. Why?
  - (a) NH<sub>3</sub> is not a strong nucleophile. Therefore, more NH<sub>3</sub> is needed.
  - (b) Cl is not a good leaving. Therefore, more NH<sub>3</sub> is needed.
  - (c) Cyclohexyl group presents large steric hindrance. Therefore, more NH<sub>3</sub> is needed.
  - (d) NH<sub>3</sub> will be protonated by HCl as reaction proceeds. Therefore, the reaction will be incomplete.
- 90. What could be the best reagents for the following reaction?

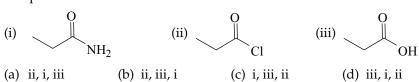
- (a) H<sub>2</sub>NEt and CH<sub>3</sub>CO<sub>2</sub>H
- (b) H<sub>2</sub>NEt and HCl

(c) H<sub>2</sub>NEt and NaOH

- (d) H<sub>2</sub>NEt and Na<sup>+</sup>-OCH<sub>3</sub>
- **91.** What could be the product for the following reaction?

$$(a) \qquad \begin{array}{c} OH \qquad O \\ OH \qquad OH \end{array} \qquad \begin{array}{c} HCl \\ OH \qquad OH \end{array} \qquad \begin{array}{c} Product \\ OH \qquad OH \qquad OH \end{array}$$

**92.** What is the order of increasing boiling points (from the lowest to highest) for the following compounds?



93. 
$$(i) CH_3CO_3H$$

$$(ii) CH_3MgBr then H_3O^+$$
 product is
$$(a) \qquad (b) \qquad (c) \qquad (d) \qquad (d)$$

(a) 
$$O$$
 (b)  $O$  (c)  $O$  (d)  $O$ 

102. 
$$C \equiv C - CH_3 \xrightarrow{\text{(i) Na, NH}_3} \text{ product is}$$

(c) 
$$\begin{array}{c} H & H \\ -C & -C - CH_3 \\ R & H \end{array}$$

OH

104. 
$$CH_3CO_2H$$
  $(i)$   $SOCl_2$   $(ii)$  3-methylaniline  $(iii)$   $LiAlH_4$ , then  $H_3O^+$ 

(a) 
$$H_3C$$
  $NH_2$   $CH_3$ 

(c) 
$$H_3C$$
  $N$   $H$ 

# LEVEL 2

## **Single and Multiple-choice Type**

### 1. The product is

2. 
$$(i) O_3 \longrightarrow (A) \xrightarrow{\text{dil. OH}} \text{Products}$$

In the above sequence the final products of the reaction is/are

Correct option is

(a) 
$$A = B = H_3C$$
—CH<sub>2</sub>CH<sub>2</sub>F; C = CH<sub>2</sub>OH

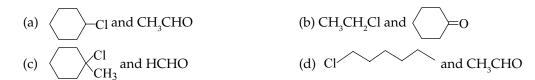
(b) 
$$A = H_3C$$
 —  $CH=CH_2$ ;  $B = H_3C$  —  $CH_2CH_2F$ 

(c) 
$$C = HOCH_2 - CH_2CH_2F$$

(d) 
$$B = H_3C$$
 —  $CH_2CH_2F$ ;  $C = HOCH_2$  —  $CH_2CH_3$ 

4. (A) 
$$(ii) Ph_3P$$
  $(ii) BuLi$   $(iii) (B)$   $(iii) CH-CH_3$ 

In the above reaction, (A) and (B) will respectively be



- 5. Which of the following pairs will form the same product with phenyl hydrazine/H<sup>®</sup>?
  - (a) CH<sub>2</sub>OH-CO-CH<sub>3</sub> and CHO-CHOH-CH<sub>3</sub>
  - (b) Glucose and mannose
  - (c) Glucose and fructose
  - (d) Glucose and sucrose
- **6.** Which is/are untrue statement(s)?
  - (a) Protonation increases electrophilic nature of carbonyl group
  - (b)  $CF_3SO_3^-$  is a better leaving group than  $CH_3SO_3^-$
  - (c) Benzyl carbonium ion is stabilised by resonance
  - (d)  $CCl_3CH \stackrel{OH}{\underset{OH}{<}}$  is unstable
- 7. Identify the product in the following reaction

$$O \longrightarrow O + Br_2 + KOH \longrightarrow A + B$$

A and B are

(a) 
$$CHBr_3$$
 (b)  $CODE = CODE = CODE$ 

**8.** In the following reaction

$$\begin{array}{c}
O \\
& \\
& \\
\hline
C_2H_5ONa
\end{array}$$

$$A \xrightarrow{(i)H_3O^{\oplus}} B$$

$$A \xrightarrow{(ii)} Soda \lim_{\to} \Delta$$

Product A and B are

(a) 
$$OC_2H_5$$
 (b)  $OC_2H_5$  (c)  $OC_2H_5$ 

9. 
$$CHO^+$$
 (CH<sub>3</sub>CO)<sub>2</sub>O  $CH_3COONa \rightarrow A \xrightarrow{SOCl_2} B \xrightarrow{H_2-Pd (BaSO_4)} C;$ 

Product (C) is/are

(a) 
$$(b)$$
  $(c)$   $(c)$ 

10. 
$$\langle P \rangle = O + H_2N - OH \xrightarrow{pH = 4.5} A \xrightarrow{H^{\oplus}} B \xrightarrow{H_2O, 260^{\circ}C} (polymer [X]).$$

Correct statements about [X] are

- (a) the polymer is bakelite
- (b) the polymer is Nylon-6
- (c) the polymer contains six carbon atoms in the repeating units
- (d) it is condensation polymer(s)

11. 
$$\xrightarrow{\text{CH}_3}$$
 OH  $\xrightarrow{\text{C=N}}$  Product; The product formed is  $\text{NO}_2$ 

(a) 
$$NO_2$$
  $CH_3$   $Br$   $NHCOCH_3$   $CONHCH_3$   $NO_2$   $NO_2$   $NO_2$   $NO_2$   $NO_2$   $NO_2$ 

12. Select the correct reactions

(c) 
$$Ph$$
  $CH_3$   $(i)$   $SeO_2$   $Ph$   $ONa$   $ONa$ 

(d) PhCHO + 
$$(CH_3CH_2CO)_2O$$
 (i)  $CH_3CH_2COONa$  Ph  $OH$ 

13. Choose the alkene(s) that would give the two products of the following ozonolysis reaction.

alkene 
$$(1) O_3$$
  $(2) Me_2S$   $(2) Me_2S$   $(3) i$   $(4) iii and iv$ 

#### **14.** Choose the major product of the following reaction

OCH<sub>3</sub> + CuLi 
$$\xrightarrow{Pd}$$
 Major product?

