

**M.Sc. DEGREE END SEMESTER EXAMINATION APRIL 2016**  
 SEMESTER -2: **CHEMISTRY (Pure & Applied)**  
 COURSE: **P2CHET06-P2CPHT06 - ORGANIC REACTION MECHANISM**  
*(Common for Regular- 2015 Admission /Supplementary-2014 Admission)*

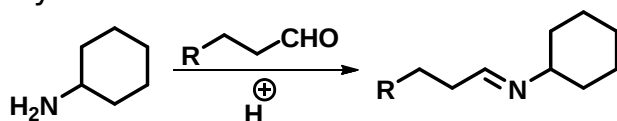
Time: Three Hours

Maximum Marks: 75

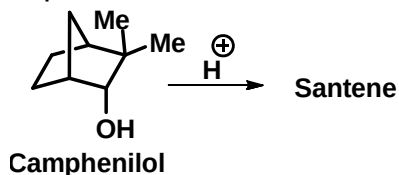
**SECTION A**

(Answer any **10** questions, Each question carries **2** marks)

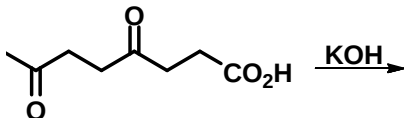
1. Draw a mechanism for the formation of the imine from cyclohexylamine and the following aldehyde.



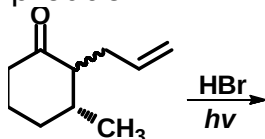
2. Describe Sommelet-Hauser rearrangement with suitable example.  
 3. Describe the Markovnikov's and anti-Markovnikov's rule for addition reaction with suitable example.  
 4. Write the structure of the product and the name of the reaction.



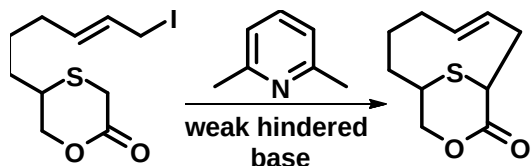
5. What is auto-oxidation? Illustrate with examples.  
 6. Complete the following reaction and name the reaction.



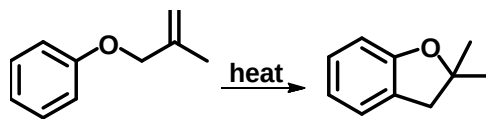
7. Describe Cannizzaro reaction with suitable example.  
 8. Predict the structure of the product.



9. What are carbenes? Explain the two types of carbenes briefly.  
 10. Suggest a mechanism for this formation of a nine-membered ring.  
 (Note: The weak hindered base is not strong enough to form an enolate from the lactone.)



11. Predict the mechanism for the following reaction and name the reaction.



12. What are free radicals? Describe the generation and stability of free radicals.
13. Describe in brief the  $S_Ni$  mechanism with suitable example.

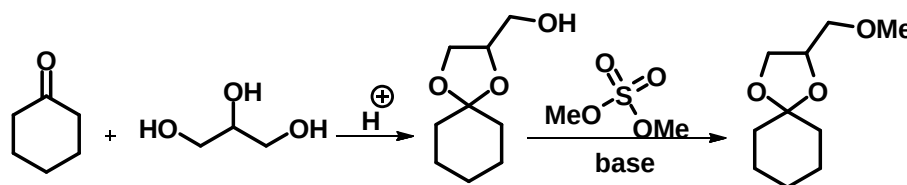
(2 × 10 = 20)

### SECTION B

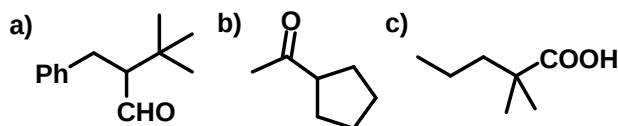
(Answer 5 questions by attempting not more than 3 questions from each of the following bunches. Each question carries 5 marks)

#### Bunch 1

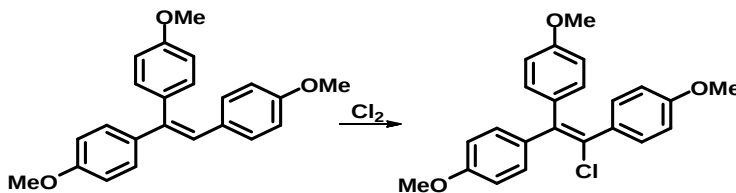
14. Draw mechanisms for the following reactions. Why were acidic conditions chosen for the first reaction and basic conditions for the second?



