## **ALDOL AND CANNIZARO REACTION**



# LEVEL- 21

**1.** Compound *A* and *B*, both were treated with NaOH, producing a single compound *C*.

OH
OH
$$(A)$$
 $CH_3$ 
 $HO^-$ 
heat
 $C$ 
Compound  $(C)$  is:

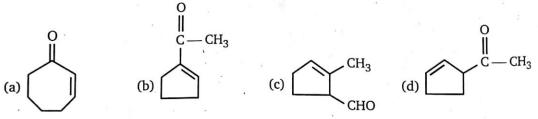
2. 
$$CH_3$$
 ?  $CH_3$  ; This conversion can be achieved by :

- (a) Dehydration, Hydrolysis
- (b) Retro aldol and further condensation
- (c) Perkin condensation & Clemmensen reduction
- (d) Clemmensen and Perkin condensation
- 3. This is an example of an intramolecular aldol reaction :

(a) 
$$H_2SO_4 \rightarrow (A)$$
; Product  $(A)$  is :

(b)  $C$ 
(c)  $C$ 
(d)

4. 
$$CH_3 - C - CH_2 -$$



- **5.** Ph CH = CHCHO + CH<sub>3</sub>CH = CHCHO  $\xrightarrow{\text{base}}$  (A) 87%; Product of this reaction is:
  - (a)  $Ph (CH = CH)_2 CHO$
- (b)  $Ph (CH = CH)_3CHO$
- (c)  $Ph (CH = CH)_4CHO$
- (d)  $Ph CH = CH CH = CH CH_3$
- **6.** CH<sub>3</sub>CHO  $\xrightarrow{10\% \text{ NaOH}} \xrightarrow{\Delta} \xrightarrow{\text{H}_2} (A)$ ; Product (A) of the reaction is:
  - (a) propanol
- (b) ethanol
- (c) butanol
- (d) pentanol

7. (A) 
$$\xrightarrow{\text{NaOH}} \Delta$$

Reactant (A) is:

(d) 
$$CH_3 - C - (CH_2)_4 - CH_2 - OH$$

8. 
$$CH_3 - C - CH_2 - C - CHO \xrightarrow{KOH, H_2O} (A)$$
; Product A is:

9. 
$$\underbrace{\frac{\text{LDA}}{\text{CH}_3-\text{CH}_2-\text{I}}}_{\text{CH}_3-\text{CH}_2-\text{I}} (A); \text{ Product } A \text{ is:}$$

$$CHO$$
 + conc. NaOH  $\xrightarrow{heat}$ , products Identify the product.

**11.** Compare enolate A with enolate B.

Which of the following statements is true?

- (a) A is more stable than B
- (c) B is more stable than A
- (b) A and B have the same stability
- (d) No comparison of stability can be made

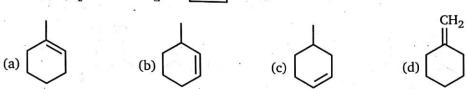
12. Benzalacetone is the product of mixed aldol condensation between benzaldehyde  $(C_6H_5CH=O)$  and acetone  $[(CH_3)_2C=O]$ . What is its structure?

(a) 
$$C_6H_5CH = CHCCH_3$$
 (b)  $C_6H_5CH = C(CH_3)_2$  (c)  $C_6H_5CCH = CHCCH_3$  (d)  $C_6H_5CCH = CH_2$ 

**13.** Identify the major product *P* in the following reaction:

Product (B) is:

15. 
$$(A) \xrightarrow{(i) O_3} (B) \xrightarrow{NaOH} C - CH_3$$
 the reactant (A) will be:



**16.** Identify the principal product of the following reaction?

17. Which one of the following compounds is the best choice for being prepared by an efficient mixed aldol addition reaction?

**18.** Identify the major product *P* in the following reaction:

OLi OLi
$$(i) CH_3CH_2I/THF \rightarrow F$$
OEt

20.