(a) OCH<sub>3</sub> (b) OMe

(c) OCH<sub>3</sub> (d) OCH<sub>3</sub>

#### 15. Which of the following is correct for the final product of the given sequence of reaction

- (a) Compound  $P_3$  on oxidation with  $(CrO_3 + H_2SO_4)$  gives a compound which gives 2, 4 DNP test
- (b) Compound  $P_3$  on reaction with  $I_2$  + NaOH gives yellow ppt
- (c) Compound P<sub>3</sub> on reaction with cerric ammonium nitrate gives red colouration
- (d) Compound P<sub>3</sub> on reaction with MnO<sub>2</sub> gives carboxylic acid

## 16. Identify correct method of preparation of acetaldehyde from reaction of cyanide

(a) 
$$Me - C \equiv N \xrightarrow{(i) DIBAL}$$
 (b)  $Me - C \equiv N \xrightarrow{(i) SnCl_2 + HCl}$ 

(c) 
$$Me - C \equiv N \xrightarrow{(i) Conc. H_2SO_4}$$
 (d)  $Me - C \equiv N \xrightarrow{(i) Pd/BaSo_4 / H_2}$ 

#### 17. Identify compounds that give iodoform test

(a) 
$$\bigcup_{\text{Me}-C-OPh}^{\text{O}}$$
 (b)  $\bigcup_{\text{C}}^{\text{O}}$  (c)  $\bigcup_{\text{C}}^{\text{O}}$ 

#### 18. Identify compounds which give PPT with Tollen's reagent

(a) 
$$\bigoplus_{\text{CINH}_3 - \text{NH}} - \bigvee_{\text{NO}_2} - \text{NO}_2$$
 (b)  $\bigcirc$ 
(c)  $\text{Me} - \text{C} \equiv \text{C} - \text{H}$  (d)  $\bigcirc$ 

19. 
$$H-C \equiv C-H \xrightarrow{1 \text{ eq. NaNH}_2} P_1 \xrightarrow{I} P_2 \xrightarrow{1\% \text{ HgSO}_4} P_3$$

Identify the correct statement for the above reaction sequence?

- (a)  $P_3$  Product gives +ve iodoform test
- (b)  $P_2$  Product on reaction with  $HB(Sia)_2$  and  $H_2O_2/OH^{\circ}$  gives  $CH_2-C-H$

(c) 
$$P_3$$
-Product  $\xrightarrow{CH_2 = PPH_3} X \xrightarrow{\text{(i)} B_2H_6 \cdot THF} OH$ 

- (d) P<sub>3</sub> Product gives Tollen's test
- 20.  $\langle O O H \xrightarrow{H^{\oplus}}$  Products is/are

(a) (b) 
$$O$$
 (c)  $O$  (d)  $O$  (d)

- 21.  $Ph C CH_3 + CH_2 C O C_2H_5 \xrightarrow{NaNH_2} A \xrightarrow{KOH/H_2O} B$ ; Products A and B are

  - (c) Ph-CH<sub>2</sub>-C-CH<sub>3</sub>

22. O 
$$\longrightarrow$$
 dil. H<sub>2</sub>SO<sub>4</sub>  $\rightarrow$  P<sub>1</sub>+ P<sub>2</sub>

P<sub>1</sub> and P<sub>2</sub> products are identified by

- (b) Iodoform test (c)  $Br_2 + H_2O$  test (d) 1% alkaline KMnO<sub>4</sub> (a) Tollen's reagent

- (a)  $MnO_2/\Delta$
- (b) P.C.C.
- (c)  $Br_2 + H_2O$
- (d) LAH

#### 24. Among the following reactions identify lactonisation reactions

**25.** The compound which gives lactone on heating or in the presence of Conc. H<sup>®</sup> medium

**26.** The products Y and X are

27.

28. 
$$H_3C$$
  $CHO + H_2C$   $CH_3$   $(i) NaOMe / \Delta$  Identify product  $(a)$   $(b)$   $(c)$   $(d)$   $(d)$ 

(d)

30. 
$$CH_2$$
 $H_3C$ 
 $H_3C$ 
 $CH_2$ 
 $CH_3$ 
 $CH_$ 

ÓН

Conc. H<sub>2</sub>SO<sub>4</sub> Identify product

 $CH_3 \xrightarrow{Conc. H_2SO_4} Identify product$ 

(a) 
$$O \xrightarrow{CH_3} CH_3$$

$$(d) \begin{picture}(c){c} $H_3C$ & $CH_3$ \\ \hline $CH_3$ & $CH_3$ \\ \hline \end{picture}$$

 $\xrightarrow{\text{Conc. H}_2\text{SO}_4}$  Identify product

(a) 
$$H_3C$$
  $CH_3$   $CH_3$   $CH_3$ 

34. 
$$\begin{array}{c} CH_3 \\ Ph \\ H_2C = P \\ \hline Ph \\ RLi / \Delta \end{array}$$
 Identify product

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

(c) 
$$CH_3$$
  $CH_3$   $CH_$ 

35. 
$$\underbrace{\begin{array}{c} \text{(i) } CH_2N_2\\ \text{(ii) } NaH\\ \text{(iii) } MeI \end{array}}_{O} \quad \text{Identify product}$$

$$(c) \begin{picture}(600,0) \put(0,0){\line(1,0){100}} \put(0,0){\line(1,0$$

36. 
$$(i) \text{ MeMgCl} \atop \underbrace{(ii) \text{ HClO}_4 (\text{aq.})}_{\text{(iii) NaOH (aq.)}} \text{ Identify product}$$

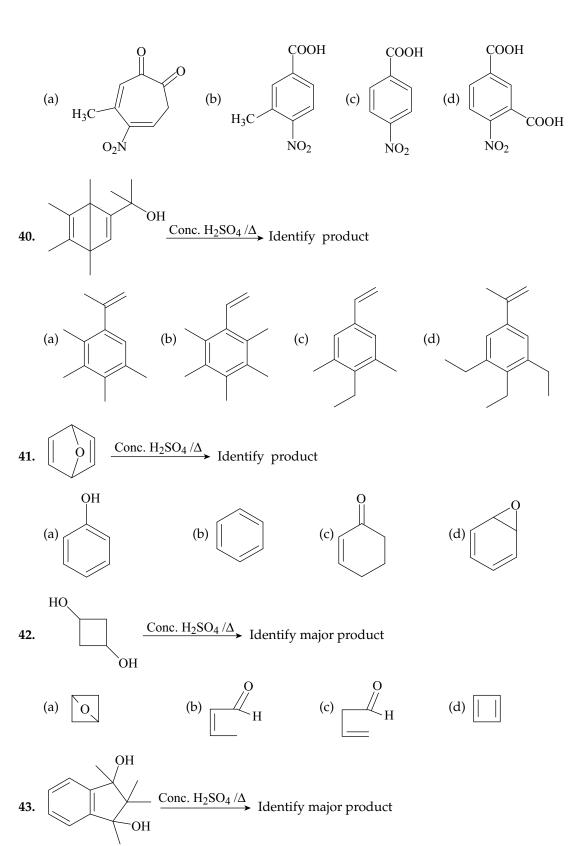
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Aq. NaOH  $/\Delta$  Identify product

