

Reg. No. :

D 1099

Q.P. Code : [D 07 PCHO 4]

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2013.

Second Year

Chemistry

ORGANIC CHEMISTRY — II

(ORGANIC SYNTHESIS AND NATURAL PRODUCTS)

Time : Three hours

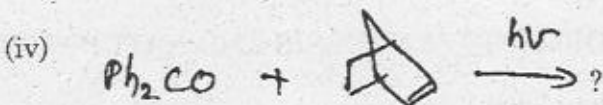
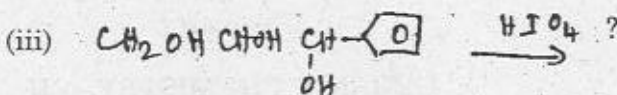
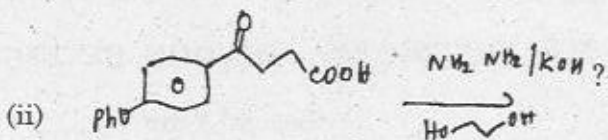
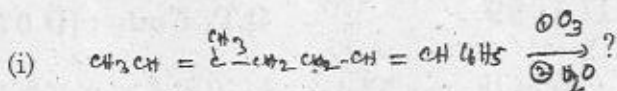
Maximum : 100 marks

Answer any FIVE questions.

(5 × 20 = 100)

1. (a) Discuss Naber rearrangement with mechanism and examples.
- (b) Establish the involvement of cyclopropanone intermediate in favorski rearrangement.
- (c) Discuss the mechanism and applications of
 - (i) Benzidine rearrangement
 - (ii) Bacyer villiger rearrangement. (4+8+8)

2. (a) Complete the following. Identify the product (Δ) formed in each case.



(b) Briefly discuss about oxidation of obtains.

(c) Explain the following

(i) Cis-trans isomerisation

(ii) Sommelet reaction. (8+4+8)

3. (a) Discuss the preparation and synthetic applications of

(i) DCC (ii) DDQ

(b) What is Barbier wienand degradation? How is it done? What are its uses? Explain with examples.

(c) Discuss smeier reaction with mechanism and examples. (10+5+5)

4. (a) How are the positions of double bonds and isopropyl group established in abietic acid?
(b) Establish the structure of carophyllene.
(c) Write a note on Juvenile Hormone. (8+8+4)
5. (a) What is diels hydrocarbon? How is it synthesised
(b) Establish the structure of equilenin. Give its synthesis.
(c) Explain the following
(i) Conversion of cholesterol to testosterone.
(ii) Position of double bonds in ergosterol. (4+8+8)
6. (a) Establish the structure of reserpine acid.
(b) How is alopine synthesized starting from suberone?
(c) How are the following elucidated?
(i) Position of methoxy group and vinyl side chain in quinine.
(ii) Position of methoxyl groups in glaucine. (4+6+10)
7. (a) What are enzymes and co enzymes?
(b) Elucidate the structure of pelargonin.
(c) Discuss the following
(i) Structure of RNA
(ii) Chemistry of flavones. (4+6+10)

8. (a) State and explain Octant rule. Give its applications.
- (b) Explain the following with examples
- (i) Metro Diels Alder seaction
 - (ii) Fragmentation pattern of carboxylic acids.
- (c) How are the three inomeric butanob distinguished using MS.
- (d) Predict the structure of an organic compound that exhibits m/e beaks at 15, 43, 57, 91, 105 and 148 in the mass spectrum. (4+8+4+4)
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Reg. No. :

D 1100

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

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2013.

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) Show how any two isomers of composition $[\text{Pt}(\text{py})(\text{NH}_3)(\text{Br})(\text{CN})]$ can be prepared?
- (b) Discuss the effect of π - bonding on 10 Dq values. Explain on the basis of CFT, why Fe_3O_4 and Mn_3O_4 are having different spinel structures?

