

(6 pages)

MAY 2016

P/ID 40121/PCHA

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Time : Three hours

Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

Answer ALL questions.

All questions carry equal marks.

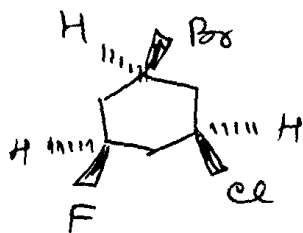
1. Indicate the correct form of fischer projection for erythro  $\text{CH}_3\text{CHBrCHClCHO}$ .
2. It is not proper to equate chiral molecules with asymmetric molecules. Explain.
3. Draw the (+)synclinal n-butane and antiperiplanar n-butane.
4. The gauche form is the most stable conformation of 1, 2-dihydroxyethane. Account.
5. Can substituent constant of Hammett equation have negative value? Explain.
6. Indicate the C-alkylation and O-alkylation products of a phenolate.
7. Discuss the action of n-butyl lithium on pyridine.
8. Explain the mechanism of chichibabin reaction.
9. Provide any one method to prove the existence of an intermediate in a reaction.
10. Indicate how m-nitrobenzoic acid can be prepared from ethyl benzoate.

PART B — (4 × 20 = 80 marks)

Answer ALL the questions.

All questions carry equal marks.

11. (a) (i) What is atropisomerism? Explain with examples.
- (ii) Provide R/S notation for all the chiral centres present in the following molecule ;



- (iii) Draw the correct stereochemical form for 2S, 3S-3-bromo-2-butanol.
- (iv) Distinguish between stereoselective and stereospecific reactions.
- (v) Write a note on Cram's rule.  
(4 + 3 + 2 + 5 + 6)

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- (b) (i) Illustrate alternating axis of symmetry with an example.
- (ii) Give a detailed account of the stereochemistry of allenes and spirans.
- (iii) Draw the different geometrical isomers of disubstituted cyclopentanes and disubstituted cyclopentanes. Identify the active compounds. (4 + 6 + 10)
12. (a) (i) In the gaseous form, diaxial form dominates over diequatorial form in trans-1, 2-dichlorocyclohexane. Explain.
- (ii) In cis-1,3-dimethylcyclohexane, the equatorial, equatorial isomer is stable than axial, axial isomer. Account for this.
- (iii) In 1-methyl-1-phenylcyclohexane, the phenyl group prefers axial position. Why?
- (iv) Compare the conformational features of cis and trans decalins.
- (v) Explain how the kinetic and steric factors influence the product ratio during the reduction of cyclic ketones. (3 + 3 + 3 + 5 + 6)

Or

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- (b) (i) Describe the situations wherein non chair conformations are preferred in cyclohexyl systems.
- (ii) Define the terms 'dihedral angle' and anchoring group.
- (iii) Write notes on : conformational effects on ester hydrolysis and acylation alcohols in six membered systems. (5 + 5 + 10)
13. (a) (i) Discuss the non kinetic methods available to determine the mechanism of organic reactions.
- (ii) Distinguish between primary kinetic isotope effect and secondary kinetic isotope effect.
- (iii) Discuss the similarities between Hammett equation and Taft equation. (10 + 5 + 5)

Or

- (b) (i) What are the features of  $S_Ni$  reaction. Illustrate with examples.
- (ii) Discuss the mechanism of acylation and alkylation of  $RNH_2$
- (iii) Write notes on Nucleophilic substitution at bridge head.
- (iv) Explain Von Braun reaction.

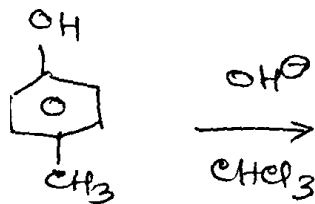
(v) What is neighbouring group participation? Why does the rate of the reaction enhance during NGP? Account for the fact that reactions involving NGP leads to retention. (5 + 4 + 5 + 6)

14. (a) (i) Nitro group is a good leaving group in aromatic nucleophilic substitution reactions, but not in aliphatic nucleophilic substitution reactions. Why?

(ii) What is the formylating agent in vilsmeier reaction? Write the mechanism of the reaction in detail.

(iii) Discuss the course of nucleophilic substitution by  $\text{NaNH}_2$  on differently substituted dichlorobenzenes predicting the major product in each case.

(iv) Write the product in the following reaction :



(v) Compare the rates of bromination of aniline, acetanilide and benzene. (3 + 4 + 6 + 3 + 4)

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- (b) (i) How can you prepare *p*-nitroaniline, *m*-nitroaniline and 1, 3, 5-tribromobenzene from aniline?
- (ii) Cl deactivates the aromatic ring towards electrophilic substitution but ortho, para orienting. NO<sub>2</sub> deactivates the aromatic the ring but ortho, para orienting. Explain in detail.
- (iii) Discuss the mechanisms of Friedel craft acylation, Gattermann formylation and aromatic nitration reactions. (6 + 6 + 8)
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