 $Ac_2O$   $\rightarrow$  Identify product

CH<sub>3</sub>

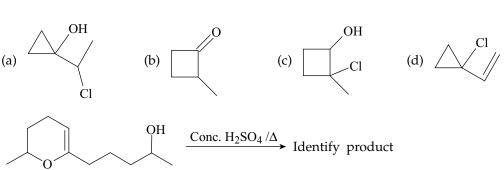
39. 
$$H_3C$$
  $\longrightarrow$  NaOH  $\longrightarrow$  Identify product

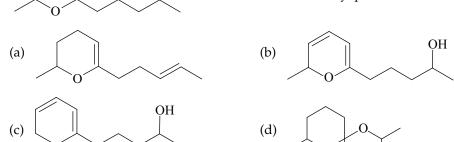


44. O Conc. 
$$H_2SO_4/\Delta$$
 Identify product

45. 
$$Conc. H_2SO_4/\Delta \rightarrow Identify product$$

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





49. 
$$_{\text{H}_3\text{C}}$$
— $_{\text{C}}$ = $_{\text{C}}$ CH<sub>2</sub>  $\xrightarrow{\text{Dil. H}_2\text{SO}_4}$  Identify product

(a) 
$$HO$$
  $OH$   $CH_2-C\equiv C-CH_2$  (b)  $O$  (c)  $CH_2$ 

50. 
$$Conc. H_2SO_4/\Delta \rightarrow Identify product$$

48.

51. 
$$\triangle$$
 COOH  $\triangle$  Product is?

(a) 
$$HO$$
 (b)  $HO$  (c)  $HO$  (d)  $O$  COOH

#### **Comprehension Type**

#### Passage 1

If we take an alcohol solution of an aldehyde (or ketone) and pass into it a small amount of gaseous HCl the hemiacetal forms, and hemiacetal reacts with a second molar equivalent of the alcohol to produce an acetal (or ketal).

$$R = O + R'OH \xrightarrow{HCl(g)} R \xrightarrow{OH} C \xrightarrow{R'OH} R \xrightarrow{R'OH} C \xrightarrow{OR'} + H_2O$$

All the steps in the formation of an acetal from an aldehyde (or ketone) are reversible. With excess of alcohol, equilibrium favours forward (acetal formation) direction.

Although acetals are hydrolysed to aldehydes and ketones in aqueous acid, they are stable in basic solution. Because of this property, it is a convenient method for protecting aldehyde and ketone from a series reaching in basic solution.

Similarily, thioacetal (ketal) formation takes place.

The final product of the reaction is

Correct statement for the given reaction is

- (a) X and Y are structural isomers
- (b) both X and Y gives only one monochlorinated product
- (c) X on oxidative ozonolysis gives gluteric acid
- (d) X and Y on reaction with  $H_2N$  OH gives oxime

#### Passage 2

In organic chemistry various reactions take palce by rearrangements. These rearrangements can be classified on the basis of migratory group and its nature. One of the well-known rearrangement is the formation of N-substituted amides by rearrangement of aldoximes or ketoximes. This is known as Beckmann rearrangement. It is catalysed by various acidic reagents. The mechanism of this reaction is given as

$$R \xrightarrow{R} C = N \xrightarrow{H^{\oplus}} R \xrightarrow{R'} C = N \xrightarrow{\oplus} R' \xrightarrow{C} = N - R \xrightarrow{H_2O} R' - C = N - R \xrightarrow{\Theta} R' - R$$

55. 
$$CH_3$$
 OH  $C=N$  Product; The product formed is

Br

 $CH_3$  OH

 $C=N$  Product; The product formed is

 $CH_3$  (b) NHCOCH<sub>3</sub> (c) CONHCH<sub>3</sub>
 $CH_3$  (d) none of these

CH=CH OH 
$$P_2O_5$$
 Product; The final product is

OH

(a) CH=CH-CN

(b) CH=CH-N=C-H

(c) CH=CH-CH<sub>2</sub>NH<sub>2</sub>

(d) N

57.  $(CH_2)(C_2H_5)C=NOH \xrightarrow{C_6H_5SO_2Cl} (A) \xrightarrow{H_2O/H^{\oplus}} CH_2NH_2 + C_2H_5COOH$ 

The formation of final product suggest the migration of

(a) -CH<sub>3</sub> group

(b)  $-C_2H_5$  group

(c)  $C_6H_5$ – $SO_2$ –group

(d) cannot predicated without structure

### Passage 3

Aldehydes and ketones show nucleophilic addition reactions. The α-hydrogens in aldehydes and ketones are acidic. Therefore, aldehydes and ketones having at least one α-H undergo aldol condensation in the presence of a base such as NaOH. Aldehydes having no α-hydrogen undergo Cannizzaro reaction in the presence of concentrated alkali. The carbonyl group of aldehydes and ketones can be reduced to methylene group by Clemmensen or Wolf Kishner reduction. Aldehydes are easily oxidised to carboxylic acids by Tollen's reagent and Fehling's solution. Functional derivatives of carboxylic acids undergo nucleophilic acyl substitution with nucleophiles.

58. In the reaction given hereunder, correct statement (s) about A and B are

$$\begin{array}{c}
R \\
H
\end{array}$$

$$\begin{array}{c}
O \\
H_2N
\end{array}$$

$$\begin{array}{c}
O \\
A \\
\end{array}$$

$$\begin{array}{c}
H_2O \\
\end{array}$$

$$\begin{array}{c}
O \\
A \\
\end{array}$$

$$\begin{array}{c}
H_2O \\
\end{array}$$

$$\begin{array}{c}
B \\
\end{array}$$

- (i) A is optically active and dextrorotatory
- (ii) A is racemic mixture and optically inactive

(iii) B is 
$$\stackrel{R}{\underset{H}{\longrightarrow}} \stackrel{N}{\underset{NH_2}{\longrightarrow}} \stackrel{N}{\underset{N}} \stackrel{N}{\underset{N}} \stackrel{N}{\underset{N}} \stackrel{N}{\underset{N}} \stackrel{N}{\underset{N}} \stackrel{N}{\underset{N}} \stackrel{N}{\underset{N}}{\underset{N}} \stackrel{N}{\underset{N}} \stackrel{N}{\underset{$$

