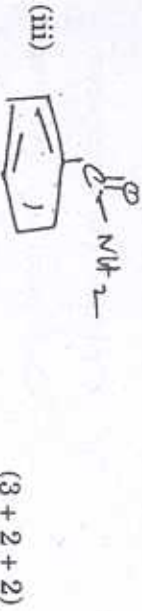


8. (a) State and explain nitrogen rule. (3)

(b) Explain McLafferty-rearrangement with two examples. (6)

(c) What is octant rule? Explain. (4)

(d) Give the fragmentations for the following compounds.



Reg. No. :

D 646

Q.P. Code : [D 07 PCH 04]

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2009.

Second Year

Chemistry

ORGANIC CHEMISTRY — II

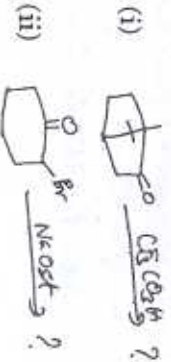
(ORGANIC SYNTHESIS AND NATURAL PRODUCTS)

Time : Three hours Maximum : 100 marks

Answer any FIVE questions.

All questions carry equal marks.

1. (a) Explain benzidine rearrangement with suitable example. (8)
- (b) Discuss the mechanism of fries rearrangement. (4)
- (c) Complete and propose suitable mechanism for the following reactions : (4 + 4)

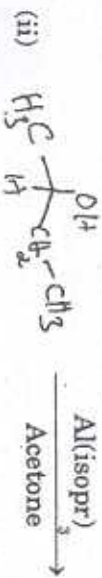


2. (a) Illustrate Jablonki diagram and explain the photophysical process viz; fluorescence and phosphorescence. (8)

(b) Write short notes on the following :
(3 × 4 = 12)

- (i) Paterno-Buchi reaction
(ii) Birch reduction
(iii) Wolt-Kishner reaction.

3. (a) Predict the product(s) and suggest suitable mechanism for the following reactions :
(5 + 3 = 8)



- (b) Explain Barbier-Wieland degradation with two examples. (5)
- (c) How will you synthesis DDQ? Explain two synthesis utility of it? (5)
- (d) Give an example for dehydrations reactions of DCC. (2)

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D 646

4. (a) Elucidate the structure of Zingiferene. (10)
- (b) Write the synthesis of the following :
(5 + 5 = 10)

- (i) Abetic acid
(ii) Eudesmol.

5. (a) How will you elucidate the structure of morphine? (12)

(b) Give the synthesis of reserpine? Explain. (8)

6. (a) Elucidate the structure of ergosterol. (10)

(b) How will you convert
(5 + 5 = 10)

- (i) Cholesterol to testosterone
(ii) Cholesterol to progesterone?

7. (a) What is meant by primary structure of protein? Explain. (2)

(b) Explain the structure of oxytocin. (8)

(c) Write the synthesis of the following :

- (i) Guanine
(ii) Cyanin
(iii) 4'-methoxyflavone. (3 + 3 + 4 = 10)

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Reg. No. :

D 647

Q.P. Code : [D 07 PCH 05]

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2009.

Second Year

Chemistry

INORGANIC CHEMISTRY — II

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

Each question carries 20 marks.

(5 × 20 = 100)

1. (a) Give any two experimental evidences to disqualify the postulates of crystal field theory. (4)
- (b) Draw the M.O. Energy level diagrams for an octahedral complex having π bonds. (6)
- (c) Calculate CFSE in Δ_0 and spin only magnetic moment for various d^n octahedral complexes. Predict those d^n configurations having orbital contribution and/or spin-orbit contribution to the total magnetic moment. (10)

6. (a) Briefly discuss the metal tropylium complexes. (4)
 - (b) Draw an M.O. diagram for metallocene. Using this diagram, predict the number of unpaired electrons in $[\text{Cp}_2\text{Ti}]^+$, $[\text{Cp}_2\text{Cr}]^+$ and $[\text{Cp}_2\text{Co}]$. (8)
 - (c) (i) The prosthetic groups of hemoglobin and cytochromes are same but their functions are different. Explain. (3)
 - (ii) Discuss the work function of cytochromes. (5)
7. (a) Explain isolobal relationship. (3)
 - (b) The isolobal relationship concept is an outgrowth of equating the Lewis Octet rule of organic and main group chemistry with the 18-electron rule of transition metal organometallic chemistry. Justify. (7)
 - (c) Elaborate applications of isolobal principle. (10)
8. (a) Describe the principles and instrumentations of electron and neutron diffractions. (8)
 - (b) With illustration, explain the use of different detectors used in HPLC. (6)
 - (c) Discuss the kinds of pumps used in HPLC. (6)

