Organic Chemistry: Endsem. 28-Feb-2023. 5pm-7pm (120 min)

- Question paper is for 100 points; as a rough guideline plan to spend 1 min per point for the length of the answer required
- This endsem is also the assignment. Submit by 06-March-2023 11:30am (handwritten only)

PART-I (40 points) All questions in this section are worth 4 points

1. (4 points) (a) Consider the n-butane molecule. Draw schematic diagram of the torsional energy of this molecule for the torsion around $C_2 - C_3$ σ bond. (b) Consider the cyclopentane molecule. Draw the stable configurations of this molecule and order them according to their stability.

2. (4 points) Discuss the various effects of the solvent on/in the various organic reactions. Illustrate with an example each.

3. (4 points) We had discussed the nucleophilic substitutions at aliphatic carbons (specifically, S_N^1 and S_N^2 mechanisms). Identify the various factors that may effect the mechanism, and write 2/3 sentences on each of the factors

4. (4 points) A very important set of examples of rearrangement involve R-N=C=O as intermediate species. Write the mechanism for one such example explicitly showing the electron-pushing scheme. Name one other such reactions, give one example (without mechanism).

5. (4 points) Ozonolysis is a common technique to identify organic compounds. Write a example reaction, illustrating the reactant, mechanism (via electron pushing diagrams) and the products.

6. (4 points) Draw the structures of the two isomers of the molecule 1-chloro 2-isopropyl cyclohexane clearly indicating the axial and equatorial substitutions. Each isomers undergo elimination reaction (of HCl molecule). Indicate the products (and expected product ratio's). Which isomer has faster rate of elimination and why?

7. (4 points) Tabulate the electrocyclic reactions on basis on the number of $\pi-$electrons involved vis-a-vis show the reaction conditions and motion required for bonding.

8. (4 points) 3,4-dimethyl hexa 1,5-diene is known to undergo pericyclic reaction; predict all the possible products and their respective yields, and the reaction conditions.

9. (4 points) What are kinetic and thermodynamic control of a reaction? Explain clearly the differences and origin of these differences. Give a real example/s which demonstrate the concept/s.

10. (4 points) Carbocations and their rearrangements to form new carbocations is important set of reactions. Give reasons/ conditions for such rearrangements, illustrate each one with a suitable example.

PART II (60 points)

11. (10 points) (a) Write a note on various types of elimination reactions with one example each indicating clearly the mechanism. (b) It is well known that elimination and substitution reactions compete with each other. Why and explain factors that determining which of the two dominates.

12. (10 points) Cannizarro reaction is the base catalysed disproportionation of aldehydes that do not have any $\alpha-$hydrogens (for ex, phenyl). Write the possible mechanism of this multistep reaction and explain each step. What are the products? Isotopic labelling has been used to figure out the mechanism of reaction; demonstrate specifically how for this reaction/s.

13. (10 points) Answer the following questions for Hammet polt/equation.
(a) (1 points) What is Hammet equation? Provide a short derivation.
(b) (2+2=4 points) Write a short note on the substituent constant, and reaction constant with examples.
(c) (5 points) The cyclodehydration of substituted 2-phenyl tri aryl methanol (see fig. 1) by 80% ethanoic acid containing 4% H_2SO_4 was briefly explainedin class as a demonstration of use of Hammet plot in a multi-step reaction; discuss with steps, the mechanism of the reaction and how Hammet plot is used to provide mechanistic insight for this reaction.

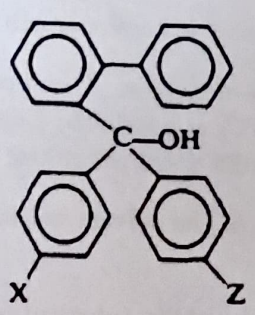
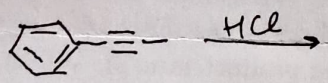


Figure 1: Substituted 2-phenyl triaryl methanol

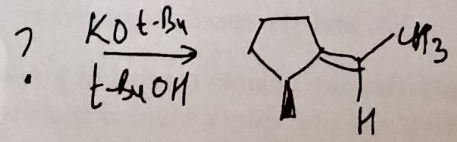
14. (6 points) Write a note on (a) electropillic addition (b) nucleophillic addition reactions indicating clearly the mechanism.

15. Answer the following questions:

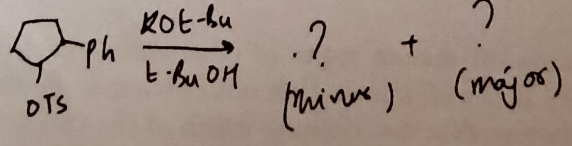
(a) (3 points) Write mechanism, reason for regioselectivity



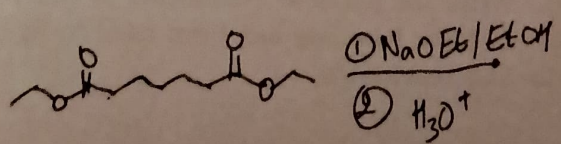
(b) (3 points) Identify reactant of the elimination reaction and clearly indicate reason



(c) (3 points) Identify major and minor products:

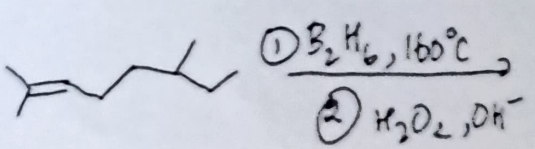


(d) (3 points) Write mechanism of Deikman condenstation reaction:

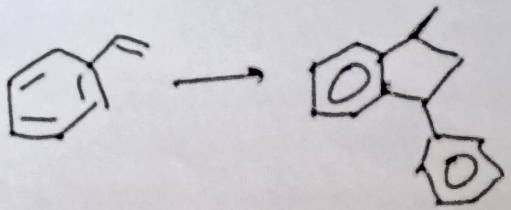


(e) (3 points) What are the products of E2 elimination reaction for 2-bromo butane. Comment on stereospecificity and stereoselectivity of the reaction.

(f) (3 points) Identify the products, show mechanism with electron pushing.



(g) (3 points) Identify mechanism of dimerisation of sterene in the below reaction; identify steps, mechanism with electron



(h) (3 points) Identify the product/s of the reaction, show mechanism