- (a) i and iii
- (b) ii and iv
- (c) ii and iii
- (d) i and iv
- **59.** To convert CH<sub>2</sub>=CH-CH<sub>2</sub>CHO to CH<sub>2</sub>=CH-CH<sub>2</sub>COOH, the best reagent will be
  - (a) KMnO<sub>4</sub>
- (b) P.C.C.
- (c)  $[Ag(NH_3)_3]OH$
- 60. The reactivity order of the following toward nucleophilic substitution will be

(a) i > iii > iv > ii

(b) ii > iii > i > iv

(c) iii > iv > i > ii

(d) iii > i > iv > ii

Identify the missing products in the following sequence of reactions.

$$\begin{array}{c}
O \\
\hline
(i) \text{ aq. NaOH} \\
(ii) \text{ H}^{\oplus}
\end{array}$$
(A) 
$$\begin{array}{c}
HCCl_3 \\
NaOH
\end{array}$$
(B) 
$$\begin{array}{c}
PhNH_2 \\
\hline
\end{array}$$
(C) + (D)

- 61. Which statements about compound A are correct?
  - (i) Compound A is used in the formation of phenolphthalein
  - (ii) Compound A is used in the formation of aspirin
  - (iii) Compound A gives colour with FeCl<sub>3</sub>
  - (a) i and iii
- (b) i and ii
- (c) ii and iii
- (d) i, ii and iii

**62.** Compound B will be

(a) 
$$OH$$
  $CHO$  (b)  $OH$   $OH$   $OH$   $CHCl_2$ 

- 63. Compounds C and D are
  - (a) Identical

(b) Geometrical isomers

(c) Functional isomers

(d) Optical isomers

### Passage 5

Given hereunder is the mechanism of Beckmann rearrangement.

$$\begin{array}{c} CH_3-C=N- \\ \hline OH \\ \end{array} \begin{array}{c} CH_3-C=NH-Ph \\ \hline \end{array}$$

- **64.** Rate-determing step in Beckmann rearrangement is
  - (a) i

(b) ii

(c) iii

(d) iv

65. 
$$CH_3$$
  $C=N$  OH

On treatment with H<sub>2</sub>SO<sub>4</sub> followed by hydrolysis in acidic medium, the above compound gives

(a) CH<sub>3</sub>-CO<sub>2</sub>H, Ph-NH<sub>2</sub>

(b)  $Ph-CO_{2}H + CH_{3}-CO_{2}H$ 

(c)  $Ph-CH_2-NH_2+Ph-CO_2H$ 

(d) CH<sub>3</sub>-NH<sub>2</sub>, Ph-CO<sub>2</sub>H

66. 
$$C=N$$
 $C=N$ 
 $C=N$ 

(c) 
$$CH_3$$
—(d)  $CH_3$ —(d)  $CH_3$ —(e)  $CH_3$ —(e)  $CH_3$ —(e)  $CH_3$ —(f)  $CH_3$ 

Ethanal is heated with a base in two separate testtubes. In one testtube nothing except the two mentioned reactants were present. In another testtube, malonic ester,  $CH_2(COOR)_2$  was also added. The final products of both testtubes add easily 1, 3-butadiene molecule. The product obtained in the first test tube can be converted into second product identical in all respects with that obtained in the second testtube.

- 67. The respective reaction involved in the two testtubes are
  - (a) Aldol condensation and Cannizaro reaction
  - (b) Aldol condensation and Perkin reaction
  - (c) Aldol condensation and Knoevenagel reaction
  - (d) Aldol reaction and Claisen condensation
- **68.** Which feature is common in the products of both reactions?
  - (a) presence of an acidic group
  - (b) presence of an aldehydic group
  - (c) presence of  $\alpha$ ,  $\beta$  unsaturation
  - (d) presence of a ketonic group
- **69.** What would have been the final product when ethanal of the first testtube is replaced by propanal?
  - (a) CH<sub>3</sub>CH<sub>2</sub>CH=CHCH<sub>2</sub>CHO

(b) 
$$CH_3$$
  $CH_3$   $CH_3$   $CH_2$   $CH_3$ 

(c) 
$$CH_3$$
  
 $CH_3CH_2C=CH-CHO$ 

Aldehydes and ketones react with phosphorous ylides to yield alkenes and triphenylphosphine oxide. (An ylide is a neutral molecule having a negative carbon adjacent to appositive heteroatom).

Phosphorous ylides are also called phosphoranes.

$$\begin{array}{c} R \\ R' \\ \hline \\ Phosphorous \ ylide \\ or \ phosphorane \\ \end{array} \xrightarrow{\begin{array}{c} \Theta \\ R''' \\ \hline \\ R''' \\ \hline \end{array} \xrightarrow{\begin{array}{c} R \\ R''' \\ \hline \\ R''' \\ \hline \end{array}} \begin{array}{c} R \\ R''' \\ \hline \\ R'''' \\ R'''' \\ \hline \\ R'''' \\ R'''' \\ \hline \\ R'''' \\ R'''' \\ \hline \\ R'''' \\ R'''' \\ \hline \\ R'''' \\ R'''' \\ \hline \\ R'''' \\ \hline \\ R'''' \\ R'''' \\ \hline \\ R'''' \\ R''''$$

Through reaction, known as the Witting reaction, phosphorus ylides are easily prepared from triphenylphosphine and alkyl halides. Their preparation involves two reactions:

Reaction 1: 
$$Ph_3\ddot{P} + CH_3 - CH - X \longrightarrow \left[ (C_6H_5)_3\dot{P} - CH \stackrel{CH_3}{\searrow} X^{\ominus} \right]$$

Reaction 2: 
$$(C_6H_5)_3P + C - H + :Base \longrightarrow Ph_3P - C : + H - B$$

$$C_2H_5 \qquad (B)$$

Specific example:

$$Ph_{3}P + CH_{3}Br \xrightarrow{C_{6}H_{6}} [Ph_{3}P - CH_{3}] \overset{\odot}{Br}$$
[Methyl triphenyl phosphorium bromide]

$$[Ph_{3}\overset{\oplus}{P}-CH_{3}]\overset{\odot}{Br}+C_{6}H_{5}Li \longrightarrow Ph_{3}\overset{\oplus}{P}-\overset{\bullet}{C}H_{2}\overset{\odot}{C}_{6}H_{6}+Li\;Br$$
 ylide

Mechanism of Witting reaction

The mechanism suggested that the ylide, acting as a carbonion, attacks the carbonyl carbons of the aldehydes or ketone to form an unstable intermediate with separated change called a betaine. In the next step, betaine forms oxaphosphetane, which spontaneously loses triphenylphosphine oxide to become an alkene.

