

2018

2nd Semester

CHEMISTRY

PAPER—C4T

(Honours)

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

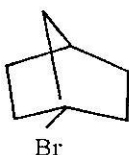
Group-A

1. Answer any five questions :

2×5

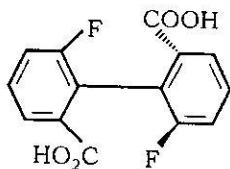
- (a) Between $(\text{CH}_3)_2\text{CHBr}$ and $(\text{CH}_3)_3\text{C-Br}$ which one results in higher ratio of elimination (E2) to substitution ($\text{S}_{\text{N}}2$) when treated with NaOEt/EtOH ?

(Turn Over)

- (b)  is extremely unreactive towards

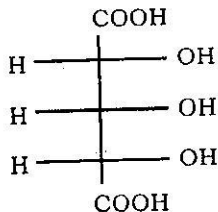
nucleophilic substitution either by S_N1 or S_N2 mechanism — Explain.

- (c) Draw energy profile diagram of three step exothermic reaction in which the second step is r.d.s and the first unstable intermediate is more stable than the second.
- (d) The following compound is chiral but undergoes easy racemisation— Explain.

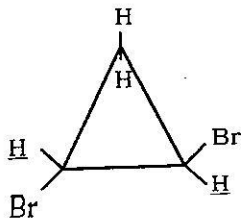
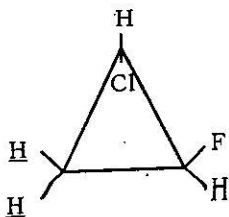


- (e) Draw the (-)sc and (+) ap conformation of active butane -2, 3-diol.

- (f) Assign absolute configuration of the pseudoasymmetric centre of the following :



- (g) 3, 5 - Dimethyl - 4 - nitro aniline is a stronger base than the corresponding 2, 6 dimethyl isomer — Explain.
- (h) Assign topical relationship between the underlined hydrogen atoms.

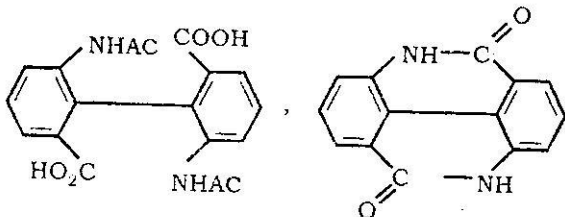


Group-B

Answer any *four* questions.

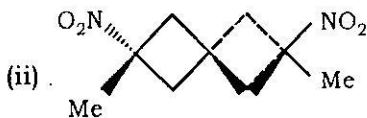
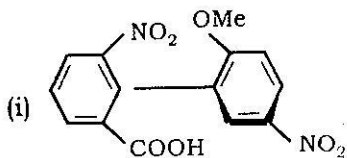
4×5

2. (a) Presence of a chiral centre is not always essential for a compound to show chirality. Explain.
- (b) What do you mean by the term 'Atropisomerism'? Which of the following compounds are resolvable at room temperature and why? 2+(1+2)

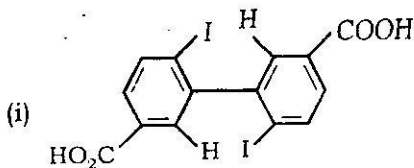


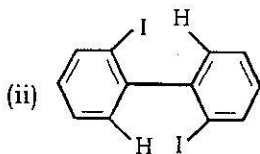
3. (a) The observed order of basicity of aminos in aqueous medium is $\text{Me}_2\text{NH} > \text{MeNH}_2 > \text{Me}_3\text{N}$, whereas in gas phase the order is $\text{Me}_3\text{N} > \text{Me}_2\text{NH} > \text{MeNH}_2$ — Explain with reason.
- (b) R Br reacts with AgCN to produce R - Nc, but it reacts with NaCN to produce R - CN — why? 3+2

4. (a) 'Acid catalysed dehydration of (R) - 2- hydroxybutan-1, 4-dicarboxylic acid gives a pair of geometrical isomers. Identify the products with proper explanation.
- (b) The rate of reaction of 1-bromobutane with azide ion increased 5×10^3 times on changing the solvent from methanol to acetonitrile — Explain. 3+2
5. (a) Assign R/S nomenclature of the followings :



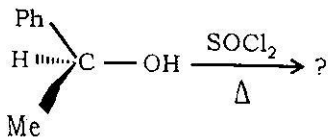
- (b) Which one will racemise faster and why ?





$$(1\frac{1}{2} \times 2) + 2$$

6. (a) Draw the potential energy diagram of 1-bromopropane.
- (b) Write one difference between torsional angle and dihedral angle.
- (c) What do you understand by the term "Walden Inversion"?
7. (a) Predict the product (with stereochemistry) and explain the mechanism involved in the reaction.



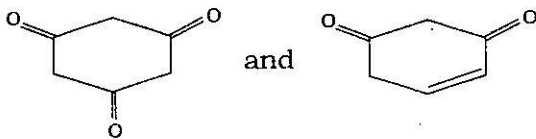
- (b) How can E_1CB pathway be distinguished from the kinetically indistinguishable E_2 pathway?

Group-C

Answer any one question.

1×10

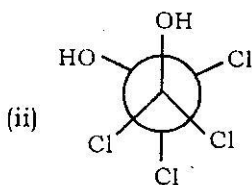
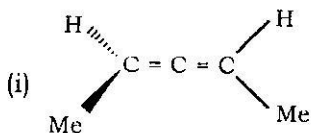
8. (a) Unsymmetrically substituted cumulenes with odd number of double bonds cannot show chirality, rather these can show geometrical isomerism—Explain.
- (b) Arrange in the increasing order of nucleophilicity.
 $\ominus\text{OC}_2\text{H}_5$, $\ominus\text{OC}_6\text{H}_5$, $\text{CH}_3\text{C}\overset{\ominus}{\text{O}}$, $\text{NO}_3\ominus$
- (c) Rate of solvolysis of tertiary butyl chloride in 60% aqueous ethanol is faster than that of the analogous compound containing Deuterium instead of hydrogen; observed $K_H / K_D = 2.32$ —Explain.
- (d) Which one has the higher enol content ?



- (e) Explain mechanistically what happens when erythro-3-bromo-2-butanol is heated with HBr.

2+2+3+1+2

9. (a) Draw the most stable configuration of the following compounds
- (i) 2-amino ethanol (ii) 1, 2-dichloroethane
- (b) What is phase transfer catalyst?
- (c) Assign configuration of the following compounds with P/M descriptors



- (d) Define pseudoasymmetric centre. Give example of 2 molecules with enantiomorphous groups along with pro-r hydrogen atoms on a pseudoasymmetric centre.
- (e) What do you mean by kinetically controlled reactions and thermodynamically controlled reactions? Explain with energy profile diagram.

$$2+1+(1\frac{1}{2}\times 2)+(1+1)+2$$