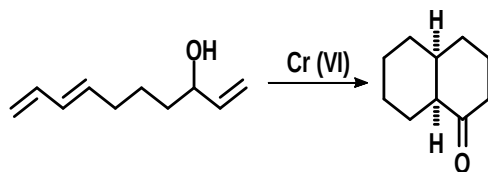
15. Suggest how the following products might be made using enol or enolate alkylation as at least one step. Explain your choice of specific enol equivalents.



16. Chlorination of this triarylethylene leads to a chloro-alkene rather than a dichloroalkane. Suggest a mechanism and an explanation.



17. This unsaturated alcohol is perfectly stable until it is oxidized with  $Cr(VI)$ ; it then immediately cyclizes to the product shown. Explain.



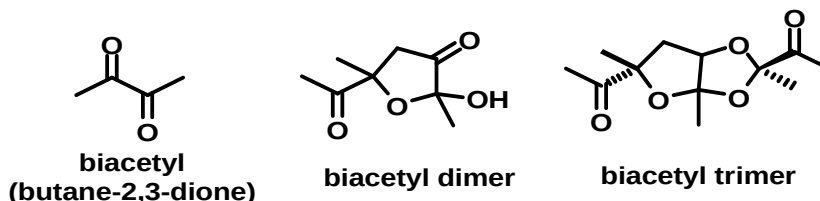
### Bunch 2 (Short Essay Type)

18. Show, by construction of both a transition state orbital array and an orbital symmetry correlation diagram, which of the following electrocyclisations are allowed.
  - a. disrotatory cyclization of the pentadienyl cation to the cyclopent-2-enyl cation.
  - b. disrotatory cyclization of the pentadienyl anion to the 3-cyclopentenyl anion.
19. Methylcyclopropane shows strikingly different reactivity toward chlorine and bromine under radical chain conditions in  $\text{CH}_2\text{Cl}_2$  solution. The main product with chlorine is chloromethylcyclopropane (56%), along with smaller amounts of 1,3-dichlorobutane and 1,3-dichloro 2-methylpropane. Bromine gives only 1,3-dibromobutane. Offer a mechanistic explanation.
20. a) Explain neighbouring group effect with suitable example.  
 b) The rates of solvolysis of the *cis* and *trans* isomers of 2-acetoxycyclohexyl-p-toluenesulfonate differ by a factor of 670, the *trans* compound being more reactive. Explain.
21. What is benzyne? Explain the mechanism of generation, structure and stability of benzyne with one suitable example.  
 (5 × 5 = 25)

### SECTION C

(Answer any **Two** questions, Each question carries 15 marks)

22. The unstable liquid diketone 'biacetyl' deposits crystals of a dimer slowly on standing or more quickly with traces of base. On longer standing the solution deposits crystals of a trimer. Suggest mechanisms for the formation of the dimer and the trimer. Why are they more stable than the monomer?



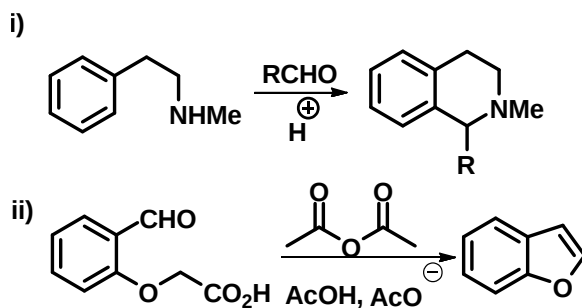
23. a) What is a concerted reaction? Describe the types of concerted reaction with suitable examples.

b) Briefly describe the Diels-Alder and Ene reactions with two suitable examples. Using the orbital diagrams discuss the endo-rule for the Diels-Alder reaction.

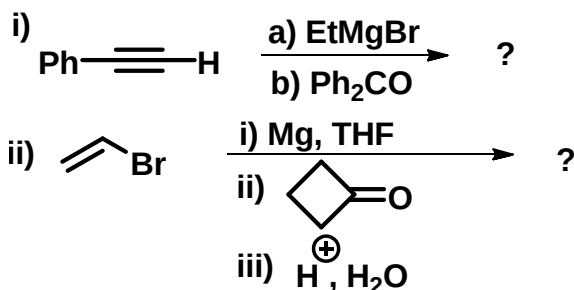
24. Describe the following named reaction with one suitable example.

- a) Wittig reaction
- b) Peterson olefination
- c) McMurry coupling
- d) Robinson annulation reaction
- e) Favorskii rearrangement

25. a) Suggest the mechanism for the product formation and name the reaction.



b) Complete the following reaction with mechanism.



(15 × 2 = 30)

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