LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

SECOND SEMESTER – **APRIL 2015**

CH 2819 - ORGANIC REACTION MECHANISMS & HETEROCYCLICS

Date : 16/04/2015 Dept. No. Max. : 100 Marks

Time : 01:00-04:00

Part-A

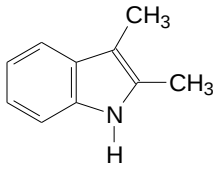
Answer all questions. Each question carries two marks. ***(10x2=20)***

1. Which of the following compounds have aromatic character and write the basis of your answer?
   (a) $C_4H_4^{2+}$ (b) $C_7H_7^{+}$ (c) C_8H_8
2. Predict the mechanism of aliphatic diazotisation reaction with one example.
3. Explain S_N1 reaction with an example.
4. How is the formation of benzyne intermediate confirmed in aromatic nucleophilic substitution reaction?
5. What are the conditions that favour E1cB mechanism?
6. Write the role of inhibitors in free radical reaction.
7. Give evidences for the formation of arenium ion in aromatic electrophilic substitution reaction.
8. What is oxymercuration-demercuration reaction?
9. Compare the basicity of imidazole and pyridine.
10. Mention the biological importance of pyrimidines.

Part-B

Answer any eight questions. Each question carries five marks. ***(8x5=40)***

11. Discuss various factors affecting the aliphatic electrophilic substitution reaction mechanisms.
12. Give reason for the following **(3+2)**
    a) Halogens are ring deactivators but *o*-,*p*-directors.
    b) Aniline is more reactive than acetanilide in electrophilic substitution.
13. a) Predict the mechanism of Stork – enamine reaction. **(3+2)**
    b) What is meant by *ipso* substitution reaction?
14. Explain the ion-pair mechanism of nucleophilic substitution reaction with suitable example.
15. Discuss the mechanism of von-Richter reaction. How does the nature of Z group affect the reaction rate?
16. Compare the reactivity of alkenes and alkynes towards electrophilic, nucleophilic and free radical addition reactions.
17. Account for the following: **(2½ × 2)**
    a) In E2 reaction *threo* form gives *trans* alkene while *erythro* form gives *cis* olefin.
    b) Acid catalysed dehydration of *neo*pentyl alcohol yields 2-methyl-2-butene as the majorproduct.
18. Discuss the reactivity of aliphatic and aromatic substrates in free radical reaction.
19. How are carbenes synthesized? How do they undergo reaction with alkenes and conjugated dienes?
20. What are the conditions for a compound to undergo Michael 1,2- and 1,4-addition reactions? Give suitable examples.
21. How is the following compound synthesized?



22. Explain the following. **(2+3)**
    a) Chichibabin reaction b) Smiles rearrangement

Part-C

Answer any four questions. Each question carries ten marks. ***(4x10=40)***

23a. Derive the Hammett equation to correlate the substituent and reaction constant.
  b. Write the mechanism and limitations of Friedel- Crafts alkylation reaction. **(6+4)**

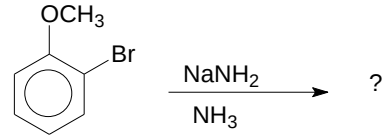
24a. Explain the mechanism of prototropic rearrangement reaction with an example.
  b. S_N1 reaction involves neighbouring group participation by H, CH_3, C_6H_5 or aryl groups. How does the order of priority vary among the group? **(5+5)**

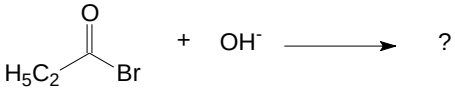
25a. Explain the mechanism of Rosenmund von Braun reaction. How do oxidative addition and reductive elimination take place in this reaction?
  b. How is amination of 1-butene done? What are the products formed? **(6+4)**

26a. What is E1 reaction? Explain the stereo specificity of E1 elimination reaction.
  b. Discuss the mechanism of free radical rearrangement reaction with evidences**.** **(4+6)**

27a. Discuss briefly **(3+3)**
    (i) electrophilic substitution of pyrrole.
    (ii) nucleophilic substitution of pyridine.
  b. Explain in detail the synthesis of thiamine. **(4)**

28. Predict the products for the following.

a) 

b) 

c) 

d) 3-Methyl-2-hexene $\xrightarrow{\text{Hydroboration}}$?

(4 × 2½)

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