## 2018

(Pre-CBCS)

(5th Semester)

### **CHEMISTRY**

FIFTH PAPER (CHEM-351)

(Organic Chemistry—II)

Full Marks: 55

Time: 2½ hours

( PART : A—OBJECTIVE )

( *Marks*: 20 )

The figures in the margin indicate full marks for the questions

SECTION—A

( *Marks*: 5)

Tick (✓) the correct answer in the brackets provided :

 $1 \times 5 = 5$ 

- 1. The increasing order of acidity of the following compound is
  - (a) m-nitrophenol < p-nitrophenol < 2,4-dinitrophenol ( )
  - (b) 2,4-dinitrophenol < p-nitrophenol < m-nitrophenol ( )
  - (c) p-nitrophenol < 2,4-dinitrophenol < m-nitrophenol ( )
  - (d) m-nitrophenol < 2,4-dinitrophenol < p-nitrophenol ( )

2.		reaction between aldehyde and HCN to form cyanohydrin is an mple of	
	(a)	nucleophilic substitution ( )	
	(b)	nucleophilic addition ( )	
	(c)	addition-elimination ( )	
	(d)	elimination ( )	
3.	Primary amine when treated with aldehyde gives		
	(a)	alcohols ( )	
	(b)	Schiff's base ( )	
	(c)	2°-amine ( )	
	(d)	carbylamine ( )	
4.	Ace	tal is formed by the reaction between	
	(a)	aldehyde and carboxylic acid ( )	
	(b)	aldehyde and alcohol ( )	
	(c)	ketone and alcohol ( )	
	(d)	ketone and carboxylic acid ( )	
5.	The	order of aromaticity of five-membered heterocycle is	
	(a)	pyrrole < thiophene < furan ( )	
	(b)	furan < pyrrole < thiophene ( )	
	(c)	pyrrole < furan < thiophene ( )	
	(d)	furan < thiophene < pyrrole ( )	

# SECTION—B

( *Marks* : 15 )

Answer the following questions:

 $3 \times 5 = 15$ 

- 1. Draw the molecular orbital picture of benzene with proper labelling.
- 2. Complete the following reaction with suitable mechanism:

2HCHO 50% NaOH ?

- 3. Describe nitrous acid test to distinguish between 1°, 2° and 3° amines.
- 4. Explain Mannich reaction taking suitable example.
- **5.** Electrophilic substitution of pyridine takes place primarily at C-3 than C-2 and C-4. Explain.

# ( PART : B—DESCRIPTIVE )

( Marks: 35)

The figures in the margin indicate full marks for the questions

**1.** (a) State Hückel's rule of aromaticity. Indicate whether the following compounds are aromatic or not: 1+4=5

$$\triangle$$
 ,  $\bigcirc$  ,  $\bigcirc$  ,  $\bigcirc$ 

(b) "Phenols are more acidic than alcohols." Explain.

2

OR

**2.** (a) Complete the following reactions (mechanisms not required):  $1 \times 2 = 2$ 

(i) 
$$\sim$$
 Cl + NaOH  $\sim$  ?

(ii) 
$$O_2N$$
—C1  $\xrightarrow{NH_3}$  ?  $NO_2$ 

(b) Complete the reactions with suitable mechanisms (any two):  $2\frac{1}{2} \times 2=5$ 

(i) 
$$Cl + NaNH_2 \xrightarrow{liq. NH_3}$$
?

(ii) 
$$\langle - \rangle$$
 OH + CHCl<sub>3</sub>  $\longrightarrow$  ?

(iii) 
$$\sim$$
 OH + NaOH  $\longrightarrow$  ?  $\sim$  ?

**3.** (a) Complete the following reactions with suitable mechanisms (any *two*):

$$2\frac{1}{2} \times 2 = 5$$

(i) 
$$CH_3COCH_3 + NH_2OH \xrightarrow{H^+}$$
 ?

(ii) Ph—CHO + KCN 
$$\xrightarrow{\text{EtOH}}$$
 ?

(iii) 
$$CH_3COOH + C_2H_5OH \xrightarrow{H^+}$$
 ?

(b) "Aldehydes are more reactive than ketones towards nucleophile." Explain.

