

U.G. 4th Semester Examination - 2025

CHEMISTRY

[MAJOR]

Course Code : CHEM-MJ-T-4

(Organic)

[NEP-2020]

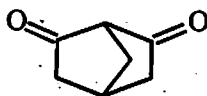
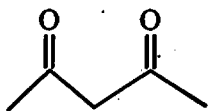
Full Marks : 40

Time : $2\frac{1}{2}$ Hours

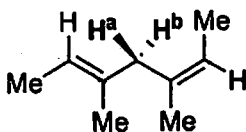
*The figures in the right-hand margin indicate marks.
Candidates are required to give their answers in their
own words as far as practicable.*

1. Answer any five questions : 2×5=10

- a) 2, 6-di-butylpyridine is a specific proton Scavenger—explain.
- b) What is Valence tautomerism? Mention the higher *enol-content* of the following:

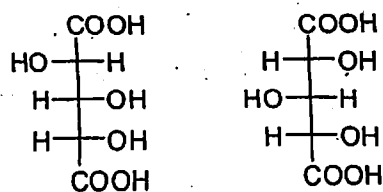


- c) Designate the marked hydrogens as *pro-R* or *pro-S*:

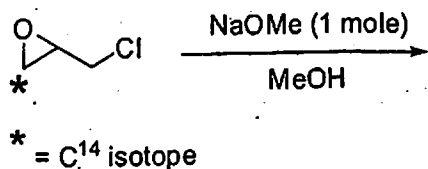


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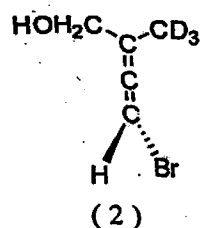
- d) Oxidation of isopropanol with chromic acid shows huge primary kinetic isotope effect. What information can you get regarding the mechanism of this conversion?
- e) Explain the role of Li^+ ion in LiAlH_4 mediated reduction of carbonyl compounds. What is the nucleophile involved in this reaction?
- f) Label the C-3 carbon atom of the following compounds in terms of chirotopicity and stereogenicity:



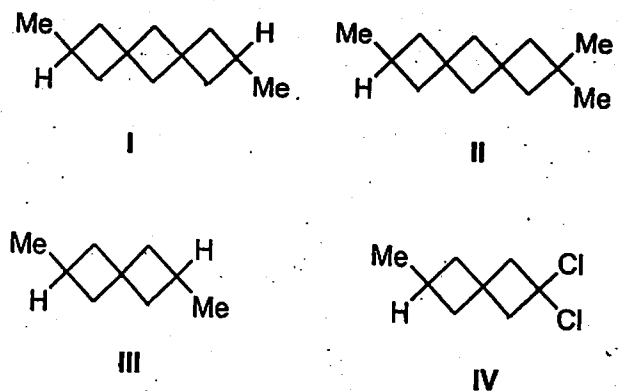
- g) Predict the product and give mechanism:



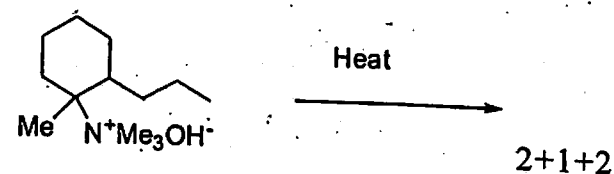
- h) The following compound is found to be optical active inspite the absence of chiral centre, why? What is the absolute configuration of it?



2. Answer any **two** questions : 5×2=10
- a) i) Comment on the optical activity of the following spiro-compounds with reason:

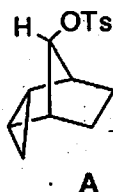


- ii) Give one example of a molecule containing pseudo asymmetric centre.
- iii) Write down all the possible products in the following reaction and indicate the major product among them with explanation:



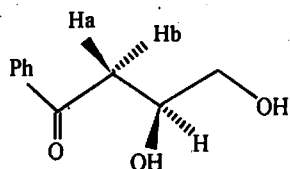
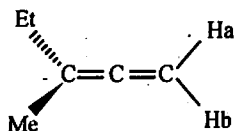
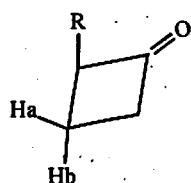
- b) i) Considering the sulphonation reaction of naphthalene as an example, explain KCP and TCP with suitable energy profile diagrams.

- ii) Compound A undergo acetolysis reaction 10^{11} time faster than compound B explain:

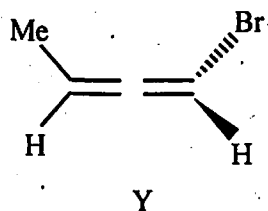
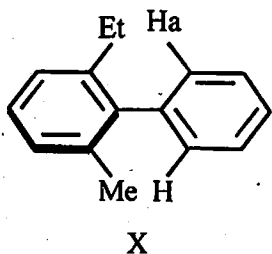


3+2

- c) i) Designate the marked atoms in the following compounds by homotopic, enantiotopic or diastereotopic relationship with reason:



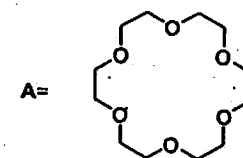
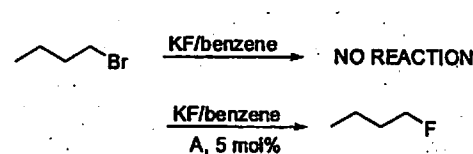
- ii) Assign R/S description for the following compounds:



3+2

- d) i) The reaction rate of MCl with NaN_3 at 0°C increased 4.5×10^4 fold on changing the solvent from MeOH to DMF —explain.