2. (a) Citing suitable examples, explain the types of the charge transfer spectra encountered among the transition metal complexes. (3)
- (b) State Jahn-Teller theorem. How is the existence of Jahn-Teller distortion in a complex verified? (6)
- (c) (i) Arrive at the ground state term symbol for Ni^{2+} ion. Indicate the splitting of the high spin multiplicity terms of Ni^{2+} in octahedral field. From the splitting, predict the number of d-d transitions possible for Ni^{2+} in octahedral field. Assign the transitions. (8)
- (ii) Write a note on nephelauxetic effect. (3)
3. (a) Sketch the structure of cyanocobalamin. (4)
- (b) How are the following prepared?
- (i) Iron penta carbonyl
- (ii) Carbonyl halide
- (iii) Vaska's complex
- (iv) Zeise's salt. (6)
- (c) (i) Draw the structure of chlorophyll. (3)
- (ii) Correlate the work function of hemoglobin and myoglobin with respect to their structures. (7)

4. (a) Outline the synthesis of trans $[Pt(Py)(P \text{ and } t_3)Cl_2]$ starting from $[PtCl_4]^{2-}$. (2)
- (b) Depict the catalytic loop for explaining the mechanism of homogeneous hydrogenation of olefin using Wilkinson's catalyst. Explain each step. (6)
- (c) (i) Compare the inner and outer sphere electron transfer reactions. (4)
- (ii) Why are transition metallic compounds extremely used as catalysts? Detail the mechanism involved in Monsanto acetic acid process. (8)
5. (a) Compare the bonding modes in cyano- and isocyano-complexes. (4)
- (b) Discuss the preparation, bonding and structure of allyl complexes. (6)
- (c) (i) Give an account of bonding in nitrosyl complexes with linear, bent and bridging mode. (6)
- (ii) Why is a special significance attached to the study of dinitrogen complexes? Explain the role of titanium complexes in such study. (4)

Reg. No. :

D 648

Q.P. Code : [D 07 PCH 06]

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2009.

Second Year

Chemistry

PHYSICAL CHEMISTRY — II

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

All questions carry equal marks.

(5 × 20 = 100 Marks)

1. (a) Discuss the deviation from simple collision theory. (5)
 - (b) State the Arrhenius Law. How is it tested? (5)
 - (c) Give a detailed account of isotope effects on reaction rates. (10)
2. (a) How is the stock method used to study the rates of dissociation of simple molecules? (5)

- (b) Discuss the significance of the entropy of activation. (5)
- (c) Discuss the influence of ionic strength on reaction rates. (10)
3. (a) Illustrate Bronsted Catalysis law. (5)
- (b) Distinguish between physisorption and chemisorption. (5)
- (c) Discuss the influence of pH and temperature on enzyme catalysis. (10)
4. (a) What is known as the Wien effect? (5)
- (b) How is equivalent conductance at infinite dilution determined? (5)
- (c) Describe the stern's theory of the double layer. (10)
5. (a) Discuss the effect of complex formation on polarographic waves. (5)
- (b) Sketch the typical forms of amperometric titration curves and explain. (5)
- (c) Write a detailed note on coulometric titrations. (10)
6. (a) List the assumptions made by Brewster. (5)
- (b) Explain the Octant rule. (5)
- (c) Discuss the principles involved in DSC. (10)

7. (a) What do you mean by photoionization? Explain. (5)
- (b) What do you mean by K.L.L Anger transition? (5)
- (c) What are the characteristics of an ideal detector in GC? Explain the function of flame ionization detector. (10)
8. (a) What is the basis of the structural technique of electron diffraction? Explain. (5)
- (b) Discuss the structure of diamond. (5)
- (c) What is called the Fourier synthesis of the electron density? Explain. (10)
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