

Total number of printed pages-7

14 (CHM-1) 102

2022

CHEMISTRY

Paper : CH-102

(Organic Chemistry-1)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

PART-A

1. Draw labelled reaction profile diagrams for an exothermic reaction that proceeds via a stable intermediate. Identify the rate determining steps. 3

OR

How does maleic anhydride react with butadiene? Write the complete reaction. How do you ascertain whether the product is thermodynamically favoured? Give reasons. 1+2=3

Contd.

2. Taking the example of butane, define the terms 'conformer' and 'conformation'. Draw the *cis*- and *trans*- conformers of 1-bromo-4-*t*-butyl-cyclohexane. Which of these two conformers undergo dehydrohalogenation in the presence of base faster? Give suitable justifications. $2+1+2=5$

OR

Examine the conditions of kinetic and thermodynamic control of product formation for a given chemical reaction. For the reaction of but-3-en-2-one with NaCN in the presence of HCN , give the structures of the possible products. Identify the product formed under kinetic control, by giving suitable justifications. $2+2+1=5$

3. How can primary and secondary isotope effects be differentiated? Give illustrative examples. Considering the unimolecular thermal dissociation of C-H(D) bond, explain how the zero point energy (ZPE) is responsible for the deuterium isotope effect. $3+2=5$

OR

Briefly explain the significance of the concave upward deviation of the Hammett plot. Illustrate your answer with an appropriate example. 5

4. What is the Anomeric Effect and why is it called a stabilizing effect? Explain why the position of the equilibrium given below is dependent on the solvent. $2+3=5$

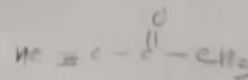


OR

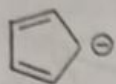
Using an illustrative reaction profile diagram, state the Curtin-Hammett principle. Base catalysed dehydrobromination of 2-bromobutane can produce a mixture of *cis*- and *trans*-but-2-ene. Explain the product selectivity on the basis of the Curtin-Hammett principle. $2+3=5$

PART-B

5. Give the mechanistic steps for the hydrolysis of *t*-butyl chloride, $(\text{CH}_3)_3\text{C-Cl}$, leading to the formation of *t*-butanol, showing the orbital structure of the carbocation intermediate. Draw the reaction profile diagram for the reaction and identify the rate limiting step. $3+2=5$



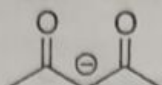
6. Using suitable examples, list the important factors that stabilize carbanion intermediates. Account for the stability of the following carbanions (6A-C). 3+2=5



6A



6B

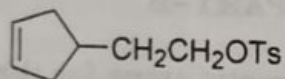


6C

7. Under what conditions can stabilized phosphorus ylides be prepared? Compare the reactivity of stabilized and non-stabilized phosphorus ylides, using appropriate examples. 2+3=5

OR

Provide a mechanistic explanation for the formation of bicyclo[2.2.1]heptane derivative during solvolysis of 2-cyclopent-3-enylethyl tosylate (7A) with sodium acetate, CH_3COONa . 5

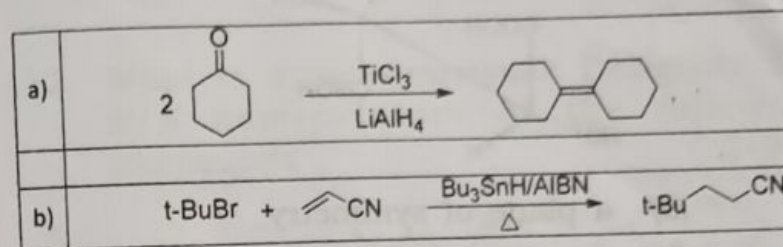


7A

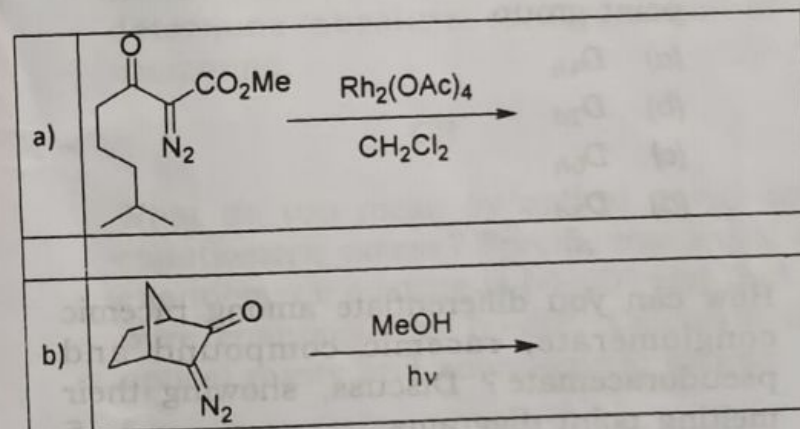
8. Using suitable illustrations, point out the important characteristics of singlet and triplet carbenes. Provide appropriate methods for the preparation of each type of carbene, along with the mechanism. 2+3=5

OR

Give mechanistic explanations for the following transformations (**any one**) by highlighting the nature of the intermediates formed in each case : 5



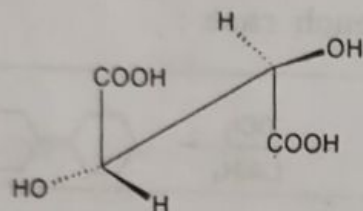
9. Predict the major products of the following reactions (**any one**) and write the plausible mechanism in each instance : 5



PART-C

10. Choose the correct option from the following :
1+1=2

(i) The structural representation of tartaric acid as shown below :



- (a) a plane of symmetry
- (b) a centre of symmetry
- (c) no symmetry
- (d) both plane of symmetry and centre of symmetry

(ii) Benzene, C_6H_6 molecule belongs to the point group

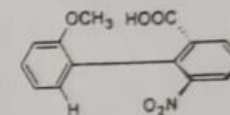
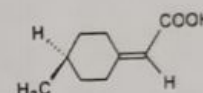
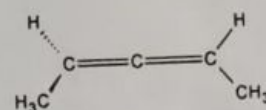
- (a) D_{4h}
- (b) D_{2d}
- (c) D_{6h}
- (d) D_{3d}

11. How can you differentiate among racemic conglomerate, racemic compound and pseudoracemate? Discuss, showing their melting point diagrams. 5

OR

Write the mechanism of ring inversion for cyclohexane molecule. Draw the energy profile for the ring inversion of cyclohexane showing the intermediate conformers. 2+3=5

12. What is atropisomerism? Designate the *R/S* nomenclature of the following compounds : 2+3=5



13. What do you mean by absolute configuration and relative configuration? Name *two* instrumental methods to determine absolute configuration of a compound. 5

OR

What do you mean by optical purity and enantiomeric excess? Specific rotation of an enantiomeric mixture is $(+)-25^\circ$ and that of pure enantiomer is $(+)-50^\circ$. Calculate the optical purity and enantiomeric excess. 5