In the given sequence of reaction, the product (B) is

(a) 
$$_{\mathrm{H_3CO}}$$
 CHO (b)  $_{\mathrm{H_3CO}}$  CH3  $_{\mathrm{C=CH_2}}$ 

71. Which of the following cannot be used in the preparation of ylide?

(b) 
$$(CH_3)_3C-1$$

(a) 
$$CH_3CH_2Br$$
 (b)  $(CH_3)_3C-I$  (c)  $CH_3-CH-Br$  (d) Both (b) and (c)  $CH_3$ 

72. 
$$C=O+Dh_3$$
 Alkene +  $Ph_3P=O$  (X)

In the given reaction, the correct statement for alkene (X) is

- (a) X on reaction with Br<sub>2</sub>/CCl<sub>4</sub> forms an optically inactive mixture
- (b) X on reaction with alk. KMnO<sub>4</sub> forms an optically inactive mixture
- (c) X on reaction with alk. KMnO<sub>4</sub> forms an optically active mixture
- (d) Both (a) and (b)

#### Passage 8

Active methylene compounds are of great importance in synthetic chemistry. When -CH<sub>2</sub> (methylene) group is flanked between two electron withdrawing groups, then its hydrogen becomes acidic and can be replaced easily. The acidity of methylene hydrogen depends upon the strength of electron withdrawing group. Acetoacetic ester, malonic ester, etc. are the examples of active methylene compound. In synthetic application acidic hydrogen is trapped by a strong base to get resonance stabilised anion which reacts accordingly to give the desired product.

$$H_2C$$
  $\stackrel{\bigcirc{COOEt}}{COOEt}$   $\stackrel{\bigcirc{OEt}}{\longrightarrow}$   $\stackrel{\bigcirc{CH}}{\hookrightarrow}$   $\stackrel{COOEt}{COOEt}$  Resonance stabilised

73. 
$$CH_3COCH_2COOEt \xrightarrow{(i) \text{ NaOEt}} A \xrightarrow{(i) \text{ dil. HCl}} Products; Products are not in excess}$$

- (a) CH<sub>2</sub>COCH<sub>2</sub> + CO<sub>2</sub> + EtOH
- (b) 2 mol of CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>+CO<sub>3</sub>
- (c) CH<sub>2</sub>COCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> + 2EtOH
- (d) CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> + EtOH + CO<sub>2</sub>

74. Which one of the following is most effective as an active methylene compound?

(a) 
$$O$$
 (b)  $CH_3COCH_2COOEt$  (c)  $O$  (d)  $O$ 

75. 
$$Ph-CH + CH_2 < C-OC_2H_5 \xrightarrow{Base} A \xrightarrow{(i) H_3O^{\oplus}} Product$$

The final product is

(a) Ph-COOH

(b) Ph–Ph–C–CH=CH–COOH

(c) Ph-CH=CH-COOH

(d) Ph-CH=CH-CHO

### Passage 9

Compound A 
$$(C_{11}H_{22})$$
  $O_3$   $E(C_6H_{12}O)$   $O_3$   $O_3$   $O_4$   $O_5$   $O_5$   $O_6$   $O_7$   $O_8$   $O_$ 

76. 
$$D(C_5H_{12}O_2) \xrightarrow{SOCl_2} x \xrightarrow{CH_2=N=N} \bigoplus_{H_2O/Ag_2O} \bigcirc y$$
; product y is

### 77. Compound A is

78. 
$$PH_3P$$
 $Bu^+O^-K^+$  W + H(C<sub>4</sub>H<sub>8</sub>O)  $\longrightarrow$  T; Product T is

$$(\text{evolves H}_2 \text{ gas}) \leftarrow \underbrace{\begin{array}{c} \text{Na} \\ \text{Na} \\ \text{Optically active} \end{array}}_{\text{optically active}} \underbrace{\begin{array}{c} \text{Conc. H}_2\text{SO}_4 \\ \text{O} \\ \text{No stereoisomerism} \\ \text{is exhibited} \end{array}}_{\text{O}_3} \underbrace{\begin{array}{c} \text{HBr} \\ \text{C(C}_{11}\text{H}_{15}\text{Br}) \\ \text{(Resolvable)} \\ \text{is exhibited} \end{array}}_{\text{(Resolvable)}} D(\text{Isomer of C})$$

$$\underbrace{\begin{array}{c} \text{C}_{11}\text{H}_{15}\text{Br} \\ \text{(Resolvable)} \\ \text{Somer of C} \\ \text{NaOH/I}_2 \underbrace{\begin{array}{c} \text{C}_1 \\ \text{AlCl}_3 \\ \text{(anhydrous)} \\ \end{array}}_{\text{(anhydrous)}} D(\text{Somer of C})$$

79. Compound (C) is

(a) 
$$CH_3$$
 (b)  $H_3C$   $CH_3$  (c)  $H_3C$   $Br$   $CH_3$  (d)  $CH_3$ 

**80.** Compound (E)  $\xrightarrow{\text{Mg-Hg}}$  (X)  $\xrightarrow{\text{(i) } H^{\oplus}}$  (Y); compound (Y) is (ii) F<sub>3</sub>C-C-OOH

Co) 
$$CH_3$$
— $C$ — $O$ — $C$ — $Ph$   $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

81. Compound (A)  $\xrightarrow{\text{H}_2\text{CrO}_4}$  (R)  $\xrightarrow{\text{NaOI}}$  (S) + (T) . Compound (S) and (T) respectively are

(a) 
$$\bigcirc \begin{matrix} O \\ -C - O N a + C H I_3 \end{matrix}$$
 (b) 
$$\bigcirc \begin{matrix} C H_3 & O \\ -C H_3 & C - O N a + C H I_3 \end{matrix}$$

(c) 
$$CH_3 \parallel C - \bar{O}N_a^+ + AgI$$
 (d)  $CH_2 - CH_2 - CH_2 - CH_3 + CHI_3$ 

**82.** Match the reactions in column I with their reagents in column II.

### Column I

- (a) CH<sub>3</sub>-CH<sub>2</sub>=CH-CHO → CH<sub>3</sub>CH=CHCOOH
- (b)  $CH_3$ -CH=CH-CHO  $\rightarrow$  CH<sub>3</sub>CH=CH-CH<sub>2</sub>OH
- (c) Ph-CH=CH-CHO → Ph-CH<sub>2</sub>-CH<sub>2</sub>-CHO
- (d)  $CH_2=CH-CH_2CHO \rightarrow CH_2=CH-CH_2CH_2OH$

### Column II

- (p) LiAIH<sub>4</sub>
- (q) NaBH<sub>4</sub>
- (r)  $Pd-C/H_2$
- (s)  $Ag(NH_3)_2^{\oplus}$

83. Match the columns.

### Column I

# Column II (In the given sequence)

(p) Formation of six member ring takes place

- (a)  $\xrightarrow{\text{HCN}}$  (A)  $\xrightarrow{\text{LiAIH}_4}$  (B)  $\xrightarrow{\text{NaNO}_2}$  (C)
- (d)  $Ph \xrightarrow{CH_3} H^{\oplus}$  (A) OH OH

- (r) Final product formed will give positive Tollen's test
- (s) Final product formed will react with 2,4-DNP. (2, 4-di-nitrophenyl hydrazine)
- **84.** Match the chemical compounds in Column I with the reagents used to test them in Column II.

