2018

2nd Semester

CHEMISTRY

PAPER—C4T

(Honours)

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

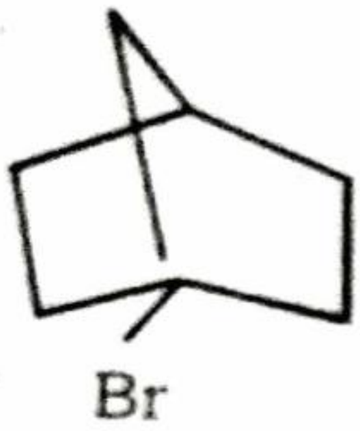
Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

Group-A

1. Answer any *five* questions : 2×5

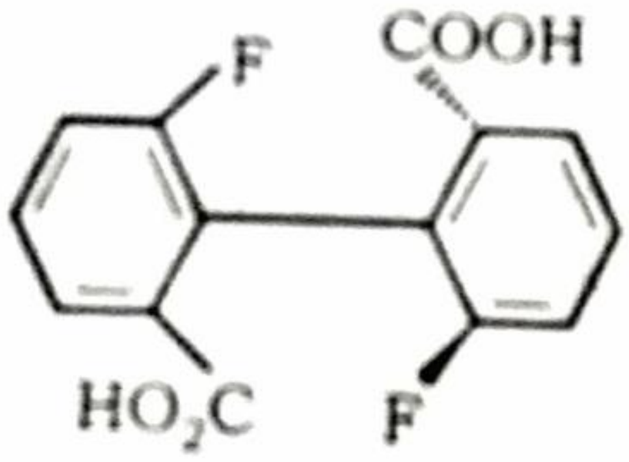
(a) Between $(CH_3)_2$ CHBr and $(CH_3)_3$ C–Br which one results in higher ratio of climination (E2) to substitution (S_N2) when treated with NaOEt/EtOH ?

(b) 

is extremely unreactive towards nucleophilic substitution either by S_N1 or S_N2 mechanism — Explain.

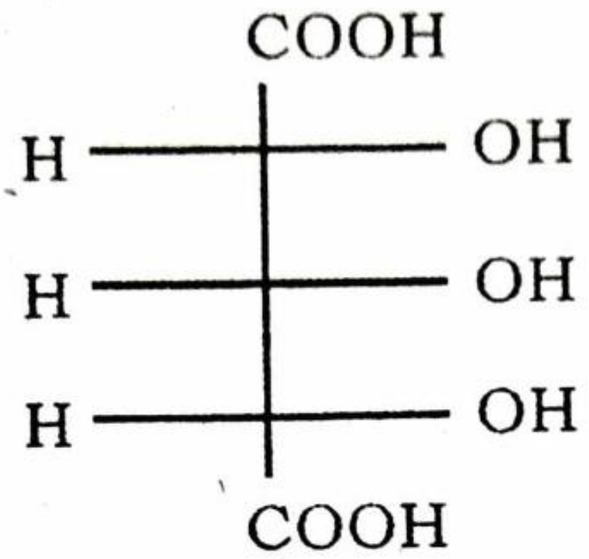
(c) Draw energy profile diagram of three slip exothermic reaction in which the second step is r.d.s and the first unstable intermediate is more stable than the second.

(d) The following compound is chiral but undergoes easy racemisation— Explain.



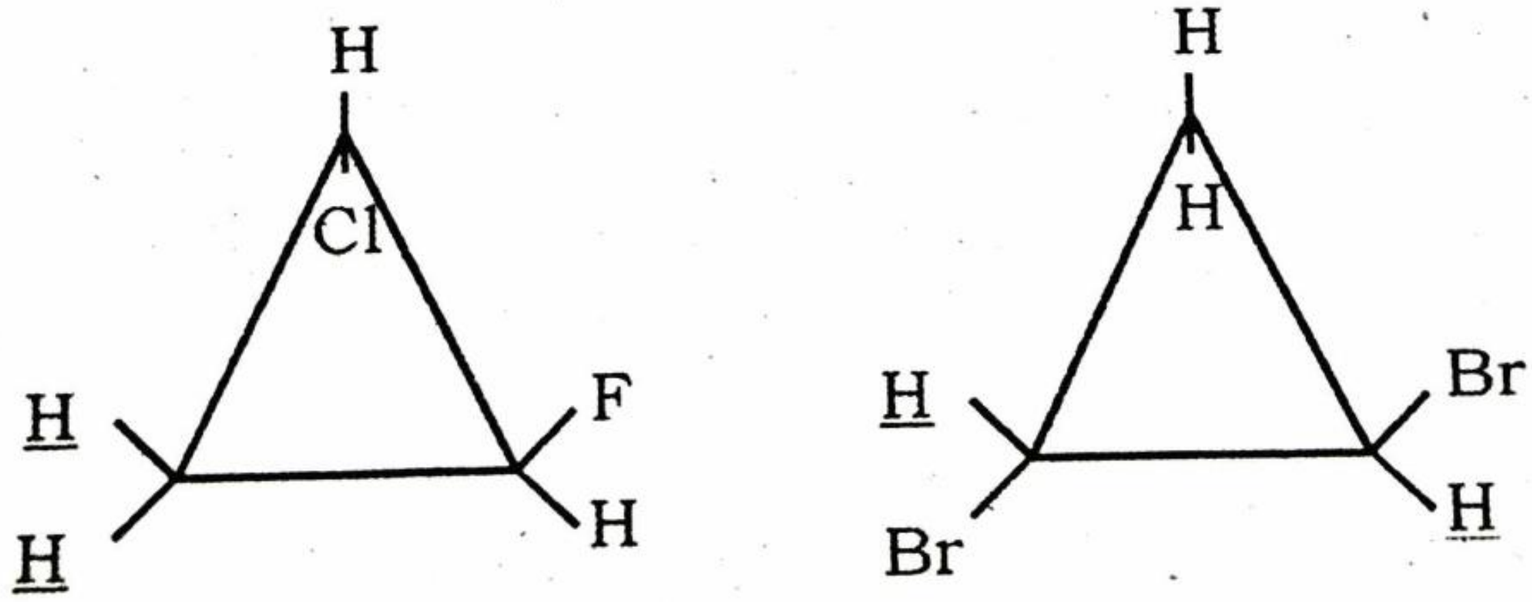
(e) Draw the (–)sc and (+) ap conformation of active butane –2, 3-diol.

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



(g) 3, 5 - Dimethyl - 4 - nitro aniline is a stranger base than the corresponding 2, 6 dimethyl isomer — Explain.

(h) Assign topical relationship between the underlined hydrogen atoms.

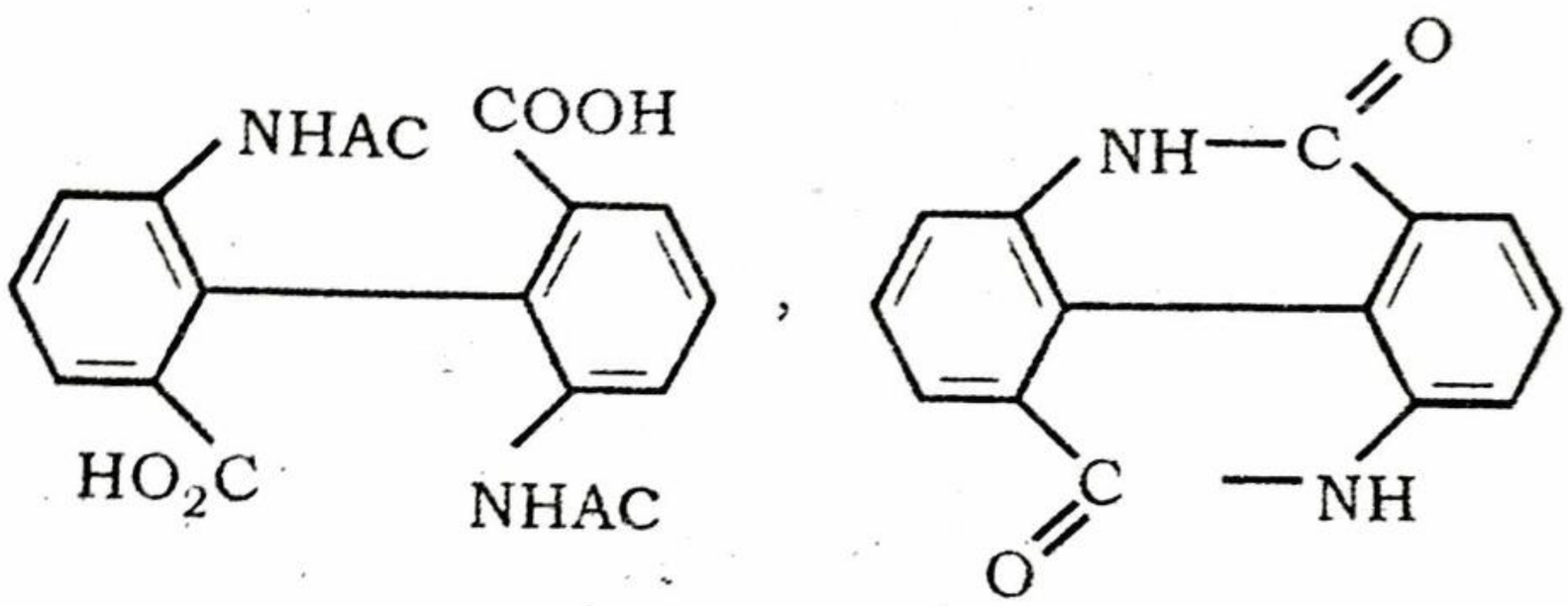


Group-B

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)



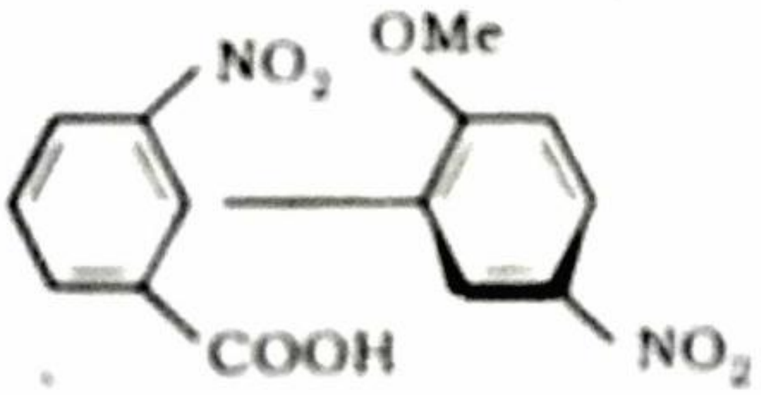
3. (a) The observed order of basicity of aminos in aqueous medium is $Me_2NH > MeNH_2 > Me_3N$, whereas in gas phase the order is $Me_3N > Me_2NH > MeNH_2$ — Explain with reason.

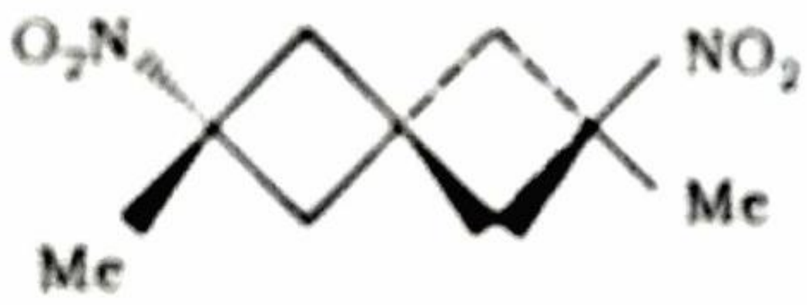
(b) *R* Br reacts with AgCN to produce R – Nc, but it reacts with NaCN to produce R – CN – why ? 3+2

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.