**19.** The enolate ion that reacts with 3-buten-2-one to form (*Y*) is :

(a) 
$$\ominus$$
(b)  $\ominus$ 
(c)  $\ominus$ 
(d)  $\ominus$ 
(d)  $\ominus$ 
(d)  $\ominus$ 
(e)  $\ominus$ 
(f)  $\ominus$ 
(f)  $\ominus$ 
(f)  $\ominus$ 
(g)  $\ominus$ 
(h)  $\ominus$ 
(h)

Product (B) in the above reaction is:

**21.**  $H - C - D \xrightarrow{HO^-}$ ; Product of this Cannizaro reaction is :

(a) 
$$D - CO_2^- + CH_2DOD$$

(b) 
$$H - CO_2^- + D - CO_2^-$$

(c) 
$$D - CO_2^- + CH_2DOH$$

(d) 
$$D - CO_2^- + CHD_2OH$$

An organic compound with the molecular formula C9H10O forms a 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizaro reaction, on vigorous oxidation it gives 1,2-benzenedicarboxylic acid. Structure of organic compound is:



23. 
$$CH_3$$
— $C$ — $CH_2$ — $C$ — $C$ 

Number of intramolecular aldol condensation product is:

- (b) 2
- (d) 4

**24.** 
$$(A) \xrightarrow{C_7 H_{14}} \xrightarrow{C_1/AcOH} (B) + (C)$$

Compound (A) exist in geometrical isomers and (B) gives Cannizaro reaction.

(*A*) will be :

(b) 
$$(CH_3)_3CCH_2 - CH = CH_2$$

(c) 
$$(CH_3)_3C - CH = CH - CH_3$$

$$CH_3$$
  $CH_3$   $CH_3$   $CH_3$   $CH_3 - CH_2 - CH = CH_2$   $CH_3 - CH_2 - CH = CH_2$ 

- Which of the following compounds will not undergo Cannizaro reaction, when treated with 25. 50% aqueous alkali?
- (c) Me<sub>2</sub>CHCHO
- (d)  $Ph CH_2 CHO$

26. 
$$H = C - D \xrightarrow{H^{18}O^{-}} D = C - 18O^{-} + CH_{2}D = OH$$

Above reaction is known as:

- (a) Cannizaro reaction, Disproportionation reaction
- (b) Tischenko reaction, Disproportionation reaction
- (c) Cross Cannizaro reaction, Redox reaction

, Aldol condensation

, Perkin reaction

, Cannizaro reaction

$$\mathrm{CH} = \mathrm{CH} - \mathrm{CO_2H}$$
 , Claisen-condensation

29. Choose the most reasonable reaction intermediate for the following reaction.

30. 
$$CH_3 - CH - CH_2 - C - H \xrightarrow{HO^-} (A)$$
; 3HCHO +  $A \xrightarrow{Na_2CO_3} (B)$  (82%)

Product (B) of the above reaction is:

$$\begin{array}{c} \text{CH}_2-\text{OH} & \text{CHO} \\ | \\ \text{(a) HO}-\text{CH}_2-\text{C}-\text{CH}_2\text{OH} & \text{(b) HO}-\text{CH}_2-\text{C}-\text{CHO} \\ | \\ \text{CH}_2-\text{OH} & \text{CH}_2-\text{OH} \end{array}$$

$$\begin{array}{c} \text{CH}_2\text{OH} & \text{CHO} \\ | & | \\ \text{(c)} \text{ HO} - \text{CH}_2 - \text{C} - \text{CH}_2\text{OH} \\ | & | \\ \text{CHO} & \text{CH}_2 - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH} \\ | & | \\ \text{CH}_2 - \text{OH} & \text{CH}_2 - \text{OH} \\ \end{array}$$

**31.** CH<sub>3</sub>CH = CHCHO 
$$\xrightarrow{\text{OH}^-} \xrightarrow{\Delta} A$$
; Product A is:

- (a)  $CH_3(CH = CH)_3CHO$
- (b)  $CH_3CH_2CH_2(CH = CH)_2CHO$
- (c)  $CH_3(CH_2CH_2)_3CH = CH CHO$
- (d) none is correct

32. 
$$\underbrace{\frac{HO^{\bigcirc}}{H_2O}}_{(A)} B.$$
 (A) and (B) are isomer: Identify (B).

(c) 
$$C - CH_3$$

34. 
$$+ \longrightarrow H$$
  $\xrightarrow{HCl/heat} A$ . Product (A) is

(b) 
$$Ph - C - CH_2 - CH_2 - Ph$$

(c) 
$$Ph - CH = CH - CH - Ph(d)$$
  
OH

(d) 
$$Ph - CH = C = CH - Ph$$

**35.** Which of the following reactant on reaction with conc. NaOH followed by acidification gives the following lactone as the product ?