- ii) Account for the following observations:



- iii) In gaseous state at 22°C , 1,2-dichloroethane contains 73% anticonformer while in liquid state anti and gauche conformations are equally populated—explain.

$$1\frac{1}{2} + 2 + 1\frac{1}{2}$$

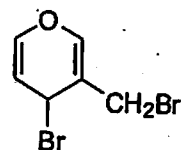
3. Answer any two questions:

$$10 \times 2 = 20$$

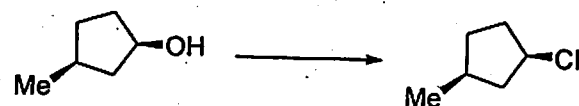
- a) i) The *threo*-isomer of 1-bromo-1,2-diphenylpropane undergoes base-induced dehydrobromination at a much faster rate than *threo*-isomer. Give explanation.
- ii) First pK_a of maleic acid lower than that of fumaric acid, however second pK_a of fumaric acid is lower than that of maleic acid. Justify.

iii) Give one example in each for an alkene having *Re-Si* face and *Re-Re* faces.

iv) Predict the bromine atoms in terms of S_N1 reactivity:



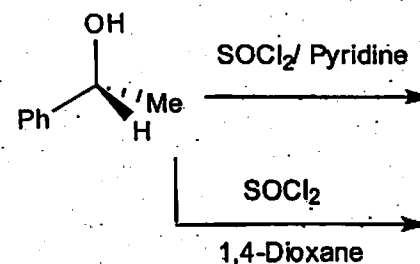
v) Carry out the following conversion and give mechanism.



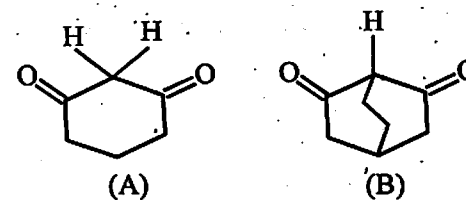
4+2+1+1+2

b) i) *Cis*-isomer of 3-bromocyclohexanecarboxylic acid in presence of NaOH gives the elimination products, however the *trans*-isomer of it gives a facile nucleophilic substitution product. Briefly discuss this observation with mechanism.

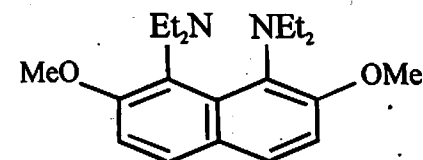
ii) Write down the product with stereochemistry:



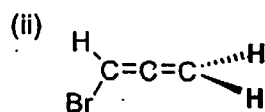
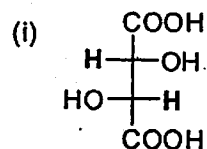
iii) In aqueous alkali cyclohexane-1,3-dione (A) is readily soluble while bi-cyclo-[2,2,2]-octane-2,6-dione (B) is poorly soluble—why?



iv) Why the following compound shows unexpected basicity?

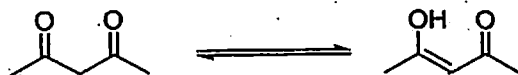


- v) Find topicity of the marked H's of the following compounds:



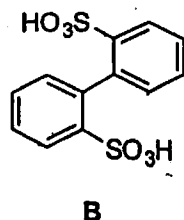
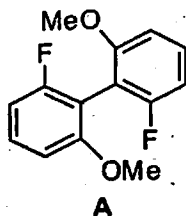
2+2+2+2+2

- c) i) The keto-enol composition of acetyl acetone is found to vary with different solvents. Deduce the following results:

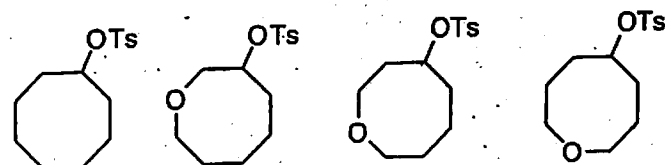


Gas phase:	8%	92%
In Hexane:	8%	92%
In CH ₃ CN:	42%	58%
In H ₂ O:	85%	15%

- ii) Front side attack of nucleophile is not favourable in S_N2 process. Explain with FMO approach.
- iii) Define buttressing effects. Biphenyl A is non-resolvable while the compound B is resolvable, explain.



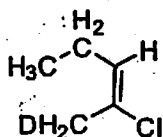
- iv) 2,3-Dibromobutane on treatment with KI gives mainly trans 2-butene rather than cis-2-butene—explain.
- v) Arrange the following tosylates in order of increasing rate of hydrolysis. Give reasons:



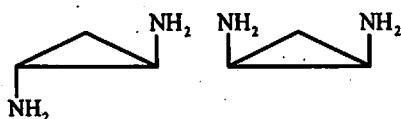
3+2+1+2+2

- d) i) State and explain Hammond postulate.
- ii) Nitration of benzene shows $k_H/k_D = 1.0$ With C₆H₆ and C₆D₆ respectively. What information you obtain from this data? Suggest mechanism with rate law for this reaction.
- iii) What is the stereoelectronic condition E2 elimination? Give one example of α -elimination reaction.

- iv) Indicate the (pro)²-chiral & pro-chiral centre of the following:



- v) Which of the following is a stronger base and why?



- vi) Account for the fact that in DMSO the order of reactivity of halide ions with methyl bromide is $F^- > Cl^- > Br^- > I^-$ which is opposite to their observed rate in methanol solution. 2+2+2+1+1+2