LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - **CHEMISTRY**

SECOND SEMESTER – **APRIL 2013**

CH 2819 - ORGANIC REACTION MECHANISMS & HETEROCYCLICS

Date : 26/04/2013 Dept. No. Max. : 100 Marks

Time : 9:00 - 12:00

PART-A

Answer ***ALL*** questions. (10 × 2 = 20)

01. Predict the sign of Hammett constant for the following substituents.

m-NO_2,*p*-OMe, *p*-COOH, *m*-OH, *p*-OH

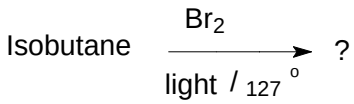
02. Suggest a suitable method to differentiate S_E2(front) and S_Ei reaction.

03. What is Grunwald-Winstein relationship?

04. 'The effect of attacking nucleophile in S_N1 reaction kinetics is negligible.' Why?

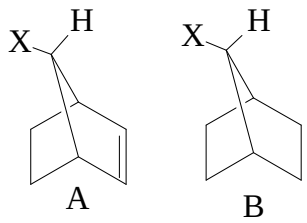
05. What will be the product when trans-1,4-dibromocyclohexane reacts with a metal Zinc?

06. Predict the product and explain the stereochemistry of the reaction?



07. Predict the products for the reaction of *o*- &*m*-dichlorobenzene with KNH_2 in liq. NH_3.

08. Between A & B which will undergo solvolysis very readily and why?



09. Give the product for the reaction between purine and four moles of CH_3I.

10. How is uric acid converted into caffeine?

PART-B

Answer ***ANY EIGHT*** questions. (8 × 5 = 40)

11.Draw the structure and predict the aromaticity of the following compounds;

(a) heptalene (b) azulene (c) pentalene (d) biphenyl (e) [14] annulene

12.Explain the following with suitable example.

(a) Stork-enamine reaction (b) Aliphatic diazonium coupling

13. What is Ipso substitution? Explain with examples.

14. Between $(C_6H_5)_2CHBr$ and $(CH_3)_3CBr$ which will undergo solvolysis more readily and why?

15.Explain SET mechanism with evidences.

16. Predict the product for the reaction of HI with the following compounds.

(a) Ethylmethylether (b) t-butylmethylether

17.Prove that the E2 reaction of erythro-1-bromo-1,2-diphenyl propane is stereospecific.

18. Explain the free-radical mechanism of an aromatic substrate.

19. The addition rate of $Br_2$to ethylene increases by adding $AlBr_3$, but decreases by the KBr. Justify the above statement.

20. Explain von Ritcher rearrangement with mechanism.

21. Write the Hantzsch synthesis of pyridine derivatives.

22. Convert ethylcyanoacetate into xanthine.

PART-B

Answer ***ANY FOUR*** questions. (4 × 10 = 40)

23. a) Account for the following observation:"Benzoic acid is *meta*-directing in aqueous or acidic solutions but *ortho*- and *para*-directing in the presence of base"

b) Write the mechanism of the following reaction:

(i) Fiedal-Crafts arylation (ii) $S_E1$reaction

24. a) Explain the linear free energy relationship in ArSE reactions.

b) Write the mechanism of aliphatic electrophilic substitution reaction involving the following as electrophile with a suitable example.

(i) Halogen (ii) Sulphur

25. Explain the following with evidences.

(a) Ion Pair mechanism (b) Benzyne mechanism

26. a) Neomenthyl chloride undergoes dehydrochlorination when treated with sodium ethoxide in ethanol is about 200 times faster than menthyl chloride under similar conditions. Furthermore, neomenthyl chloride gives a mixture of 75% 3-menthene and 25% 2-menthene, whereas menthyl chloride produces only 2-menthene. Account for these observations.

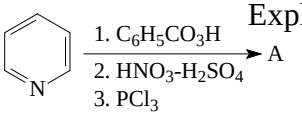
b) Explain the following with mechanism.

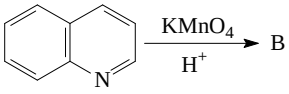
(i) Birch reduction (ii) Chlorination of neopentane

27.a) Explain neighboring group participation mechanism with suitable example.

b) Give the Baeyer's synthesis of uric acid from urea.

28. Predict the product for the following.

i) 

ii) 

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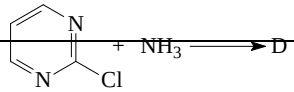
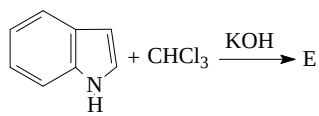
iv) 

v) 

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