LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

SECONDSEMESTER – APRIL 2018

CH 2814- ORGANIC SUBSTITUTION, ADDITION & ELIMINATION RXNS

Date: 17-04-2018 Dept. No. Max. : 100 Marks

Time: 01:00-04:00

Part-A

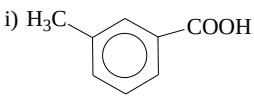
Answer ALL questions. **(10 × 2 = 20)**

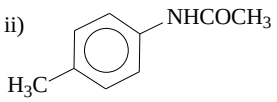
1. Give evidences for the formation of σ and πcomplexes in aromatic electrophilic substitution reaction.
2. The rate of acid-catalyzed hydrolysis of benzamide is -0.298 and the relative electron withdrawing effect of $-NO_2$ substituent is + 0.710. Calculate the relative reactivity of nitrobenzamide.
3. What is Swain-Scott relationship?
4. Predict the products for the reaction between *m*-dichlorobenzene with KNH_2 in liq. $NH_3$and mention the intermediate involved.
5. Write the mechanism of Bucherer reaction.
6. When does Hofmann elimination take place in E2 reaction?
7. What is Cope reaction? Give an example.
8. Write a note on Wohl-Ziegler bromination.
9. Why does the addition of hydrogen bromide to an alkene by free radical mechanism seem to follow anti-Markonikoff's rule?
10. "Stereospecificity of bromination reaction of $PhCH=CHCH_3$ decreases as the polarity of the solvents increases. Justify.

Part-B

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

11. Which of the following compounds have aromatic character? Give reason.
    (a) $C_4H_4^{2+}$ (b) $C_7H_7^{+}$ (c) C_8H_8
12. Predict the major product formed on nitration of the following compounds.





13. Discuss various factors affecting the aliphatic electrophilic substitution reaction mechanisms.
14. Compare the acid and base catalysed halogenation reaction of methyl ketones with mechanisms and evidences.

15a. Write the mechanism of Stork – enamine reaction.

b. What is meant by *ipso* substitution reaction? Give an example. (3 + 2)

16. Discuss the mechanism of Sommelet-Hauser reaction. How does it compete with Steven's rearrangement?
17. Explain ion-pair mechanism with evidences.
18. Discuss the mechanism and stereo chemistry of E1 elimination reaction with an example.

19a. How does the catalytic hydrogenation of a double bond follow *syn* addition? Give an example.

b. What is cheletropic reaction? Cite an example. (2 × 2.5)

20. Discuss the reactivity of aliphatic and aromatic substrates in free radical reaction.

21. Compare the reactivity of alkenes and alkynes towards electrophilic, nucleophilic and free radical addition reactions.
22. How are carbenes synthesized? How do they undergo reaction with alkenes and conjugated dienes?

Part-C

Answer any FOUR questions. **(4 × 10 = 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 von-Richter reaction.

b. How is amination of 1-butene carried out? What are the products formed? (5 + 5)

25. Explain the following with examples.

a) Benzyne mechanism b) Smiles rearrangement (6 + 4)

26a. Prove that the E2 reaction of erythro-1-bromo-1,2-diphenyl propane is stereospecific.

b. Explain Hofmann degradation reaction with an example. (5 + 5)

27a. Explain Bucherer reaction with mechanism.

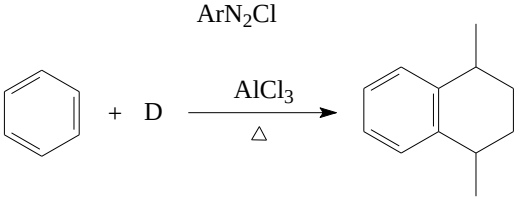
b. Discuss in brief the mechanism and stereochemistry of E2 elimination reaction. (5 + 5)

28. Predict A, B, C, D, and, E for the following reactions. (2 × 5)

i) $CH_3CH_3 + A \xrightarrow[CH_3CN]{} BrCH_2CH_2CONCO$

ii) $CH_3CH{=}CH_2CH_2C{\equiv}CH + NBS \xrightarrow{(C_6H_5COO)_2} B$

iii) $CH_2{=}CHCN \xrightarrow[ArN_2Cl]{CuCl_2} C$

iv)  + D $\xrightarrow[\triangle]{AlCl_3}$

v) $CH_2(COOEt)_2 + CH_2{=}CHCHO \xrightarrow{NaOEt} E$

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