



Register Number:

Date:

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27
M.Sc. CHEMISTRY- I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2019
CH 7218 : ORGANIC CHEMISTRY

Time- 2½ hrs

Max Marks-70

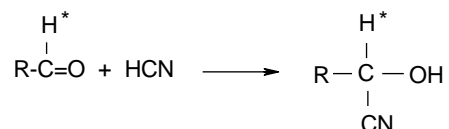
This paper contains **FOUR** printed pages and **THREE** parts

PART A

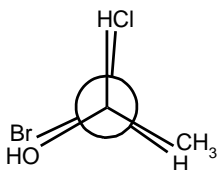
Answer any **SIX** questions. Each question carries **2** marks.

6x2=12

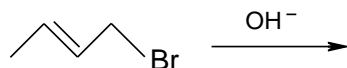
1. State Curtin-Hammett principle.
2. What type of kinetic isotopic effect could be observed if the asterisked hydrogen is replaced with deuterium in the following reaction? Give reason for the isotope effect.



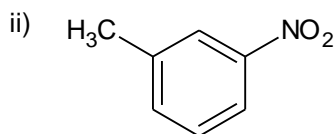
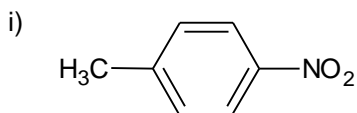
3. Rewrite the following structure in perspective formula and assign R/S configuration notation to the stereocentres.



4. Write the structure of the following compounds i) 5-methylbicyclo[2.1.1]hexane
ii) bicyclo[3.1.1]heptane
5. Complete the following reaction if it takes place under conditions that favour S_N1 mechanism:



6. What is an ambident substrate? Give an example.
7. Write the mechanism for E1cB reaction.
8. Predict the major product(s) formed when the following molecules undergo nitration reaction.

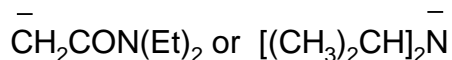


PART B

Answer any FOUR questions. Each question carries 12 marks.

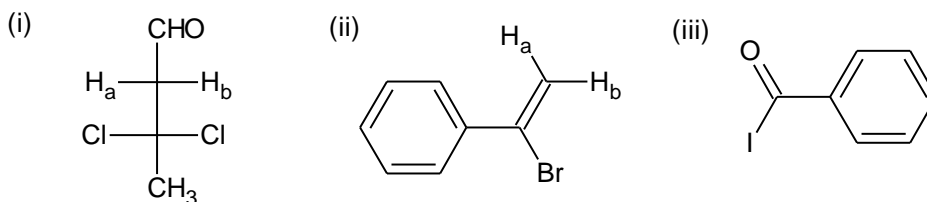
4x12=12

9. a) Give one method of obtaining carbenes. Distinguish between different types.
 b) The C-N bond distances for the *o*- and *p*-nitro groups in 2,4,6-trinitroiodobenzene are quite different. Which of the two C-N bonds has a higher bond length? Give reason.
 c) Which of the following is more basic? Justify your answer.



- d) Taking the addition of HBr to 1,3-butadiene as an example, illustrate the terms kinetically controlled and thermodynamically controlled reactions. (3+3+3+3)
10. a) How is isotopic labelling useful in determining the mechanism of a reaction? Explain with an example.
 b) Give an example each (structure only) for the following types of compounds. Indicate molecule(s) with chiral plane if any.
 (i) an optically active allene derivative. (ii) a cyclophane that is optically active.
 (iii) atropisomer that is optically active. (iii) a molecule with stereogenic centre.
 c) Write in Fischer projection formula all the isomers of 2,3,4-trifluoropentandioic acid. Identify the *meso* compounds among these. Identify the pseudoasymmetric centers and give configuration notations to these centers. (3+5+4)

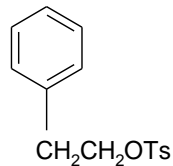
11. a) Discuss the conformations of cyclohexane with the help of a potential energy diagram.
 b) Write the structure for the i) least stable conformer of butane in sawhorse formula ii) most stable conformer of ethane-1,2-diol in Newman projection formula iii) stable conformer of *cis*-1-*tert*-butyl-4-chlorocyclohexane iv) chair form of *cis*-decalin.
 c) Assign *pro-R*/*pro-S*/*pro-E*/*pro-Z* to H_a and H_b hydrogens in (i) and (ii). Indicate the *Re* and *Si* face in (iii).



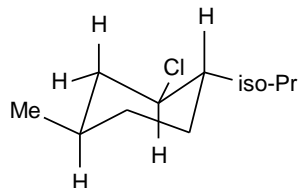
(5+4+3)

12. a) The reaction of (*S*)-2-bromobutane with a nucleophile under S_N1 conditions leads to the formation of about 50-70% of the inverted product. Suggest a mechanism to support this observation.
 b) Write the A_{AC}2 mechanism of ester hydrolysis.

