

2010  
CHEMISTRY - II (Optional)

200042

Standard : Degree

Total Marks : 200

Nature : Conventional

Duration : 3 Hours

Note :

- (i) Answers must be written in English.
- (ii) Question No. 1 is **Compulsory**. Of the remaining questions, attempt **any four** selecting one question from each section.
- (iii) Figures to the **RIGHT** indicate marks of the respective question.
- (iv) Use of log table, non-programmable calculator is permitted, but any other table/code/reference book are not permitted.
- (v) Make suitable assumptions, wherever be necessary and state the same.
- (vi) Number of optional questions upto the prescribed number in the order in which they have been solved will only be assessed. Excess answers will not be assessed.
- (vii) Credit will be given for orderly, concise and effective writing.
- (viii) Candidate should not write roll number, any name (including their own), signature, address or any indication of their identity anywhere inside the answer book otherwise he/she will be penalised.
- (ix) For each slab of 10 and 15 marks, the examinee is expected to write answers in 125 and 200 words respectively.

1. Answer **any four** of the following questions.

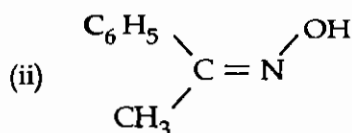
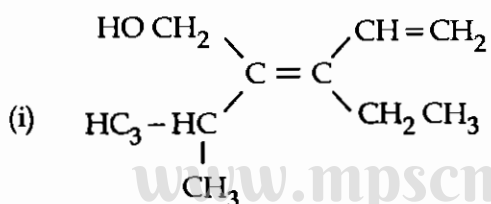
- (a) State Markownikov's rule. Explain the mechanism with suitable example. Give 10 the following reactions of
  - (i)  $\text{KMnO}_4$  oxidation (alkaline medium)
  - (ii) Ozonolysis
- (b) Explain Bischler-Napieralski synthesis of isoquinoline. What is the action of following 10 reagents on pyridine.
  - (i)  $\text{H}_2\text{O}_2 + \text{CH}_3\text{COOH}$
  - (ii)  $\text{C}_2\text{H}_5\text{COCl} + \text{I}_2$
- (c) How is polypeptide synthesised? Explain the structure of deoxyribonucleotide 10

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- (d) Differentiate between fluorescence and phosphorescence. Explain Jablonski diagram 10
- (e) Explain acidity of terminal alkynes with examples. Give the reaction of 10
- (i) 1, 3-butadiene with HCl
- (ii) 1, 3-cyclohexadiene with maleic anhydride.

## SECTION - A

2. (a) Explain the structure and stability of carbenes. Give the different method of preparation of carbocations. Explain 10
- (i) Unusual stability of cyclopentadienyl anion
- (ii) Why acetylene is more acidic than ethylene
- (b) Explain erythro and threo enantiomers with example. Label E or Z for the following 10



Explain Baeyer's strain theory

- (c) What are the different types of molecular vibrations in IR Spectra? Explain the terms chromophore and auxochrome. What do you mean by chromophore - auxochrome interaction? 10
- (d) What is magnetic anisotropy? Explain the effect of magnetic anisotropy on acetylenic molecule. Give the number of signals, approximate positions and splitting pattern of 10
- (i) ethanol
- (ii) ethyl acetate

3. (a) What are the different methods of determining reaction mechanism? Explain trapping of intermediates and isotopic labeling with example. Give the structure and two methods of preparation of benzyne. 10
- (b) Label R or S 10  
 (i) 1, 2-dichloropropane  
 (ii) 1-bromo-2-methylbutane  
 Explain the terms  
 (i) 1, 3-diaxial interaction  
 (ii) flipping of the ring
- (c) Explain Beer-Lamberts law. Why is UV Spectroscopy useful in studying conjugated carbonyl compounds? Give reasons 10  
 (i) Alcoholic solution of aniline shows  $\lambda_{\max}$  at 230 nm while dilute acidic solution of aniline  $\lambda_{\max}$  at 203 nm  
 (ii)  $\text{CCl}_4$  does not absorb radiation for IR region.
- (d) What is chemical shift? The IR spectrum of a compound with molecular formula  $\text{C}_7\text{H}_6\text{O}$  shows absorption bands in the following region  $1730\text{ cm}^{-1}$  in  $1470\text{ cm}^{-1}$   $304\text{ cm}^{-1}$  and 2 IR bands between  $690\text{--}750\text{ cm}^{-1}$ . NMR spectrum gave a singlet  $\delta$  (9-10ppm) and a multiplet  $\delta$  (7-8ppm). Assign the structure. 10

