

[6]

- e) The rate of semicarbazone formation of substituted benzaldehyde shows a non-linear Hammett plot with a ρ value of +3.35 for the electron donating groups and ρ value of -4.4 for electron withdrawing groups. Explain the mechanism and find out the r.d.s. Draw the Hammett plot of this reaction taking reaction rate vs total substituent effect. 2

Ex/SC/CHEM/PG/CORE/TH/XIII-O/2023

M. Sc. (CHEMISTRY) EXAMINATION, 2023

(4th Semester)

PAPER: XIII-O

[ORGANIC CHEMISTRY SPECIAL]

Time : Two Hours

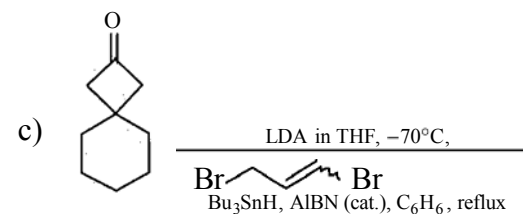
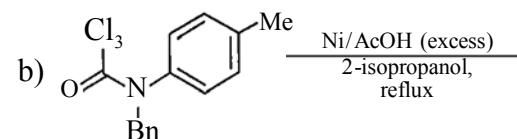
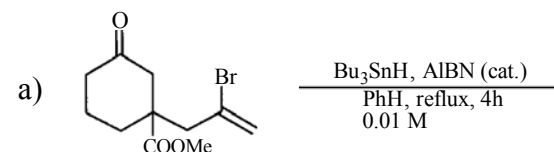
Full Marks : 40

(20 marks for each unit)

Use a separate answer script for each unit.

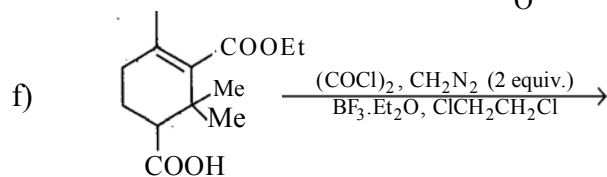
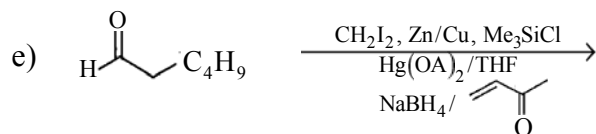
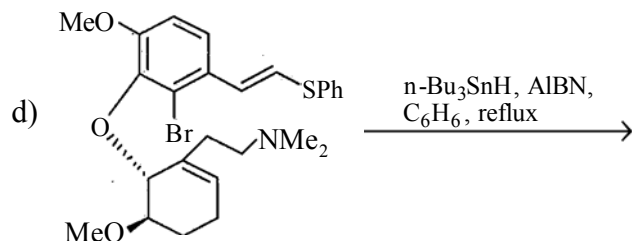
Unit: O-4131

1. Indicate the product(s) with proper stereochemistry and explain their formation with probable mechanism of the following reactions (answer *any four*): 3×4

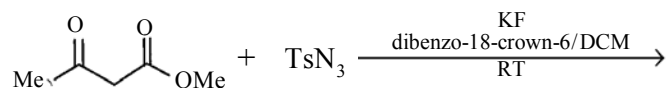


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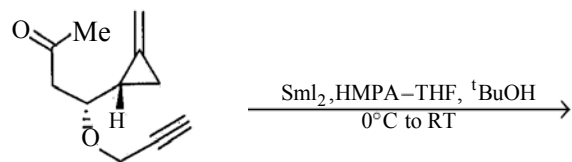
[2]



2. a) Indicate the products in the following reaction and explain with mechanism. Discuss the role of crown ether in this reaction. 2

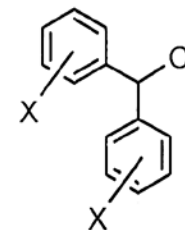


- b) Identify the major product with probable mechanism. Discuss one method of preparation of Kagan's reagent. 2+1

