



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.*

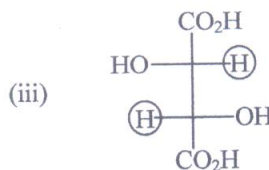
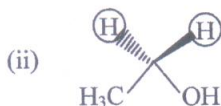
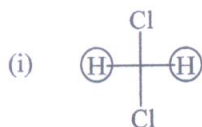
Answer any three questions taking one from each unit

Unit-I

1. (a) Define the following terms with suitable example(s). 2×2=4
 - (i) Buttressing effect (ii) Thorpe-Ingold effect.
 - (b) Define chiral (stereo) axis and illustrate it with suitable examples in allene and biphenyl system. 3
 - (c) Draw all possible stereoisomers of the compound [A] and write the relationship (enantiomer/diastereomer) among them. 3

$$\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$$

(A)
 - (d) Indicate the topicity of the ligands and/or faces as directed for the following examples. 3
 - (i) *pro-S* and *pro-E* **Hs** of 1-butene (ii) *pro-S* **H** and **Si face** of butanone.
2. (a) Give the proper designation R/S of following spiro-compounds: 2
 - (i)
 - (ii)
- (b) Draw the most populated conformer of the following molecules. Account for your choice. 3
 - (i) ethyl chloride (ii) 1, 2-dibromoethane (iii) ethylene glycol
- (c) Identify the encircled hydrogens as homotopic, enantiotopic, or diastereotopic in the following molecules. 3

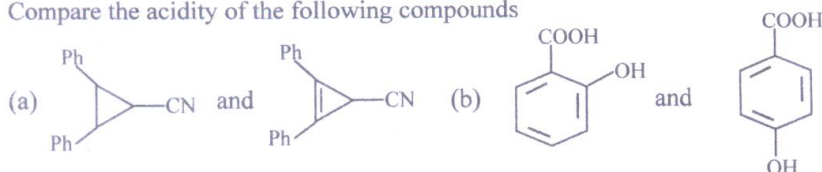


- (d) What is torsion angle? Why is it distinct from dihedral angle? Draw *M*-gauche butane and give its conformational descriptor in Klyne-Prelog terminology. 3
- (e) Draw the *s-cis* and *s-trans* conformations of (3*Z*, 5*Z*)-4,5-dimethyl-3,5-octadiene. 2

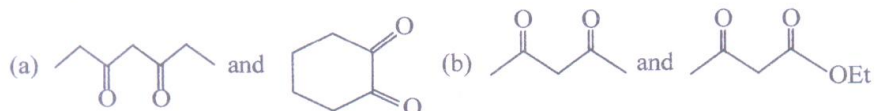
Unit-II

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. 4

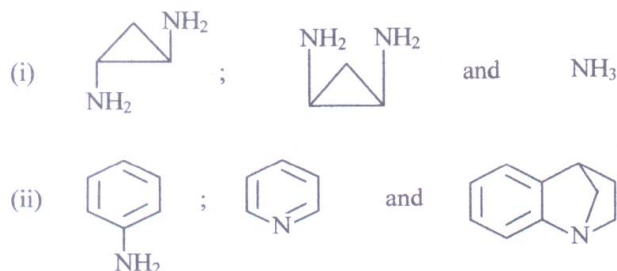
- (b) Compare the acidity of the following compounds 3



- (c) Hydrolysis of methyl bromide is accelerated in the presence of sodium iodide. Explain with energy profile. 3
- (d) Illustrate with an example the application of primary kinetic isotope effect study in establishing the rate determining step of a reaction mechanism. 2
- (e) Which one of the following pairs of compounds has higher enol content? — Explain. 2

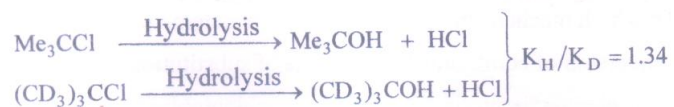


4. (a) Identify the alkane in each of the following pairs that has the lower carbon-carbon bond dissociation energy (BDE) and explain the reason for your choice: 2
- (i) Ethane and propane (ii) Propane and isobutane
- (b) What is Hammond's postulate? Apply this postulate to determine the orientation of chlorination and bromination of isobutene. 1+2
- (c) Arrange with increasing basicity with explanation in each case. 4



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

3



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

2

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?

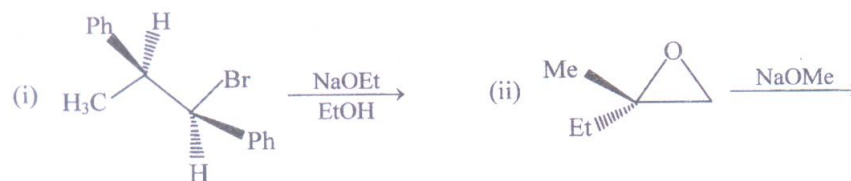
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(b) Write the expected substitution product(s) for each reaction and predict the mechanism by which each product is formed.

3



(c) Predict the product with proper configuration.

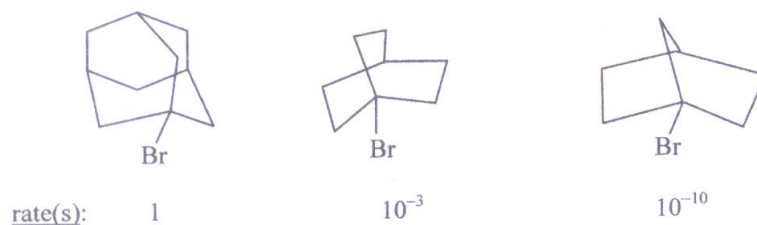
 $1\frac{1}{2} \times 2 = 3$


(d) Explain why Grignard reagent could not be formed from 1,2-dibromoethane.

2

(e) The relative rates for solvolysis of the following compounds in 80% ethanol at room temperature are as follows:

3



How could you explain the observation?

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? 4
- Involves inversion of configuration at the site of substitution.
 - Is greatly accelerated in protic solvents of increasing polarity.
 - Is first order in haloalkane and first order in base.
 - Order of reactivity of haloalkanes is $3^\circ > 2^\circ > 1^\circ$.
- (b) Which of the two substrates gives better yield of 1-alkene and why? 3
- $$\text{MeCH}_2\text{CMe}_2 \xrightarrow{\text{NMe}_3\text{I}^\oplus}$$

[A]

OR

$$\text{MeCH}_2\text{CMe}_2 \xrightarrow{\text{Br}}$$

[B]
- (c) Bromination is more selective than chlorination of 2-methylpropane: 2
—Explain with reason.
- (d) Which one is more nucleophilic and why? [**any two**] 2
- (i) RO^- and RCOO^-

(ii) NH_3 and H_2O

(iii) NH_3 and NH_2NH_2
- (e) Write a mechanism for the hydrolysis of the nitrogen mustard bis(2-chloroethyl) methylamine $[\text{ClCH}_2\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{Cl}]$. 2

—x—