#### Column I

- (a) Ethanol
- (b) Glucose
- ` '
- (c) Glyoxal
- (d) Acetone

### Column II

- (p)  $[Ag(NH_3)_2]OH$
- (q) Fehling's solution
- (r) H<sub>2</sub>N= Ph-NHSOOH
  Ph-NHSOOH
  SO<sub>3</sub>H
- (s) I<sub>2</sub>/NaOH

**85.** Match the columns.

### Column I (Reaction)

# Column II (Reducing reagent)

(a) O= 
$$\sim$$
 CH<sub>2</sub>C-OPh  $\xrightarrow{A}$  HO-  $\sim$  CH<sub>2</sub>C-OPh

(b) 
$$O = CH_2 - CH - Ph \xrightarrow{B} HO - CH_2 CH_2 Ph$$

(c) 
$$O = CH = CH - Ph \xrightarrow{C} HO - CH_2CH_2Ph$$
 (r)  $NaBH_4$ 

(d) 
$$O = CH_2-C-Ph \xrightarrow{D} CH_2CH_2Ph$$
 (s) Red P + HI O (t) Ni/H<sub>2</sub>

**86.** Match the columns.

### Column I

### Column II

$$(p) \longrightarrow \bigcap^{\operatorname{Br}}$$

(q) 
$$MeC \equiv CMe \longrightarrow Me \longrightarrow C = C \longrightarrow Me$$

$$(r) \begin{array}{c|c} OH & OH & OH \\ \hline \end{array}$$

(s) 
$$CH_3COOH \longrightarrow CH_2 = C = O$$

### 87. Match column I with column II.

### Column I

### Column II

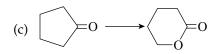
- (p) 2, 4-DNP test
- (q) Tollen's reagent test
- (r)  $I_2$  + NaOH (Iodoform test)
- (s) Fehling's solution test
- 88. Match column I with column II.

### Column I (conversion)

(b) 
$$\bigcirc$$
 0  $\longrightarrow$   $\bigcirc$  0

### **Column II (reagents)**

- (p) HCN; H<sub>2</sub>/Ni; HNO<sub>2</sub>
- $(q) CH_2N_2$



(r) m-CPBA (Meta-chloroperbenzoic acid)

(s) 
$$P=CH_2$$

89. Match Column I with Column II.

### Column I

- (a) Aldol condensation
- (b) Cannizzaro reaction
- (c) Reformatsky reaction
- (d) Benzoin condensation

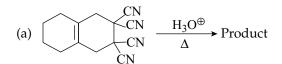
### Column II

- (p) Hydride ion transfer
- (q) Zinc enolate
- (r)  $\overline{C}N$  as catalyst
- (s) Enolate ion

90. Match the coloumns.

### Column I

### Column II



(p) Anhydride

- (q) Carboxylic acid
- (r) Alkene
- (s) Optical active compound
- (t) Ester

91. Match the columns.

### Column I (compound)

(a) 
$$C \stackrel{\bigcirc{}}{\searrow} C \stackrel{\bigcirc{}}{\searrow} H$$

- Column II (Tests)
- (p) 2, 4-DNP test

(b) CH<sub>3</sub>-C-

(q) Yellow ppt. with NaOH +  $I_2$ 

(r) Red ppt. with Fehling's solution

(d)  $H_3C$  CH<sub>3</sub>

(s) Silver mirror with Tollen's reagent

**92.** Match the columns.

### Column I (Reagents)

### Column II

- (a) Tollen's reagent give white ppt. with
- (p) Me-CH=CH-Me

(b)  $Br_2 + H_2O$  test given by

- (q) Me-C≡C-H
- (c) Product of reaction of acetylene with 1%
- (r)  $Cl_{N}^{\oplus}H_{3}-NH_{2}$

HgSO<sub>4</sub> and dil. H<sub>2</sub>SO<sub>4</sub>

O || (s) Me–C–H

(d) Pd/H<sub>2</sub> reacts with

- O || (r) Me–C–Me
- 93. Match column I with column II.

### Column I

### Column II

(a) 
$$CH_3CHO + CH_3CH_2CHO \xrightarrow{\text{dil. OH}}$$

(p) CH<sub>3</sub>-CH<sub>2</sub>CH=CH-CHO

(b) PhCHO + CH<sub>3</sub>-C-CH<sub>3</sub> 
$$\stackrel{\bigcirc}{\overset{\bigcirc}{OH}}$$
  $\stackrel{\triangle}{\overset{}{\overset{}{O}}}$ 

(q) CH<sub>3</sub>–C=CH–CH<sub>3</sub> CHO

(c) PhCHO + HCHO  $\stackrel{\odot}{OH}$   $\stackrel{}{\Delta}$ 

(r) HCOO

(d) 
$$\langle \bigcirc \rangle$$
 OH + CHCl<sub>3</sub>  $\xrightarrow{\bigcirc OH}$ 

- (s) Ph-CH=CH-C-Me
- (t) CHC
- 94. Match the column I with column II.

### Column I

### Column II

(a) Schimdt reaction

(p) RCOOH  $\xrightarrow{\text{NaOH/CaO}}$  RH

(b) Curtius reaction

(q) R-CH<sub>2</sub>COOH  $\xrightarrow{\text{Red P/X}_2}$  R-CH-COOH

(c) Decarboxylation

(r) RCOCl  $\xrightarrow{\text{(i) NaN}_3}$  RNH<sub>2</sub> RNH<sub>2</sub>

(d) HVZ reaction

(s) RCOOH  $\xrightarrow{N_3H}$  RNH<sub>2</sub>

### **Integer Type**

- 95. How many products are possible when ethanal and phenyl ethanal (mixture) is treated with dil. NaOH at about 10°C.
- **96.** For the given sequence of reaction

How many products are obtained finally?

