M SC DEGREE END SEMESTER EXAMINATION MAY - 2015 SEMESTER 2-M SC CHEMISTRY/ APPLIED CHEMISTRY COURSE: P2CHET06, P2CPHT06 - ORGANIC REACTION MECHANISM

Time: 3 Hours

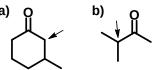
Max. Marks: 75

Section A

(Answer any ten questions, each question carries 2 marks)

1. How would you produce specific enol equivalents at the points marked with the arrows?

(not necessarily starting from the simple carbonyl compound shown)



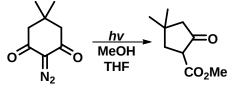
2. Explain regioselectivity in addition reactions, with special reference to Markovnikov's

addition. What are the mechanistic reasons for the selectivity?

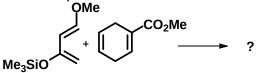
3. What is a concerted reaction? Describe the two types of concerted reaction with suitable

example.

4. Suggest a mechanism for this ring contraction.



5. Predict the structure of the product of this Diels-Alder reaction.



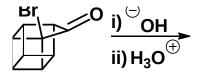
6. Briefly describe the Baldwin's rules.

7. What is **A** in the following reaction scheme and how does it react to give the final product?

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(PTO)

- 8. Describe two methods for the generation of nitrene.
- 9. Complete the following reaction with mechanism.

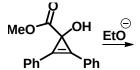


10. Write briefly on classical and non-classical carbocations.

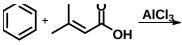
11. How will you distinguish between singlet and triplet carbenes based on their stability and

stereochemical behavior in addition reactions?

12. Complete the following reaction with mechanism.



13. Complete the following reaction and write the name of the reaction.



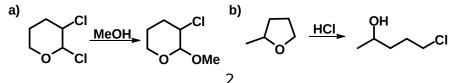
(2*10=20)

Section B

(Answer **FIVE** questions by attempting **not more than 3** questions from each of the following bunches. Each question carries 5 marks)

Bunch 1

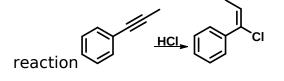
14. Draw mechanisms for these reactions, explaining why these particular products are formed.



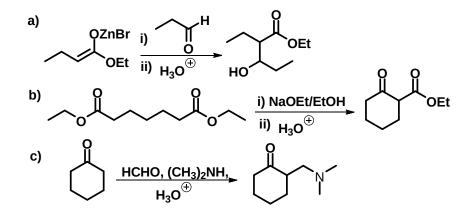
15. The aldehyde and ketone below are self-condensed with aqueous NaOH so that an unsaturated carbonyl compound is the product. Give a structure for each product and explain why you think this product is formed.

a)
$$(HO \ \underline{NaOH}_{H_2O}$$
 ? b) $(HaOH)_{H_2O}$? b) $(HaOH)_{H_2O}$?

16. The addition of HCl to 1-phenylpropyne gives predominately the *syn* product with the regiochemistry shown below. Give an explanation of what the regiochemistry and *syn* addition indicate about the mechanism of this



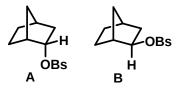
17. The following are some name reactions; give the mechanisms of these transformations showing all intermediates.



Bunch 2(Short Essay Type)

- 18. Explain the thermodynamic vs. kinetic enolates with suitable examples. What are the factors affecting the formation of thermodynamic and kinetic enolate?
- 19. What are sigmatropic reactions? Explain Cope and Claisen reactions with suitable examples. (General)

- 20. Describe the Wittig and Peterson olefination reaction with suitable example.
- 21. **A** solvolyzed \approx 350 times faster than its endo isomer **B** in acetic acid. Why? Comment on the stereochemistry of the acetylated product of **A** and **B**.



(5×5=25)

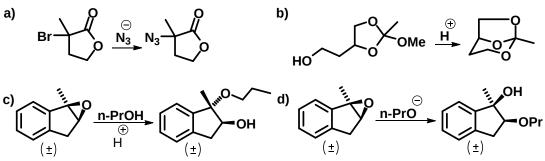
Section C

(Answer any two questions, each question carries 15 marks)

- 22. Describe the following named reaction with one suitable example.
 - a) Claisen,
 - b) Dieckmann,
 - c) Knoevenagel,
 - d) Stobbe, and
 - e) Darzen

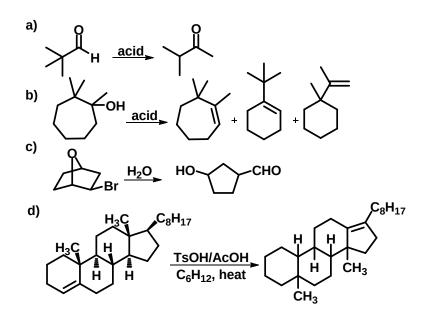
23. Write the mechanism for the following conversion and state with reasons whether these

reactions will be either $S_N 1$ or $S_N 2$.



24. Draw mechanisms for each of the following reactions involving rearrangements. In the last

example (d) predict the stereochemistry.



25. Write briefly on the molecular rearrangements involving nitrene intermediates, with special

reference to Hofmann, Curtius, Lossen and Beckmann rearrangements. Discuss the

stereochemical preferences in Beckmann rearrangement.

 $(15 \times 2 = 30)$