#### OR

**4.** (a) Arrange the following in their increasing order of acidity and explain : 2 HCOOH, CH $_3$ COOH, ClCH $_2$ COOH

2

- (b) Complete the following reactions (mechanisms not required):  $1 \times 5=5$ 
  - (i)  $CH_3COCH_3 \xrightarrow{Conc. HCl}$  ?

(ii) C + CH<sub>3</sub>MgBr 
$$\longrightarrow$$
 ?  $\xrightarrow{\text{H}_2\text{O}/\text{H}^+}$  ?

(iii) 
$$\stackrel{O}{\parallel}$$
  $\stackrel{KMnO_4/H^+}{\longrightarrow}$  ?  $\stackrel{SOCl_2}{\longrightarrow}$  ?

(iv)  $CH_3COCH_3 + NH_2CONHNH_2 \longrightarrow ?$ 

(v) 
$$H + \text{LiAlH}_4 \xrightarrow{H_2O/H^+}$$
?

- **5.** (a) Arrange the following in their increasing order of basicity and explain :  $3 \text{ CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_3\text{N}$ 
  - (b) Differentiate between tautomerism and resonance. 2
  - (c) Complete the following reactions: 1×2=2
    - (i)  $CH_3$ — $NH_2 + CH_3COC1$   $\longrightarrow$  ?
    - (ii)  $R-NH_2 + CHCl_3 \xrightarrow{KOH} ?$

- **6.** (a) How will you synthesize the following compounds from ethylacetoacetate? 2×2=4
  - (i) Butanoic acid
  - (ii) 2-Pentanone
  - (b) What are active methylene compounds? Give examples.
  - (c) Complete the following reactions: 1×2=2

(i) 
$$CH_3$$
— $NH_2 + CS_2 \rightarrow ? \xrightarrow{HgCl_2} ?$ 

(ii) 
$$\sim$$
 NH<sub>2</sub> + aq. Br<sub>2</sub>  $\longrightarrow$  ?

**7.** (a) Complete the following reactions with suitable mechanisms (any two):

$$2\frac{1}{2} \times 2 = 5$$

1

(i) 
$$CH_3$$
 +  $CH_3COC1$   $AlCl_3$  ?

(ii) 
$$OEt$$
 NaOEt  $EtOH$  ?

(iii) 
$$\stackrel{\text{O}}{\longleftarrow}$$
 + CH<sub>3</sub>Br + PPh<sub>3</sub>  $\stackrel{\text{BuLi}}{\longrightarrow}$  ?

(b) Explain the  $A_{AC}2$  mechanism for the hydrolysis of ester.

**8.** (a) Complete the following reactions with suitable mechanisms (any *two*):

 $2\frac{1}{2} \times 2 = 5$ 

(i) 
$$\stackrel{O}{\longrightarrow}$$
 +  $\stackrel{H}{\longrightarrow}$  ?

$$\begin{array}{ccc}
& & \text{Ph} & \text{Me} \\
(ii) & \text{Ph} & & & \text{Me} & & & \\
& & & & & \text{HO} & \text{OH} & & \\
\end{array}$$
?

(iii) 
$$H_2O \rightarrow ?$$

- (b) How will you obtain benzilic acid from benzil? Give proper mechanism for the reaction.
- **9.** (a) How will you synthesize indole from Fischer indole method? Give chemical equations.
  - (b) Complete the following reactions (any three, mechanisms not required):

 $1 \times 3 = 3$ 

2

(i) 
$$O = \bigvee_{H \in H} O \xrightarrow{NH_3} ?$$

(ii) 
$$N + SO_3 \xrightarrow{\text{pyridine}} ?$$

(iii) 
$$\stackrel{\text{(iii)}}{\sim} + \operatorname{Br}_2 \xrightarrow{\operatorname{dioxan}} ?$$

(iv) 
$$+ \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4}$$
?

10. (a) Compare the basicity of the following:

 $2 \times 2 = 4$ 

- (i) Pyrrole vs. pyridine
- (ii) Pyridine vs. piperidine
- (b) Give the mechanism of the following transformation:

3

$$\begin{array}{c} \text{CH}_2\text{OH} \\ \text{CHOH} \\ \text{CH}_2\text{OH} \\ \end{array} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \begin{array}{c} \text{CH}_2 \\ \text{CH} \\ \text{CH}_2 \\ \end{array} \xrightarrow{\text{CH}_2} \begin{array}{c} \text{NH}_2 \\ \text{H}^+, \end{array}$$

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