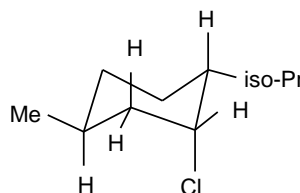
- c) The substrate given below undergoes solvolysis 3040 times faster than $\text{CH}_3\text{CH}_2\text{OTs}$ at 75°C in CF_3COOH to give a product with retention of configuration. Explain this observation giving necessary mechanistic details. (4+4+4)



13. a) What is the effect of increasing polarity of the solvent on substitution to elimination ratio? Explain with a suitable example.
 b) Molecule B undergoes E2 elimination faster than molecule A. Why? Write the product/s of E2 elimination of molecules A and B. Indicate the major product if more than one product is possible. Also, mention each elimination product as Zaitsev/anti-Zaitsev.



(A)



(B)

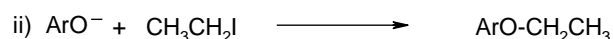
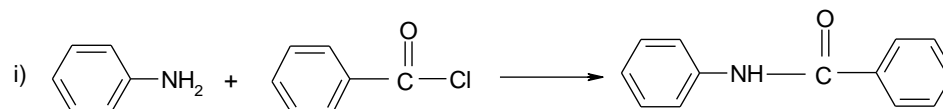
- c) What is Gatterman-Koch reaction? Write the mechanism of the reaction. (3+6+3)
14. a) Write the mechanism for the Smiles rearrangement.
 b) What major product(s) are formed when i) anthracene ii) pyrazole undergoes electrophilic substitution reaction? Explain your answer.
 c) Write the benzyne mechanism and give one evidence in support of this mechanism. (3+6+3)

PART C

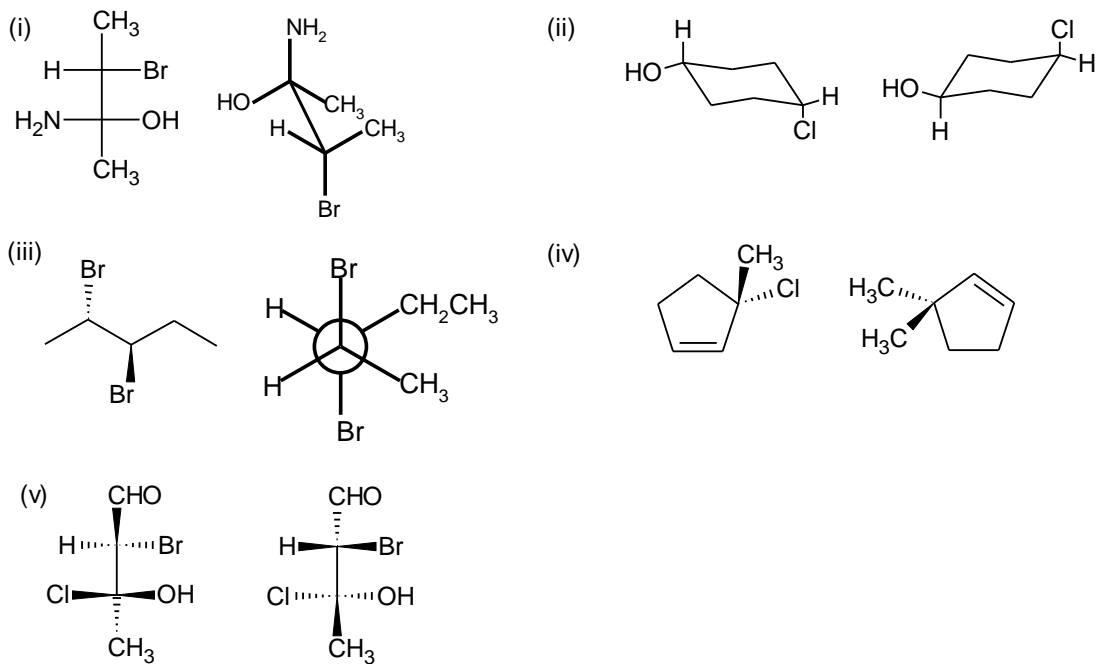
Answer any TWO questions. Each question carries 5 marks.

2x5=10

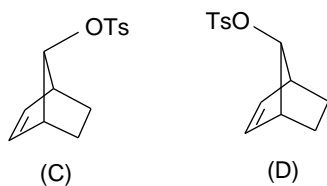
15. Two nucleophilic substitution reactions are given below. Match the correct Hammett reaction constant, ρ value, with each of the reactions. Explain how you arrive at the answer. (The ρ values given are -0.99 and -2.69)



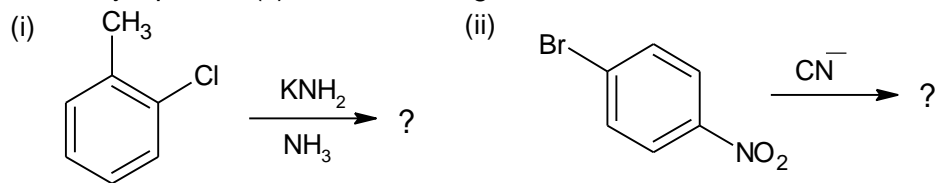
16. Indicate the relationship between the following pairs of molecules as enantiomers / diastereomers / constitutional isomers / identical / unrelated.



17. a) *Anti*-7-norbornyl tosylate (C) undergoes acetolysis 10^7 times faster than its *syn* isomer (D). Suggest a suitable mechanism to explain the relative rates of the reaction.



b) Write the major product(s) in the following reaction.



(3+2)
