

U.G. 2nd Semester Examination - 2020

CHEMISTRY

[HONOURS]

Course Code : CEMH/CC-T-04

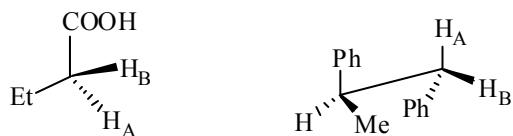
(Organic Chemistry)

Full Marks : 40

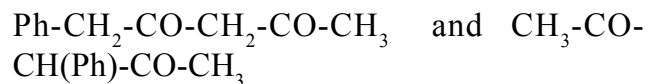
Time : 2½ Hours

*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) Identify pro-S and pro-R hydrogen atoms in the following molecules:



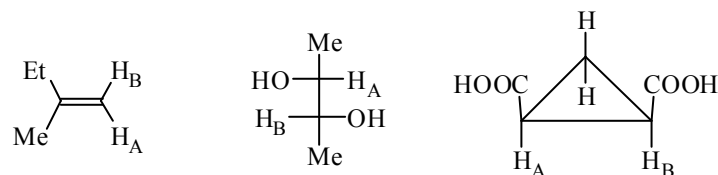
- b) Indicate the pro-R methyl group and Re-face in isobutyraldehyde.
- c) Which one has higher enol content of the following compounds and why?



- d) What are the electrophilic and nucleophilic catalysts? Give one example of each.
- e) E-2 elimination of 2-bromobutane with NaOEt in EtOH yields 19% of 1-butene whereas same NaOEt in t-BuOH increases the yield of 1-butene to 38%. Explain.
- f) Which one will react faster in S_N1 reaction CH₂=CHCH₂Cl or Ph₃C-Cl and why?
- g) CH₃CH=CHCH₂-Cl and CH₃-CH(Cl)-CH=CH₂ give same product when treated with diethylamine. Give the structure of the product and explain its formation.
- h) Draw the most stable conformation of 1,2-dibromoethane and ethylene glycol – justify your answer.

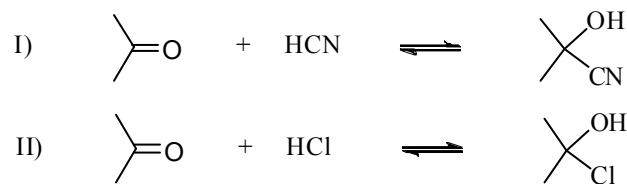
2. Answer any **two** questions: 5×2=10

- a) i) Identify H_A and H_B in each of the following structures as homotopic, enantiotopic or diastereotopic ligands and explain.



[Turn Over]

- ii) Predict configuration of products when pro-R hydrogen of propanal is replaced by Br and CN⁻ is attacked from the Re-face of propanal. 3+2
- b) i) Draw the energy profile diagram of a two-step exothermic reaction, activation energy of the 1st step is greater than that of 2nd step but the 2nd step is rate determining step. Justify your drawing.
- ii) 2,4,6-trinitro-N,N-dimethylaniline is 4x10⁴ times stronger base than 2,4,6-trinitroaniline – explain. 3+2
- c) i) Calculate ΔH° for the following two reactions from the bond dissociation energy data provided and identify with reasoning which one is preferred thermodynamically.

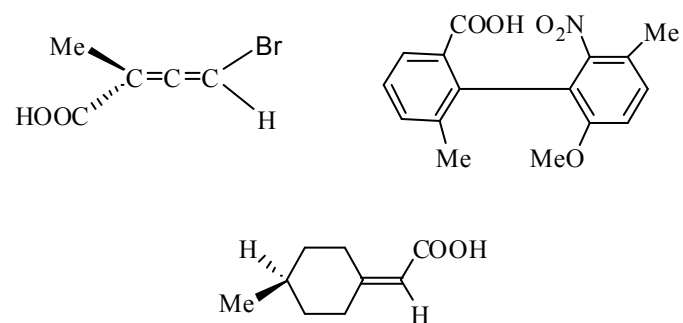


BDE (kcal/mole) : H-Cl (103), H-CN (130), C-Cl (84), C-CN (122).