97. Identify the total number of compounds that give positive test with Tollen's reagent

$$H_3C$$
 $H_3C$ 
 $H_3C$ 

98. Identify the total number of compounds that give positive iodoform test

**99.** Identify the total number of compounds that give diastereomeric product on reaction with MeMgCl

100. Identify that compounds that give Cannizaro reaction

# **Answer Keys**

# LEVEL 1

| 1  | 2    | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10  | 11  | 12  | 13  | 14  | 15 |
|----|------|----|----|----|----|----|----|----|-----|-----|-----|-----|-----|----|
| С  | d    | d  | b  | d  | С  | a  | d  | с  | bd  | b   | a   | a   | С   | С  |
| 16 | 17   | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25  | 26  | 27  | 28  | 29  | 30 |
| ab | d    | d  | с  | a  | b  | d  | a  | bc | b   | d   | с   | b   | a   | b  |
| 31 | 32   | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40  | 41  | 42  | 43  | 44  | 45 |
| ab | abcd | d  | d  | с  | a  | d  | с  | b  | с   | a   | b   | с   | abd | b  |
| 46 | 47   | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55  | 56  | 57  | 58  | 59  | 60 |
| b  | a    | b  | с  | d  | d  | с  | b  | b  | с   | a   | a   | d   | с   | bc |
| 61 | 62   | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70  | 71  | 72  | 73  | 74  | 75 |
| b  | b    | С  | a  | с  | b  | d  | b  | с  | b   | a   | d   | с   | b   | d  |
| 76 | 77   | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85  | 86  | 87  | 88  | 89  | 90 |
| b  | a    | b  | b  | a  | с  | b  | с  | b  | b   | a   | с   | a   | d   | b  |
| 91 | 92   | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 | 104 |    |
| d  | d    | a  | b  | a  | a  | d  | d  | b  | a   | d   | с   | d   | d   |    |

# LEVEL 2

| 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    | 14    | 15    |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| С     | ac    | bc    | ab    | abc   | d     | ab    | bd    | bd    | bcd   | b     | bcd   | a     | b     | abc   |
| 16    | 17    | 18    | 19    | 20    | 21    | 22    | 23    | 24    | 25    | 26    | 27    | 28    | 29    | 30    |
| abd   | bcd   | ac    | abc   | abc   | bd    | ab    | ab    | bc    | ab    | bd    | a     | С     | d     | b     |
| 31    | 32    | 33    | 34    | 35    | 36    | 37    | 38    | 39    | 40    | 41    | 42    | 43    | 44    | 45    |
| a     | a     | b     | b     | b     | d     | a     | с     | b     | a     | a     | b     | С     | a     | b     |
| 46    | 47    | 48    | 49    | 50    | 51    | 52    | 53    | 54    | 55    | 56    | 57    | 58    | 59    | 60    |
| a     | b     | d     | b     | a     | a     | с     | b     | b     | b     | a     | a     | b     | с     | b     |
| 61    | 62    | 63    | 64    | 65    | 66    | 67    | 68    | 69    | 70    | 71    | 72    | 73    | 74    | 75    |
| d     | a     | b     | b     | d     | b     | с     | с     | b     | d     | b     | d     | d     | a     | С     |
| 76    | 77    | 78    | 79    | 80    | 81    | 82(a) | 82(b) | 82(c) | 82(d) | 83(a) | 83(b) | 83(c) | 83(d) | 84(a) |
| a     | С     | b     | b     | С     | b     | s     | p     | r     | pq    | pqs   | p     | pqs   | pqs   | s     |
| 84(b) | 84(c) | 84(d) | 85(a) | 85(b) | 85(c) | 85(d) | 86(a) | 86(b) | 86(c) | 86(d) | 87(a) | 87(b) | 87(c) | 87(d) |
| pq    | pqr   | s     | r     | qr    | t     | ps    | r     | pr    | s     | q     | pr    | qs    | pq    | p     |
| 88(a) | 88(b) | 88(c) | 88(d) | 89(a) | 89(b) | 89(c) | 89(d) | 90(a) | 90(b) | 90(c) | 91(a) | 91(b) | 91(c) | 91(d) |
| r     | pq    | r     | s     | s     | р     | q     | r     | pr    | st    | qs    | ps    | pq    | pqrs  | pq    |
| 92(a) | 92(b) | 92(c) | 92(d) | 93(a) | 93(b) | 93(c) | 93(d) | 94(a) | 94(b) | 94(c) | 94(d) | 95    | 96    | 97    |
| qr    | pq    | s     | pqst  | pq    | s     | r     | t     | s     | r     | р     | q     | 12    | 11    | 6     |
| 98    | 99    | 100   |       |       |       |       |       |       |       |       | -     |       |       | -     |

# **WORKBOOK EXERCISES**

# **EXERCISE 1**

# Identify reagents (1 to 10) used in the following conversion from reagent present in second Column II (A to P).

### Column I (Conversion)

# 

ΗÓ

### Column II (Reagent)

### Reagent

- A.  $CH_3CH_2CH_2CH_2Li$  / THF
- B. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br
- C. Et<sub>3</sub>SiCl / Et<sub>3</sub>N
- D. Et<sub>3</sub>SiH / pyridine
- E. CH<sub>3</sub>CHO
- F. CH<sub>3</sub>CH<sub>2</sub>CHO
- G. PDC
- H. PPH<sub>3</sub>
- I.  $CH_2 = CHCH_2Br$
- $J.~H_3O^+\,/\,\Delta$
- K. Conc.  $H_2SO_4/\Delta$
- L. NaOEt then Br(CH<sub>2</sub>)<sub>3</sub>Br
- M. Et<sub>3</sub>N
- N. NaBH<sub>4</sub> then H<sub>3</sub>O<sup>+</sup>
- O. Bu<sub>4</sub>NF then H<sub>2</sub>O
- P. KMnO<sub>4</sub> / aq. NaOH / 0°C

# Identify reagents (1 to 10) used in the following conversion from reagent present in second Column II (A to T).

### **Column I (Conversion)**

### COOEt CO<sub>2</sub>H <u>ii</u> iii CO<sub>2</sub>Et CO<sub>2</sub>H Bn. ОН vi CO<sub>2</sub>Et CO<sub>2</sub>Et CO<sub>2</sub>Et vii o´Bn Bn . ОН Br viii

CO<sub>2</sub>Et

NOTE: Bn = Benzyl group,  $PhCH_2^-$ 

CO<sub>2</sub>Et

### Column II (Reagent)

- (A) NaBH<sub>4</sub> then NH<sub>4</sub>Cl
- (B) LiAlH<sub>4</sub> then H<sub>3</sub>O<sup>+</sup>
- (C) O<sub>3</sub> then Zn / CH<sub>3</sub>CO<sub>2</sub>H
- (D) O<sub>3</sub> then H<sub>2</sub>O<sub>2</sub>
- (E) NaOH
- (F) Na dissolved in EtOH
- (G) AC. H<sub>3</sub>O<sup>+</sup>
- (H) BH $_3$  then NaOH / H $_2$ O $_2$
- (I) Na then add PhBr
- (J) Na then add PhCH<sub>2</sub>Br
- (K) Pyridinium chlorochromate
- (L)  $Na_2Cr_2O_7 / H_3O^+$
- (M) NaBr / acetone
- (N) PBr<sub>3</sub>
- (O)  $Br_2 / hv$
- (P) LDA / THF / –78°C
- (Q) Mg /  $Et_2O$
- (R) EtOH / H<sup>+</sup> / heat
- (S) CH<sub>2</sub>=CH-CH<sub>2</sub>MgBr
- (T) NaOEt then CH<sub>2</sub>=CH-CH<sub>2</sub>Br