(a) 
$$C-OCH_3$$
  $CO_2H$ 

37. (P) 
$$\xrightarrow{\text{KOH}} \xrightarrow{\Delta}$$
 Ph—CH<sub>2</sub>—OH + Ph—CO<sub>2</sub>

(R) 
$$\xrightarrow{O_3} P + Q$$
, Structure of (R) is:

(a) 
$$Ph - CH = CH - CH_3$$

(b) Ph—CH=
$$C < CH_3$$

$$CH_3$$
  
(c) Ph—C=CH—CH<sub>3</sub>

**38.** The following reaction gives:

(a) 
$$OMe$$
 +  $CH_3OH$  OMe

(b) 
$$OMe$$
 +  $HCO_2^{\circ}$ 

(d) 
$$OMe$$
 +  $CH_3OH$ 

**39.** Which of the following is not the product of an intramolecular aldol condensation?

**40.**  $x = \text{no. of compound better hydride donor than Ph} - C - O^{\Theta}$ H

(a) 
$$O_2N$$
  $O_9$ 

(d) 
$$CH_3$$
  $CH_3$   $O^{\ominus}$ 

**41.** Choose the reactant whose aldol reaction would give jasmone.

**42.** Compound *X* undergoes the following reaction sequence. What is the structure of compound *X*?

$$X \xrightarrow{\text{NaOH}} \xrightarrow{\text{Heat}} \xrightarrow{\text{H}_2/\text{Pd}} \xrightarrow{\text{1.LiAlH}_4} \xrightarrow{\text{2H}_2\text{O}}$$

$$(a) \text{ (b) HO}$$

$$(c) \text{ (d) O}$$

43. Predict the major product of the following reaction sequence

$$(a) \qquad \begin{array}{c} CH_3 + \text{NaOH} & \xrightarrow{H_3C} & \xrightarrow{H_2O} & \xrightarrow{1.} & \xrightarrow{2. H_2O} \\ \\ (b) & & & \\ CH_3 & & & \\ (b) & & & \\ CH_3 & & \\ CH_3 & & \\ CH_3 & & & \\ CH_3 & & \\ CH_5 & & \\ C$$

$$(c) \qquad (d) \qquad (d) \qquad CH_3$$

44. CHO 
$$\xrightarrow{\text{Conc. KOH}}$$
  $(A) \xrightarrow{\text{H}^{\oplus}}$   $(B)$  Cyclic product

Structure of (B) is:

						ANSW	ERS	— LE	VEL 1						
1.	(a)	2.	(b)	3.	(a)	4.	(b)	5.	(b)	6.	(c)	7.	(b)	8.	(b)
9.	(b)	10.	(c)	11.	(a)	12.	(a)	13.	(a)	14.	(b)	15.	(a)	16.	(b)
17.	(b)	18.	(a)	19.	(c)	20.	(a)	21.	(c)	22.	(b)	23.	(c)	24.	(c)
25.	(d)	26.	(a)	27.	(c)	28.	(b)	29.	(c)	30.	(c)	31.	(a)	32.	(a)
33.	(c)	34.	(a)	35.	(c)	36.	(b)	37.	(b)	38.	(b)	39.	(c)	40.	(b,c)
41.	(d)	42.	(d)	43.	(c)	44.	(a)						(-)		(2,0)



# LEVEL-2

### 1. Comprehension

Mechanism of Cannizzaros reaction of benzaldehyde is

**A.** Which of the following reactants can undergo Cannizaro's reaction.?

(b) R<sub>3</sub>CCHO

(d) All of these

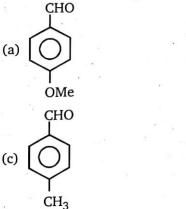
- B. Order of the above reaction is:
  - (a) 1

(b) 2

(c) 3

(d) 4

C. Which of the following is best hydride donor in Cannizaro's reaction?



(b) NO<sub>2</sub> CHO

(d) CI

- D. Cannizaro's reaction is:
  - (a) Reduction

(b) Disproportionation reaction

(c) Oxidation

- (d) Ion exchange reaction
- E. Which of the following cannot undergo intramolecular Cannizaro's reaction?

2. Aldol condensation proceeds by carbon-carbon bond formation between an enolate donor and a carbonyl acceptor. For each of the following aldol products (a through e) select a donor and an acceptor compound from the list at the bottom of the page (compounds A through H). Write the letter corresponding to your selection in the appropriate answer box.