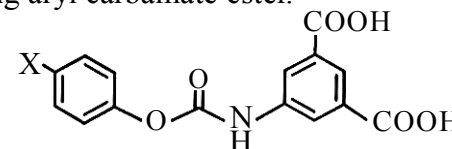


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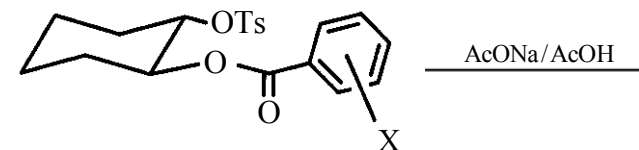
- b) Write down the Yukawa-Tsuno equation for the methanolysis reaction of the following compound. This reaction exhibits $r = 1.23$ and $\rho = -4.02$ in MeOH at 25°C. Write down the methanolysis product with suitable mechanism. 2



- c) Using a Hammett plot to explore the behavior of a catalytic antibody for the alkaline hydrolysis of the following aryl carbamate ester. 2



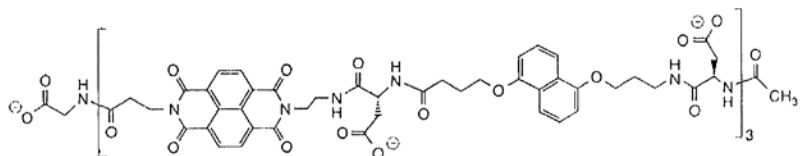
- d) The rate of acetolysis of the following *m*- & *p*-substituted compounds yield a linear Hammett plot with σ . A ' ρ ' value of -1.00 is observed. If the carbonyl oxygen is labeled with ¹⁸O and the reaction products are reduced with LiAlH₄, the obtained *trans*-1,2-cyclohexanediol retains 50% of the labeled oxygen – comment on the mechanism. 2



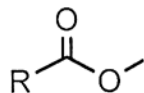
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[4]

- c) What are mechanically interlocked molecules? Write down the structure of a four wheel driven molecular car based on rotary motors. 1+2
- d) Write down the structure of a dipeptide which can self-assemble to form supramolecular nanotube in solution. The following molecule is folded in solution – explain. 1+1



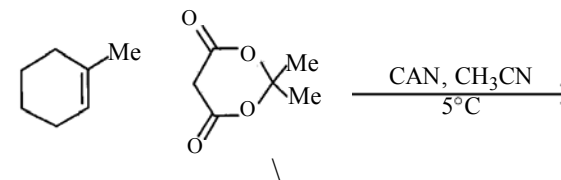
4. a) Write down the Taft equation. Predict the rate of ester hydrolysis using steric (E_S) and polar (σ^*) substituent constants of the following molecules with different R groups. 2



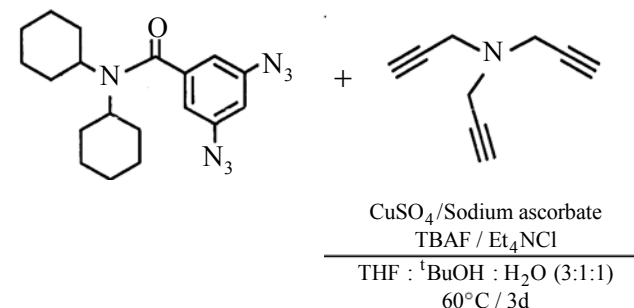
R Group	E_S	σ^*
H	1.24	0.49
CH ₃	0.00	0.00
Et	-0.07	-0.10
ⁱ Pr	-0.47	-0.19
^t Bu	-1.54	-0.30

[3]

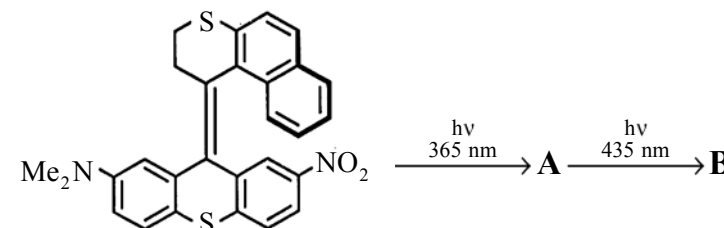
- c) Predict the products and explain with plausible mechanism. 3

**Unit: O-4132**

3. a) Write down the product of the following reaction. How will you utilize the product to capture chloride (Cl^-) using noncovalent interaction? 2+1



- b) Write down the products **A** and **B** with suitable stereochemistry. 2



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