## SECTION - B

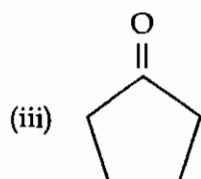
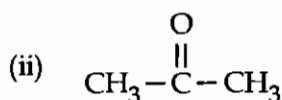
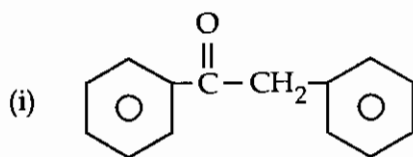
4. (a) (i) Explain Birch Reduction 5  
 (ii) Complete the following reactions 5
1.  $\text{CH}_3\text{COOH} \xrightarrow{\text{SOCl}_2} \text{A} \xrightarrow{\text{NH}_3} \text{B}$
2.  $\text{CH}_3\text{CH}_2\text{COONa} \xrightarrow[\text{sodalime}]{\Delta} \text{A} + \text{B}$
- Give the different methods of preparation of acid chlorides.
- (b) Write a short note on Claisen rearrangement. Give the mechanism for Fries rearrangement. 10
- (c) Give the mechanism for Aldol condensation. Give one reaction of the following 10  
 (i) Knoevenagel reaction  
 (ii) Wittig reaction
- (d) How is amine salt used as phase transfer catalysts? explain with examples. How is diazonium salt synthesized? How will you convert aniline to benzoic acid and chlorobenzene? 10

9. (a) Explain Arrhenius theory of electrolytic dissociation. What is hydrogen electrode? 10  
Give the conductometric titration of weak acid and strong base.
- (b) Write a note on glass electrode. Find the emf of the following cell at 298 K, 10  
 $E^\circ_{\text{Ag}/\text{AgCl}} = 0.2224$  and  $E^\circ_{\text{Ag}/\text{Ag}^+} = 0.7991$  :
- $$\text{Ag}/\text{AgCl}_{(s)}, \text{Cl}^-_{(a=0.1)} \parallel \text{Ag}^+_{(a=0.01)}/\text{Ag}$$
- (c) Give the postulates of quantum mechanics. 10
- (d) How can computers be used in chemical analysis? 10

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7. (a) How is the following prepared from dithiane derivatives. 10



Explain tautomerism in ethylacetoacetate.

- (b) Determine the configuration of glucose. Write a short note on maltose. 10
- (c) Give the preparation of epoxy resin. How is Nylon-6 synthesised? 10
- (d) (i) Give the synthesis of Methyl orange. 5  
 (ii) Give the application of green chemistry 5

#### SECTION - D

8. (a) Explain Debye-Huckel-Onsager equation. Derive Nernst equation for metal-insoluble salt electrode. 10
- (b) Set-up a cell for the following reaction 10  

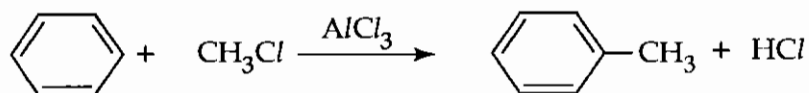
$$2\text{Al} + 3\text{I}_{2(s)} \rightarrow 2\text{Al}^{3+}_{(a=0.1)} + 6\text{I}^{-}_{(a=0.01)}$$
 Calculate the emf of the cell. Is the reaction spontaneous? Write a note on alkaline batteries.
- (c) Give quantum mechanics for particle in 1-dimentional box along with energy levels. 10
- (d) Explain active and passive applications of computer. 10

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5. (a) Explain aromatic electrophilic substitution reaction with examples. Give different methods of preparation of aliphatic carboxylic acids **10**
- (b) Describe the oxidative cleavage of vicinal diols by lead tetracetate. Give the reaction mechanism of Reimer-Tiemann reaction **10**
- (c) (i) Write the following reactions **5**
1. Benzaldehyde is treated with acetic anhydride and then hydrolysed.
  2. Benzophenone is treated with hydroxylamine
- (ii) Complete and name the following reaction and give its mechanism **5**
- $$\text{C}_6\text{H}_5\text{COCH}_3 \xrightarrow[\text{(CH}_3\text{)}_2\text{CHOH}]{\text{[(CH}_3\text{)}_2\text{CHO]}_3\text{Al}}$$
- (d) Explain Hoffmann reaction with mechanism. Write a note on reductive amination of aldehydes and ketones Give the preparation of hydroazobenzene **10**

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6. (a) Describe Claisen condensation with mechanism. Write a note on alkylation and acylation of enamines. **10**
- (b) How is furanose ring structure of D-glucose determined by Haworth method ? **10**
- (c) Explain cationic addition polymerization. Write a note on rubber. **10**
- (d) (i) Give the synthesis of Malachite green. **5**
- (ii) What is atom economy? Calculate the percentage atom economy of the following reaction **5**



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