## **Post Graduate Teaching Department of Chemistry (AUTONOMOUS)**

## Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur

## Semester I: End Semester Examination (February 23, 2022)

## Paper II (Code: 1T2): Organic Chemistry

Time: 3 h Max. marks = 60

Note: 1) All the questions are compulsory.

- 2) Figures to the right indicates marks assigned to each question.
- **Q.** 1 Suggest a plausible mechanism for the following reaction.

(A) OH  $+ CHCl_3$   $\xrightarrow{i) NaOH(aq)}$   $\xrightarrow{i) H_3O}$   $\xrightarrow{i) H_3O}$ 

(B) Classify the following molecules as aromatic, nonaromatic and antiaromatic with suitable 4 reasons.

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(C) Rank the following carbocations in order of increasing stability with suitable justification.

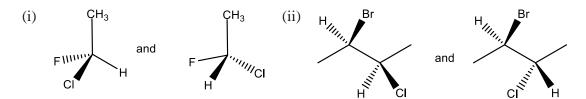
$$\bigoplus_{\oplus} \bigvee_{\oplus}$$

OR

- Q. 1 Define crown ethers with suitable examples. Explain its role in the following reaction.
- (D)  $CI \leftarrow CI + KCN \xrightarrow{18-crown-6} NC \leftarrow CN$  yield 96.8%
- (E) Predict the product(s) and its stereochemistry in the following reactions. Justify your answer.

- (F) Give any two examples of nitrene generation reactions.
- Q. 2 i) Draw all the staggered and eclipsed conformers that result from rotation about the C-2  $\neg$ C- 4
- (A) 3 bond of pentane.

- ii) Draw a potential-energy diagram for rotation of the bond of pentane through 360°, starting with the least stable conformer.
- (B) For each pair of structures shown, indicate whether the two species are constitutional isomers, 4 enantiomers, diastereomers of one another, or identical molecules.



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(C) Convert the following Newman Projections into Fischer Projections

i] 
$$H$$
  $GH_3$   $GH_3$ 

OR

- (D) Which isomer in each pair of compounds is lower in energy?
  - i) cis- or trans-1,2-diethylcyclohexane
  - ii) cis- or trans-1-ethyl-3-isopropylcyclohexane
- (E) Assign R or S configuration to the chirality center in each of the following molecules:

$$(i) \qquad \underset{\stackrel{}{\text{HO}}}{\overset{}{\text{HO}}} \text{H} \qquad (ii) \qquad \underset{\stackrel{}{\text{Cl}}}{\overset{}{\text{Cl}}}$$

(F) For each pair of structures shown, indicate whether the two species are constitutional isomers, 4 enantiomers, diastereomers of one another, or identical molecules.

Q. 3 Explain the kinetic and thermodynamic control with respect to the sulphonation of naphthalene: 4

(A) 
$$SO_3H$$

$$H_2SO_4$$

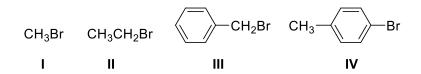
$$80 °C$$

$$H_2SO_4$$

$$165 °C$$

$$SO_3H$$

- (B) Predict the order of reactivity of the following halides with
  - i) sodium iodide in acetone
  - ii) aqueous alcoholic silver nitrate



(C) Write a suitable mechanism for the following reaction.

(D) Draw an energy diagram for each reaction. Label the axes, the starting material, product, transition state,  $\Delta H^{\circ}$ , and Ea.

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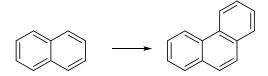
- a. A concerted, exothermic reaction with a low energy of activation.
- b. A one-step endothermic reaction with a high energy of activation.
- (E) Draw the structure of the bridged intermediate expected if each of the following were to act as 4 a neighbouring group.
  - i)  $-N(CH_3)_2$  ii)  $-C_6H_5$
- (F) In each of the following pairs of compounds, which compound will undergo faster S<sub>N</sub>1 reaction? 4
  - a. and b. Br and OBr
- Q. 4 Arrange the following in order of reactivity toward ring nitration, listing by structure the most
- (A) reactive at the top, the least reactive at the bottom. benzene, mesitylene, toluene, *m*-xylene, *p*-xylene
- (B) Predict the major product of the following reaction with suitable mechanism.

(C) Identify the major product formed in the following reaction with suitable justification.

(i) 
$$CH_3CI$$
 (ii)  $Fe, Br_2$ 

OR

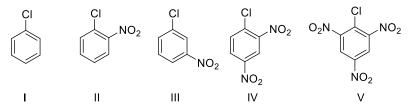
(D) How will you bring the following transformations involving more than one step?



(E) Arrange the following compounds in increasing order of reactivity towards aromatic nucleophilic substitution.

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(F) Account for the sign and magnitude of (rho) ρ-values observed for the following reactions:

	Reaction	ρ-value
i)	$X-ArH + NO_2^+ \longrightarrow X-Ar-NO_2$	- 7.3
ii)	X-PhCH2COOH	0.2

- Q 5 Attempt any six of the following.  $(2 \times 6 = 12)$
- (a) Define substituent constant
- (b) Define reaction constant
- (c) Define primary kinetic isotope effect.
- (d) Define inductive effect
- (e) Define Huckel rule
- (f) State Curtin-Hammett principle
- (g) Define hyperconjugation
- (h) Define conformation of a molecule
- (i) Define chirality of a molecule
- (j) Define nucleophie