Date:

**Registration number:** 



## Time: 2 Hours

#### ST. JOSEPH'S UNIVERSITY, BENGALURU -27 M.Sc (CHEMISTRY) – I SEMESTER SEMESTER EXAMINATION: OCTOBER 2022 (Examination conducted in December 2022) CH 7221 – ORGANIC CHEMISTRY I

Max Marks: 50

# This paper contains 3 printed pages and 3 parts

## PART-A

Answer any EIGHT questions. Each question carries 2 marks

8 x 2= 16

- 1. What are carbenes? Give one method of generating a carbene.
- 2. Write the mechanism of E1cB reaction.
- 3. What is sacrificial hyperconjugation? Give an example.
- 4. Draw the structure of i) bicyclo[3.1.1]heptane ii) chair form of *cis*-decalin.
- 5. Write the mechanism for  $S_{RN}1$  reaction.
- 6. Why is N,N,2,6-tetramethylaniline (structure I) is a stronger base than N,Ndimethylaniline (structure II)?



7. Write the geometrical isomer obtained when the following substrate undergoes dehydrohalogenation reaction with a base via E2 mechanism.

CN



8. Assign (R) or (S) designations to each of the following compounds:

ii)



9. The following substrate neither undergoes  $S_N 1$  nor  $S_N 2$  reaction. Explain.



10. What is the major product(s) formed in each case when electrophilic substitution occurs in the following?



#### <u>Part B</u>

Answer any TWO questions. Each question carries 12 marks 2 x 12= 24

11. a) Draw the i) Newman formula for the most stable conformer of 2-aminoethanol ii) most stable chair conformer of *trans*-1-*tert*-butyl-3-methylcyclohexane iii) least stable chair conformer of *trans*-1-isopropyl-4-methylcyclohexane iv) sawhorse formula for the least stable conformer of n-butane.

b) Identify the topicity relationship of  $H_1$  and  $H_2$  atoms indicated in each of the following molecules. Assign topicity descriptors (pro-*R* and pro-*S*) to these atoms.



c) Give an example each of an optically active molecule that i) is an ansa compound ii) is an atropisomer iii) has two stereocentres iv) is a benzphenanthrene

(4+4+4)

12. a) Write the A<sub>AC</sub>2 mechanism of ester hydrolysis.

b) With a suitable example, explain neighbouring group participation by aromatic  $\pi$ -electrons in nucleophilic substitution.

c) Give reasons for the following observations:

- i) Alkyl halide R-Br reacts with AgCN to give R-NC (an alkyl isocyanide) whereas it reacts with NaCN to give R-CN (an alkyl cyanide).
- ii) The rate of the following reaction increases  $4.5 \times 10^4$  times when the solvent is changed from methanol to dimethylformamide(DMF).

$$N_3^- + CH_3I \xrightarrow{S_N^2} N_3CH_3 + I^-$$
 (3+3+6)

13. a) Write Hammett equation that relates structure with reactivity and explain the terms in the equation. Show that this equation is a linear free energy relationship.

b) Using the relative stabilities of intermediates, explain the preferential position of electrophilic attack on carbon atoms of 1,2-azoles.

c) Write the major product(s) of the following reactions:



#### Part C

Answer any TWO questions. Each question carries 5 marks 2 x 5= 10

14. State whether the following reactions will show a primary or secondary(normal or inverse) kinetic isotope effect. Explain your reasoning.



15. Identify whether the pairs of molecules below are enantiomers, diastereomers, Identical, or constitutional isomers.



16. Write the major product(s) formed in the following:

