U.G. 2nd Semester Examination - 2021

CHEMISTRY

[HONOURS]

Course Code : CHEM-H-CC-T-04

(Organic Chemistry)

Full Marks : 20 Time : 1 Hour

The figures in the right-hand margin indicate marks.

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

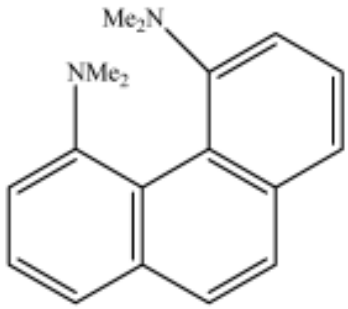
1. Answer any ***five*** questions from the following. 1×5=5

   a. Why does $H_2C=C(CH_2OH)C(F)=CH_2$ exist preferably in *s-Cis* conformation?

   b. Write down the most stable conformation of 1,2-difluoroethane.

   c. Give an example of valence tautomerism.

   d. Why does the following compound act as a proton sponge?



   e. How does a substitution, that involves intermediacy of a pyramidal radical, give rise to racemisation?

   f. KF reacts with propyl bromide only in presence of 18-crown-6. Explain.

   g. Why does higher temperature favour E2 over S_N2 reaction?

   h. What is the source of chirality of the following compound?

2. Answer any ***one*** questions from the following. 5×1=5

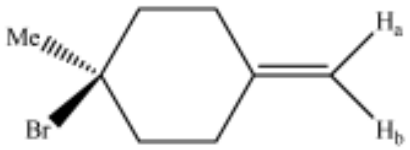
   a. i. *Meso* 2,3-dichlorobutane is optically inactive despite having chiral conformers. Explain.

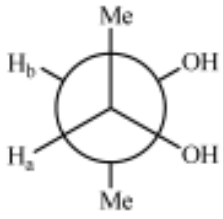
   ii. $(Me_3CO)_3CH$ exists almost exclusively in the keto form. Explain.

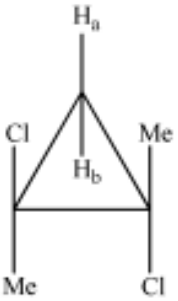
   iii. How can you convert *S*-1-phenylethanol into *S*-1-phenylethyl chloride?

   2+2+1

   b. i. Find out the topic relationship between H_a and H_b in the following compounds. (any two).

i. 

ii. 

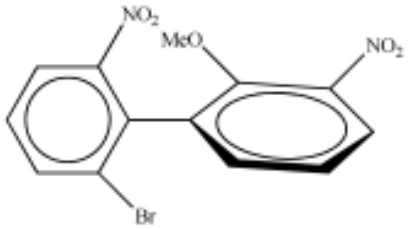
iii. 

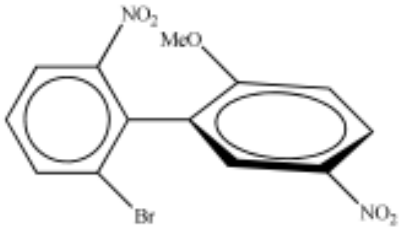
ii. Both the diastereomers of $PhCH(Me)CH(NMe_3)^+Ph$ give the same alkene as the major product when subjected to base catalysed elimination. Explain.

iii. Compare the basicity of 4-chlorophenol and 4-fluorophenol with reasons.

2 + 1½+1½

c. i. Which of the following compounds will undergo racemisation at a faster rate? Explain your choice.





ii. Hydrolysis of $EtSCH_2CH(Me)Cl$ gives two products of which the unexpected product preponderates. Explain.

iii. Which type of entropy is lost during the formation of a cyclic transition state from an open chain precursor?

2+2+1

3. Answer any ***one*** question from the following. 10×1=10

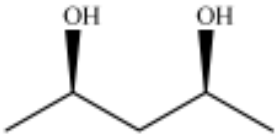
a. i. Draw an energy profile for the following reaction. Here B is the substrate and A and C are products.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$$

$k_1 > k_2$ but $(k_2/k_{-2}) > (k_1/k_{-1})$.

Identify the kinetically controlled and thermodynamically controlled products with explanation.

ii. Designate the *pro-r* and *pro-s* hydrogens in the following molecule. Also comment on the chirality of the molecule obtained by replacement of the *pro-s* hydrogen by chlorine.



iii. Isobutane undergoes bromination under photochemical conditions to furnish mainly *tert*-butyl bromide whereas chlorination of isobutane under identical conditions yields preponderantly isobutyl chloride. Explain with suitable energy profile diagram.

3+3+4

b. i. Tertiary butyl chloride undergoes S_N1 substitution and E2 elimination at a faster rate than $(CD_3)_3CCl$. Is the same type of kinetic isotope effect involved in both the cases? Explain your answer.

ii. Base catalysed dehydrobromination of (*1S, 2R*)-1-bromo-1,2-diphenylpropane furnishes *E*-1,2-diphenylpropene exclusively. Explain.

iii. What type of stereoisomerism (enantiomerism/diastereomerism) is expected for the following molecules? Explain briefly.

i. PhCH=C=C=C=C=C=CHEt ii. EtCH=C=C=CHMe

iv. In the gaseous state at 22°C, 1,2-dichloroethane contains 73% of the anti conformer but in the liquid state, the percentage of anti conformer drops to almost 50%. Offer an explanation.

3+3+2+2

c. i. Difference in acidity between benzoic acid and 4-nitrobenzoic acid is smaller than that between phenol and 4-nitro phenol. Explain.

ii. Compare the nucleophilicity and basicity of EtO^- and EtS^- with reasons.

iii. Draw an energy profile for rotation about C_2-C_3 of *active*-2,3-butanediol. Designate the conformers in terms of Klyne Prelog terminology. Comment on the relative stability of the conformers.

iv. Only 'backside' attack of the nucleophile is possible in S_N2 substitution whereas in S_E2 substitution, nucleophile can approach both from the 'front' and the 'backside'. Explain in terms of elementary molecular orbital theory. 2+2+4+2