### 3 (Sem-5) CHM M 3

# (2)

#### 2020

( Held in 2021 )

### **CHEMISTRY**

(Major)

Paper : 5.3

Full Marks: 42

Time: 2 hours

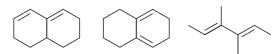
The figures in the margin indicate full marks for the questions

GROUP—A

( Marks : 21 )

**1.** Answer the following :

- $1 \times 2 = 2$
- (a) Arrange the following diene in order of increasing reactivity in a Diels-Alder reaction:



(b) 2-Methyl-2-nitropropane does not dissolve in alkali whereas 2-nitropropane dissolves. Why?

**2.** Answer the following :

 $2 \times 2 = 4$ 

(a) In the following reactions (i) is faster than (ii). Give reasons:

(i) 
$$\stackrel{\text{CONH}_2}{\longrightarrow}$$
  $\stackrel{\text{NH}_2O}{\longrightarrow}$ 

(ii) 
$$NO_2$$
 NaOBr,  $H_2O$  NO<sub>2</sub> NO<sub>2</sub>

(b) Between 2,4-dimethyl-3,5-heptanedione and 4,4-dimethyl-3,5-heptanedione which compound is more acidic and why?

- **3.** Answer any *three* of the following :  $5 \times 3 = 15$ 
  - (a) How can you carry out the following conversions? Propose mechanisms for the same:
    - (i) Butanone to butan-2-ol
    - (ii) Cyclohexene to *trans*-cyclohexan-1,2-diol

1-21**/754** (Turn Over)

1-21**/754** 

(Continued)

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(b) How can you convert benzophenone to benzanilide using a rearrangement reaction? Propose a mechanism for the conversion. What product will be obtained if p-methylbenzophenone were to undergo the same rearrangement?

1+3+1=5

2

(c) (i) Arrange the following compounds in order of increasing boiling point and provide an explanation:

N— $NH_2$   $NH_2$ 

(ii) Give the major product in each of the following reactions:  $1\times 3=3$ 

(1) 
$$\xrightarrow{\text{m-CPBA}}$$
 ?

$$(2) \bigcirc + \bigcirc \stackrel{\text{CHO}}{\longrightarrow} ?$$

(3) 
$$\frac{\text{i) KNH}_2, -70 \text{ °C}}{\text{ii) KMnO}_4, -70 \text{ °C}} \rightarrow \frac{1}{100}$$

(d) (i) What product will be obtained when the compound given below reacts with  $SeO_2$  in presence of water? Propose a mechanism for the same :

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

- (ii) Which position of pyrrole is more reactive towards electrophiles and why?
- (e) (i) Predict the product when diazoacetone is irradiated in methanol solution. Propose a mechanism. 1+2=3
  - (ii) Give the expected dominant product(s) in mononitration of each of the following compounds: 2

3

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## GROUP—B

( Marks : 21 )

- **4.** Answer any *three* of the following :  $7 \times 3 = 21$ 
  - (a) (i) Predict the major product of the following reaction and propose a mechanism: 1+3=4

$$\stackrel{\text{MeO}}{\longrightarrow} \stackrel{\text{Li, NH}_3 \text{ (l)}}{\longrightarrow} ?$$

- (ii) Write one reaction each to show that anthracene undergoes both electrophilic substitution and addition. Why does anthracene undergo addition reaction comparatively easily than other similar aromatic systems? 1+1+1=3
- (b) (i) It is extremely difficult to carry out electrophilic aromatic substitution on pyridine. How can you nitrate pyridine? Write the reactions involved.

1-21/754

(ii) Predict the product and write the mechanism of the reaction: 1+2=3

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(Turn Over)

$$\frac{1) \text{ Excess CH}_3}{2) \text{ Ago, H}_2\text{O,}} \stackrel{?}{\longrightarrow} ?$$

(iii) Both the reactions shown below give the same alkene. Which one is the favoured route and why?

(1) 
$$CH_3Br + PPh_3 \xrightarrow{NaOH} [X]$$

$$\longrightarrow ?$$

$$(2) \qquad \qquad PPh \qquad NaOH \qquad [Y]$$

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$$(2) \xrightarrow{\text{Br}} + \text{PPh}_3 \xrightarrow{\text{NaOH}} [Y]$$

$$\xrightarrow{\text{H}} \xrightarrow{\text{H}} \xrightarrow{\text{PPh}_3} \xrightarrow{\text{NaOH}} [Y]$$

(c) (i) Write the appropriate products in the following reactions: 2+2+2=6

$$(1) \bigvee_{N} \stackrel{Ph}{\overset{OH}{\longrightarrow}} \stackrel{Ph}{\overset{H^{+}}{\longrightarrow}} ?$$

(2) 
$$OH \xrightarrow{PCC} ?$$

(Take into account the fact that PCC is mildly acidic)

(3) 
$$C_6H_5S$$
  $\xrightarrow{i) C_4H_9Li, THF, -78 °C}$  ?

1-21**/754** (Continued)

- (ii) Account for the difference in boiling points between anthracene and phenanthrene.
- (d) (i) On reaction with sodium methoxide each of the compounds PhCH<sub>2</sub>COCH<sub>2</sub>Cl and PhCHClCOMe gives the same product. Use appropriate mechanisms to explain the same.
  - (ii) How can you convert diethylmalonate to 2-ethylpentanoic acid? Write the steps involved.
- (e) (i) The compound given below undergoes Claisen rearrangement followed by Cope rearrangement.

  Write the expected product:

(ii) Predict the product(s):

- (iii) When 1,3-dimethyl-isoquinoline is treated with NaOCH $_3$  in CH $_3$ OD, the protons of the C-1 methyl group are exchanged much more rapidly than those of the C-3 methyl group. Explain.
- (iv) What is the active agent which makes mustard gas poisonous?

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(v) What happens when hydrazobenzene is placed in strongly acidic solution?

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