- ii) Arrange the following compounds in order of increasing basicity in aqueous medium and explain. Methyl amine, dimethyl amine and trimethyl amine 3+2
- d) i) What is meant by primary kinetic isotope effect? Explain with an example. How this effect can be used in investigation of reaction mechanism?
- ii) Acetylacetone shows 15% enol content in water whereas 92% enol content in *n*-hexane. – explain. 3+2

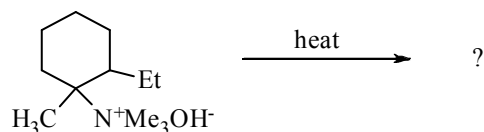
3. Answer any **two** question: 10×2=20

- a) i) Assign R/S descriptor to the following compounds:



ii) Suppose **A** and **B** can react at a certain temperature to give **C**, the rate controlled product. At a higher temperature, they react to give **D**, the thermodynamic controlled product. Explain this behaviour using an energy profile diagram.

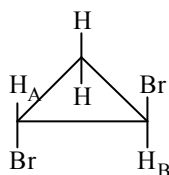
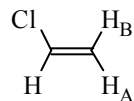
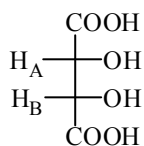
iii) Give the structure of all possible alkenes that could form in the following reaction. Indicate the major product and explain its formation.



iv) Define pseudoasymmetric centre.

3+3+3+1

b) i) Identify H_A and H_B in each of the following structures as homotopic, enantiotopic or diastereotopic ligands and explain.



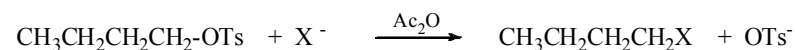
ii) Explain the following reactions with plausible mechanism and give the structure of **A** and **B**.



iii) The substitution reaction of $\text{EtSCH}_2\text{CH}_2\text{Cl}$ with ethanol proceeds at a rate many fold faster than the similar reaction of $\text{EtOCH}_2\text{CH}_2\text{Cl}$. Explain.

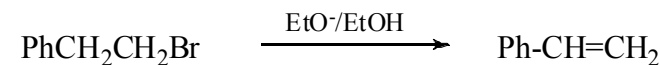
iv) Salicylic acid is much stronger than *p*-hydroxybenzoic acid but acidity of *o*-nitrophenol and *p*-nitrophenol is almost same – explain. 3+3+2+2

c) i) Explain the following observation:



In the above reaction the order of nucleophilicity for the various halides is $\text{I}^- > \text{Br}^- > \text{Cl}^-$ when LiX is used, but the order is $\text{Cl}^- > \text{Br}^- > \text{I}^-$ when $\text{Bu}_4\text{N}^+\text{X}^-$ is used.

ii) Write the E-2 and E-1cb mechanism of the following reaction:



Which mechanism is actually operative? Give evidence in favour of your answer.

- iii) Bromination of propane under photochemical condition is regioselective while chlorination is not. Explain on the basis of Hammond postulate.
- iv) Give an example of a molecule with enantiomeric groups with pro-R and pro-S hydrogen atoms on a pseudoasymmetric centre. 3+3+3+1
- d) i) Draw the potential energy diagram of 2,3-butanediol for rotation around C₂-C₃ bond showing the conformations. Explain the relative stabilities of the conformers.
- ii) Chlorination (Cl₂/hν, 25°C) of isobutene produces 1-chloro-2-methylpropane and 2-chloro-2-methylpropane in the ratio 64:36, but bromination (Br₂/hν, 127°C) furnishes 1-bromo-2-methylpropane and 2-bromo-2-methylpropane in the ratio 1:99. Explain the greater selectivity of bromination reaction.
- iii) Arrange the following compounds in order of increasing acid strength and explain.
4-Nitrophenol, 2,6-dimethyl-4-nitrophenol and 3,5-dimethyl-4-nitrophenol.
- iv) Enol content of butane-2,3-dione is slightly greater than that of acyclic ketones whereas the enol content of cyclopentane-1,2-dione is much higher than that of acyclic ketones. Explain. 3+3+2+2
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