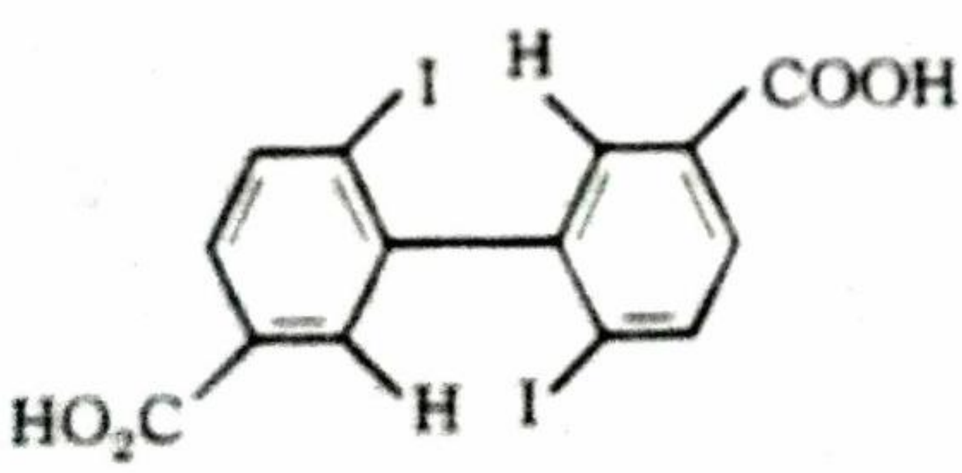
(b) The rate of reaction of 1-bromobutane with azide ion increased 5×10^3 times on changing the solvent from methanol to acetonitrile — Explain. 3+2

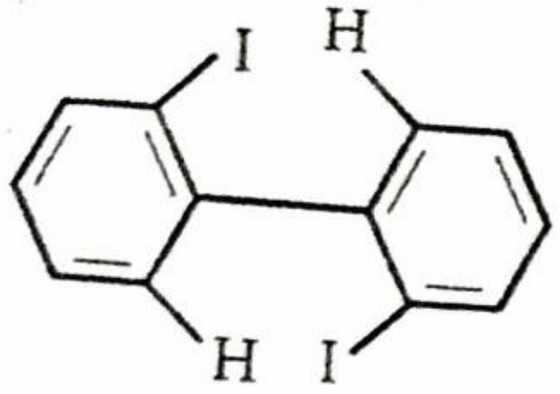
5. (a) **Assign R/S nomen calture of the followings :**

(i) 

(ii) 

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

(i) 

(ii) 

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

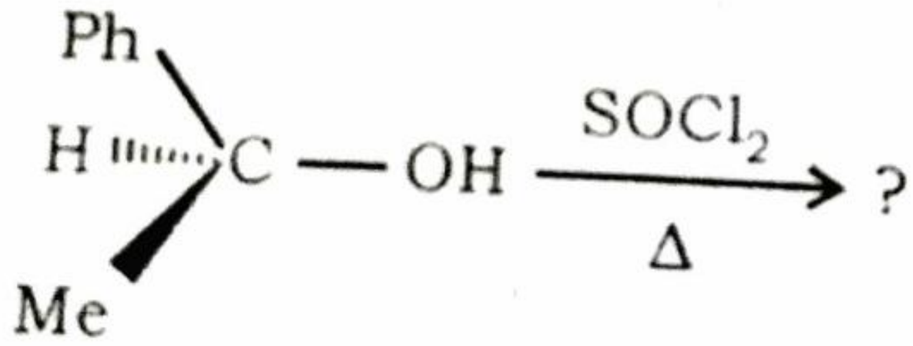
6. (a) Draw the potential energy diagram of 1-bromopropane.