9	Aldol Product	Donor	Acceptor
a.	OH		
ъ.	ОН		
c.	CH—		
d.	(CH <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> COCH <sub>3</sub>		
e.	$\begin{array}{c} CO_2C_2H_5 \\ \\ CO_2C_2H_5 \end{array}$		

#### 3. Comprehension

During an experimental workup procedure, a chemist treated a starting material with NaOH in the solvent acetone  $[(CH_3)_2C=O]$ ; however, the starting material was recovered unreacted. Instead, the chemist isolated a small amount of Product A (shown below).

#### **Product A**

The chemist determined that Product A resulted from the aldol self-condensation of acetone. Product A was identified based on the following observations.

Observations about Product A

- Elemental analysis of Product A indicated that it consisted only of carbon, hydrogen, and oxygen.
- 2. product A had a molecular weight of 116 g/mol.
- 3. Product A was a methyl ketone because it gave a positive iodoform test.
- 4. When product A was treated with Br<sub>2</sub> in CCl<sub>4</sub>, the red bromine colour persisted, because no carbon-carbon double bonds were present to react with the bromine.

The structure of Product A was further confirmed when treatment with hot sulfuric acid resulted in the corresponding dehydration product, Product B.

- A. What is the molecular weight of a compound that undergoes an aldol self-condensation reaction to result in a  $\beta$ -hydroxy ketone with a molecular weight of 144?
  - (a) 70 g/mol

(b) 72 g/mol

(c) 74 g/mol

- (d) 76 g/mol
- **B.** The aldol self-condensation of acetone is an equilibrium that favours acetone over its condensation product. Which of the following experimental modifications is most likely to shift the position of equilibrium toward Product A?
  - (a) Using only a catalytic amount of NaOH
  - (b) Using only a catalytic amount of acetone
  - (c) Removing Product A as it is formed
  - (d) Increasing the reaction temperature to the boiling point of acetone
- C. Based only on observation 1 and 2, which of the following compounds could have been Product A?

(c) 
$$CH_2 = CHCH_2 - O - CH_2CH_2CH_3$$

- **D.** When a drop of Br<sub>2</sub> in CCl<sub>4</sub> is added to Product B, the resulting solution will be:
  - (a) colourless, because Product B does not contain a carbon-carbon double bond
  - (b) colourless, because Product B contains a carbon-carbon double bond
  - (c) red, because Product B does not contain a carbon-carbon double bond
  - (d) red, because Product B contains a carbon-carbon double bond
- E. Which of the following compounds from the passage will give a positive iodoform test?
  - (a) Product A only

- (b) Product A and Product B
- (c) Product A and acetone only
- (d) Product A, Product B, and acetone

#### 4. Comprehension

- **A.** Structure of *A* is :
  - (a)  $H_2C = CH CHO$

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

- (b)  $Ph CH = CH CH_3$
- (d)  $Ph CH = C CH_3$
- **B.** Structure of (B) and (C) differentiated by:
  - (a) Tollen's reagent
  - (c) 2,4-DNP

- (b) Fehling solution
- (d) NaHSO<sub>3</sub>

**C.** Structure of *E* is :

### SUBJECTIVE PROBLEMS

X = Number of compound obtained by aldol reaction

Y =Number of compounds react with NaHCO<sub>3</sub>

Sum of X + Y is

**2.** In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is:

$$\begin{array}{c}
1 \text{ O}_{3} \\
\hline
2. \text{Zn,H}_{2}\text{O}
\end{array}$$

$$Y \xrightarrow{1. \text{NaOH} (aq)} 2 \text{ heat}$$

3. 
$$CH_3 - C - CH_3 + x HCHO \xrightarrow{KOH} HO \xrightarrow{HO} OH$$

x = moles of HCHO consumed.

Value of (x) will be

4. 
$$CH_3 - C - CH_3 + CH_3 - CH_2 - C - CH_3 \xrightarrow{KOH(aq.)} (X)$$

X = number of aldol condensation product (including stereoisomer). Find out the value of (X).

#### ANSWERS — LEVEL 2

1. 
$$A-d$$
;  $B-c$ ;  $C-a$ ;  $D-b$ ;  $E-c$ 

3. 
$$A - b$$
;  $B - c$ ;  $C - d$ ;  $D - b$ ;  $E - d$ 

**4.** 
$$A - b$$
,  $B - b$ ,  $C - c$ 

#### **Subjective Problems**

**1.** 6 **2.** 3 **3.** 6

6 4.9