- (c) Set up MO energy level diagram for $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and discuss. What would be the spin only magnetic moment for this complex species? Would you expect additional moment due to orbital contribution and spin - orbit coupling for this species? Why? (4 + 8 + 8)
2. (a) Derive ground term symbol for V^{3+} and Ni^{2+} .
- (b) KMnO_4 is coloured - Explain. Bring out the significance of nephelauxetic effect.
- (c) (i) Which of the ions $\text{Mn}(\text{III})$, $\text{Fe}(\text{III})$ and $\text{Cr}(\text{III})$ would be considered to be Jahn Teller ion when located in an octahedral field? Justify your answer.
- (ii) Give the TS diagram for Co^{3+} complexes and discuss. (3 + 6 + 11)
3. (a) What is Vasca's compound? Calculate its effective atomic number.
- (b) Discuss the stabilization of low oxidation states of metals by CO.
- (c) Describe the preparation and structure of the following :
- (i) $\text{Fe}_2(\text{CO})_9$ (ii) $[\text{HFe}_3(\text{CO})_{11}]$
- (iii) $\text{Mn}_2(\text{CO})_8$. (4 + 7 + 9)

4. (a) What is the homogeneous catalyst used for the following conversion? Discuss the mechanism involved.
- $$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$$
- (b) Distinguish between trans effect and trans influence. Write a note on the applications of trans effect.
- (c) Discuss the mechanism involved in. (i) base hydrolysis of Co(III) complexes and (ii) outer sphere electron transfer reactions. (5 + 5 + 10)
5. (a) Describe the bonding in metal – isocyanide complexes.
- (b) Bring out the biological significance of molecular absorption. Compare these with the attempts of inorganic chemists to prepare dioxygen complexes.
- (c) (i) Write a brief note on metal – allyl and dienyl complexes.
- (ii) Give the interesting structural aspects of (1) Roussin's salts and esters. (2) $[\text{Mo}(\text{C}_5\text{H}_5)_3(\text{NO})]$. (3 + 7 + 10)
6. (a) Describe the structure and biological function of chlorophyll.
- (b) Write briefly on arene complexes.

- (c) Give a method for the preparation of ferrocene. Among ferrocene and cobaltocene, which would easily get oxidized? Why? How is aromaticity of ferrocene confirmed?
(6 + 6 + 8)
7. (a) Explain the structural differences among various cytochromes. Describe the role of cytochromes in respiration.
- (b) Write briefly on :
- (i) Structural implications of isolobal analogy.
- (ii) reaction mechanisms from inorganic to organic chemistry. (8 + 12)
8. (a) Outline the principles in HPLC. Write a note on its application.
- (b) Discuss the principle and instrumentation in the X-ray and neutron diffraction methods.
(10 + 10)
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D 1101

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

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, DECEMBER 2013.

Second Year

Chemistry

PHYSICAL CHEMISTRY – II

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

All questions carry equal marks.

(5 × 20 = 100)

1. (a) Deduce the Arrhenius equation and mention its significances. (5)
- (b) Give a detailed account of absolute reaction rate theory. (10)
- (c) Write a note on kinetic isotopic effect. (5)

2. (a) Explain the influence of pressure on the reaction rates. (5)
- (b) Illustrate how fast reactions are studied by flow method. (10)
- (c) Give the significance of volume of activation. (5)
3. (a) Explain the mechanism of acid - base catalysis reactions. (5)
- (b) Discuss the mechanism and derive the Michaelis - Menton equation for enzyme catalysed reactions. (10)
- (c) Derive the Langmuir's adsorption isotherm equation. (5)
4. (a) Deduce the Debye Huckel limiting law equation. (5)
- (b) Discuss the Helmholtz - Perrin, Gouy chapmann and stern models of electrical double layers. (10)
- (c) Discuss the term activity and activity coefficient. (5)
5. (a) Discuss the principle of coulometric analysis. (5)
- (b) Explain the following
- (i) Half - wave potential
- (ii) Ilkovic equation. (10)
- (c) Explain the successive determination of halides with amperometric titration method. (5)

6. (a) Give a detailed account of axial halo ketone rule. (5)
- (b) Discuss the applications of DTA. (10)
- (c) Explain the technique of differential scanning calorimetry. (5)
7. (a) Discuss the principle of electron spectroscopy. (5)
- (b) Discuss the applications of ESCA. (10)
- (c) Explain the effect of temperature on HPLC. (5)
8. (a) Discuss the structure of rutile. (5)
- (b) Discuss the applications of electron and neutron diffraction studies. (10)
- (c) Explain the theory involved in electron diffraction studies. (5)
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