(b) Write one difference between torsional angle and diheoirel angle.

(c) What do you understand by the term "Walden Inversion" ?

2+2+1

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 in distingushable E_2 pathway?

3+2

Group-C

Answer any *one* question. 1×10

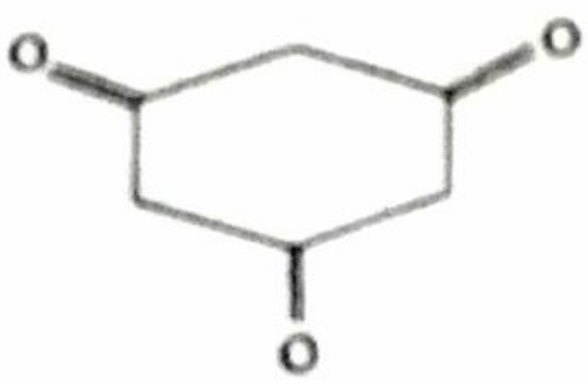
8. (a) Unsymmetrically substituted cumulenes with odd number of double bonds cannot show chirality, rather these can show geometrical isomerisis—Explain.

(b) Arrange in the increasing order of nucleophilicity.

$\overset{\ominus}{O}C_2H_5$, $\overset{\ominus}{O}C_6H_5$, $CH_3\,\overset{\ominus}{C}O$, $N\overset{\ominus}{O}_3$

(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 ?



and

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

2+2+3+1+2

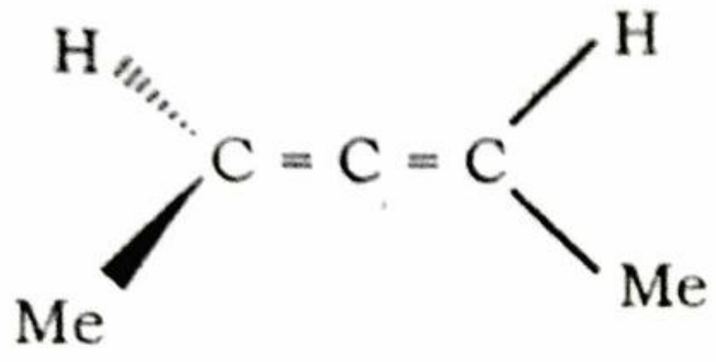
9. (a) Draw the most stable configuration of the following compounds

(i) 2-amino ethanol (ii) 1, 2-dichloroethane

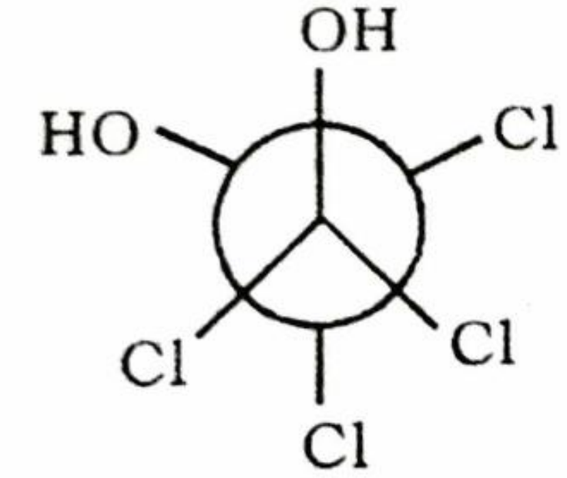
(b) What is phase transfer catalyst ?

(c) Assign configuration of the following compounds with P/M descriptors

(i)



(ii)



(d) Define pseudoasymmetric centre. Give example of 2 molecules with enantiomorphic 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.

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