

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 2nd Semester Examination, 2019



CEMACOR04T-CHEMISTRY (CC4)

Time Allotted: 2 Hours

Full Marks: 40

The figures in the margin indicate full marks.

Candidates should answer in their own words and adhere to the word limit as practicable.

All symbols are of usual significance.

Answer any three questions taking one from each unit

Unit-I

 $2 \times 2 = 4$ 1. (a) Define the following terms with suitable example(s). (ii) Thorpe-Ingold effect. (i) Buttressing effect (b) Define chiral (stereo) axis and illustrate it with suitable examples in allene and 3 biphenyl system. (c) Draw all possible stereoisomers of the compound [A] and write the relationship 3 (enantiomer/diastereomer) among them. $CH_3CH = CH - CH_2CH(OH)CH_3$ (A) (d) Indicate the topicity of the ligands and/or faces as directed for the following 3 examples. (ii) pro-S H and Si face of butanone. (i) pro-S and pro-E Hs of 1-butene 2. (a) Give the proper designation R/S of following spiro-compounds: 2 (i) NH2 3 (b) Draw the most populated conformer of the following molecules. Account for your choice. (iii) ethylene glycol (ii) 1, 2-dibromoethane (i) ethyl chloride 3 (c) Identify the encircled hydrogens as homotopic, enantiotopic, or diastereotopic in the following molecules. HO

(iii)

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- (d) What is torsion angle? Why is it distinct from dihedral angle? Draw M-gauche butane and give its conformational descriptor in Klyne-Prelog terminology.
- (e) Draw the s-cis and s-trans conformations of (3Z, 5Z)-4,5-dimethyl-3,5-octadiene.

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Unit-II

- 3. (a) Addition of HBr to 1,3-butadiene yields 1,2-addition product at low temperature whereas at higher temperature yields 1,4-addition product. Draw the mechanism and energy profile of these reactions. Explain the terms "kinetically controlled" and "thermodynamically controlled" reaction in connection with the above reactions.
 - (b) Compare the acidity of the following compounds

 COOH

 Ph

 CN (b)

 OH and

 Ph

 OH

 and
 - (c) Hydrolysis of methyl bromide is accelerated in the presence of sodium iodide.

 Explain with energy profile.
 - (d) Illustrate with an example the application of primary kinetic isotope effect study in establishing the rate determining step of a reaction mechanism.
 - (e) Which one of the following pairs of compounds has higher enol content? 2

 Explain.

(a)
$$\bigcirc$$
 and \bigcirc (b) \bigcirc and \bigcirc OEt

- 4. (a) Identify the alkane in each of the following pairs that has the lower carbon-carbon bond dissociation energy (BDE) and explain the reason for your choice:
 - (i) Ethane and propane (ii) Propane and isobutane
 - (b) What is Hammond's postulate? Apply this postulate to determine the orientation of chlorination and bromination of isobutene.
 - (c) Arrange with increasing basicity with explanation in each case.

(i)
$$NH_2$$
 NH_2 NH_2 and NH_3

$$(ii) \qquad \bigcap_{NH_2} \quad ; \quad \bigcap_{N} \quad \text{ and } \quad \bigcap_{N}$$

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(d) Explain the following observations with proper mechanism and energy profile.

$$\begin{array}{ccc} \text{Me}_3\text{CCl} & \xrightarrow{\text{Hydrolysis}} & \text{Me}_3\text{COH} & + & \text{HCl} \\ (\text{CD}_3)_3\text{CCl} & \xrightarrow{\text{Hydrolysis}} & (\text{CD}_3)_3\text{COH} & + & \text{HCl} \\ \end{array}$$

(e) What is valence tautomerism? Describe with an example.

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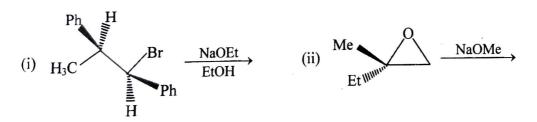
Memorial C

Unit-III

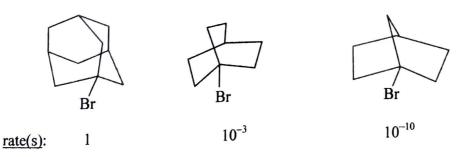
- 5. (a) Account for the fact that allylic bromination of 1-hexene by NBS gives two products. Which one is major product and why?
 - (b) Write the expected substitution product(s) for each reaction and predict the mechanism by which each product is formed.

(c) Predict the product with proper configuration.

 $1\frac{1}{2} \times 2 = 3$



- (d) Explain why Grignard reagent could not be formed from 1,2-dibromoethane.
- (e) The relative rates for solvolysis of the following compounds in 80% ethanol at room temperature are as follows:



How could you explain the observation?

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- 6. (a) Consider the following statements in reference to S_N1, S_N2, E1 and E2 reactions of haloalkanes. To which mechanism(s) if any, does each statement apply?
 (i) Involves inversion of configuration at the site of substitution.
 (ii) Is greatly accelerated in protic solvents of increasing polarity.
 (iii) Is first order in haloalkane and first order in base.
 (iv) Order of reactivity of haloalkanes is 3° > 2° > 1°.
 (b) Which of the two substrates gives better yield of 1-alkene and why?
 3
 (i) MeCH₂CMe₂ OR (ii) MeCH₂CMe₂ Br
 - [A] [B]

 (c) Bromination is more selective than chlorination of 2-methylpropane:
 - —Explain with reason.

 (d) Which one is more nucleophilic and why? [any two]

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(i) RO⁻ and RCOO⁻ (ii) NH₃ and H₂O (iii) NH₃ and NH₂NH₂
(e) Write a mechanism for the hydrolysis of the nitrogen mustard bis(2-chloroethyl) 2 methylamine [ClCH₂CH₂N(Me)CH₂CH₂Cl].

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