# Identify reagents (1 to 10) used in the following conversion from reagent present in second Column II (A to P).

### Column I (Conversion)

### Column II (Reagent)

Spirothiobarbital

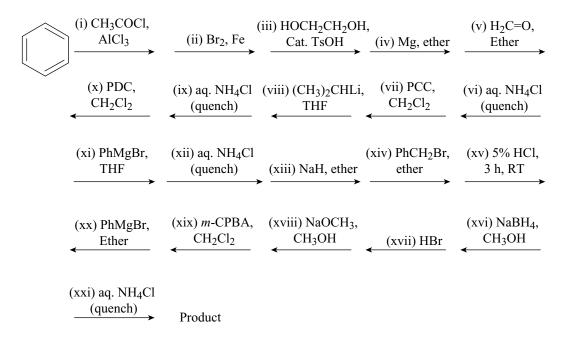
# Identify reagents (1 to 10) used in the following conversion from reagent present in second Column II (A to O).

### Column I (Conversion)

### Column II (Reagent)

### Identify the intermediate product in the following conversion

### Identify the intermediate product in the following conversion



### Identify the intermediate product in the following conversion

$$H_{3}C \longrightarrow OH \xrightarrow{\begin{array}{c} (i) \text{ Na}_{2}\text{Cr}_{2}\text{O}_{7}, & (ii) \text{ xs CH}_{3}\text{OH}, & (iii) \text{ NaOCH}_{3}, \\ H_{2}\text{SO}_{4} & \text{Cat. H}_{2}\text{SO}_{4} & \text{CH}_{3}\text{OH} & (iv) \text{ aq. NH}_{4}\text{Cl} & (v) \text{ NaOCH}_{3}, \text{ THF} \\ \hline \\ (x) \text{ LDA}, & \text{THF}, -78^{\circ}\text{C} & (ix) 180^{\circ}\text{C} & (-\text{CO}_{2}) & (viii) \text{ dil. HCl} & \text{aq. THF} & (vi) \text{ CH}_{3}\text{CH}_{2}\text{Br} \\ \hline \\ (xi) \text{ PhCH}_{2}\text{Br} & \text{Product} \\ \hline \end{array}$$

### Identify the final product in the following reaction sequence

(i) NaOH, CH<sub>3</sub>OH, Δ

(ii) (CH<sub>3</sub>)<sub>2</sub>CuLi, THF

(iii) aq.  $NH_4Cl$  (quench) Product

(d)

# SOLUTION FOR WORKBOOK EXERCISES

# **EXERCISE 1**

OSiEt, 
$$OEt$$
 $OEt$ 
 $OET$ 

Conversion

### Reagent

- (A)  $CH_3CH_2CH_2CH_2Li$  / THF
- (B) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br
- (C) Et<sub>3</sub>SiCl / Et<sub>3</sub>N
- (D) Et<sub>3</sub>SiH / pyridine
- (E) CH<sub>3</sub>CHO
- (F) CH<sub>3</sub>CH<sub>2</sub>CHO
- (G) PDC
- (H) PPh<sub>3</sub>
- (I)  $CH_2 = CHCH_2Br$
- (J)  $H_3O+/\Delta$
- (K) Conc.  $H_2SO_4/\Delta$
- (L) NaOEt then  $Br(CH_2)_3Br$
- (M) Et<sub>3</sub>N
- (N) NaBH<sub>4</sub> then H<sub>3</sub>O<sub>+</sub>
- (O) Bu<sub>4</sub>NF then H<sub>2</sub>O
- (P)  $KMnO_4$  / aq NaOH / 0°C

**NOTE:** Bn = Benzyl group,  $PhCH_2^-$ 

- (A) NaBH<sub>4</sub> then H<sub>3</sub>O<sup>+</sup>
- (B) LiAlH<sub>4</sub> then H<sub>3</sub>O<sup>+</sup>
- (C)  $O_3$  then  $Zn / CH_3CO_2H$
- (D) O<sub>3</sub> then H<sub>2</sub>O<sub>2</sub>
- (E) NaOH
- (F) Na dissolved in EtOH
- (G) AC.  $H_3O^+$
- (H) BH<sub>3</sub> then NaOH / H<sub>2</sub>O<sub>2</sub>
  - (I) Na then add PhBr
  - (J) Na then add PhCH<sub>2</sub>Br
- (K) Pyridinium chlorochromate
- (L)  $Na_2Cr_2O_7 / H_3O^+$
- (M) NaBr / acetone
- (N) PBr<sub>3</sub>
- (O) Br<sub>2</sub> / hv
- (P) LDA / THF / -78°C
- (Q) Mg /  $Et_2O$
- (R) EtOH /  $H^+$  / heat
- (S) CH<sub>2</sub>=CH-CH<sub>2</sub>MgBr
- (T) NaOEt then  $CH_2$ =CH- $CH_2Br$

OH 
$$3 = H$$
 OET  $2 = M$  OET  $OET$ 

OH  $3 = H$  OET  $3 =$ 

SPIROTHIOBARBITAL

- (A) NaH
- (B) Na / THF then MeOH
- $(C) H_2/Pd$
- (D) NaOH /Cl<sub>2</sub>
- (E)  $HC1/Cl_2$
- (F) PCl<sub>3</sub>
- (G) 1 mol. eq. LiAlH<sub>4</sub> then H<sub>3</sub>O<sup>+</sup>
- (H) Pyridinium chlorochromate
- (I) H<sub>2</sub>O<sub>2</sub>
- (J)  $H_3O^+/\Delta$
- (K) Conc.  $H_2SO_4$  /  $\Delta$
- (L) EtOH / H<sup>+</sup> /  $\Delta$
- (M) NaOEt / EtOH
- (N) Li NiPr $_2$  / THF
- (O) Aq. NaOH /  $\Delta$
- (P) NaOEt / EtOH / CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>

- (A) 1 eq NaBH<sub>4</sub> then H<sub>3</sub>O<sup>+</sup>
- (B) 1 eq LiAl $H_4$  then  $H_3O^+$
- (C) Ph<sub>3</sub>PCH<sub>2</sub>
- (D) NaOH / DMSO/ H<sub>2</sub>O
- (E) MCPBA
- (H) Pyridinium chlorochromate
- (I) Mg then  $CO_2$  then  $H_3O^+$  BC.  $H_3O^+$
- (J) Conc.  $H_2SO_4$  /  $\Delta$
- (K) TsCl / pyridine
- (L) NaOEt / EtOH
- (M) Li NiPr<sub>2</sub> / THF
- (N) LiCl / DMF
- (O) NaOH then CrO3 / pyridine