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Reg. No. :

D 2147

Q.P. Code : [D 07 PCH 01]

(For the candidates admitted from 2007 onwards)

M.Sc. DEGREE EXAMINATION, MAY 2014.

First Year

Chemistry

ORGANIC CHEMISTRY — I

Time : Three hours

Maximum : 100 marks

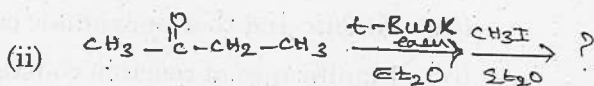
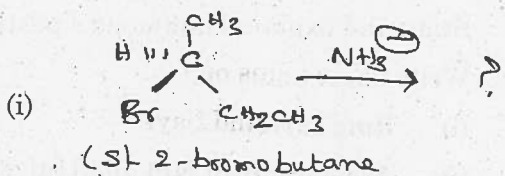
Answer any FIVE questions.

All questions carry equal marks.

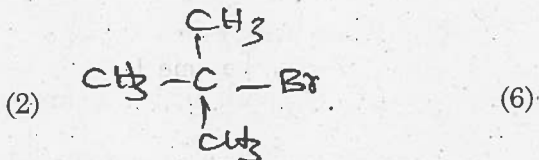
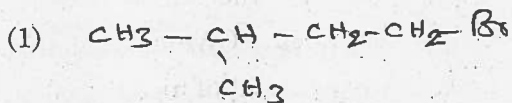
(5 × 20 = 100)

1. (a) What are antiaromatic compounds? Give examples. (2)
- (b) State and explain Hammond's postulate. (3)
- (c) Write short notes on :
 - (i) Ring current
 - (ii) Aromaticity of [10] and [18]-annulenes
 - (iii) Kinetic and thermodynamic control
 - (iv) Significance of reaction constant ' ρ '
 - (v) Primary kinetic isotopic effect. (15)

2. (a) Explain ortho/para ratios. (3)
- (b) Outline the mechanism of nitration of benzene. Give the evidences for the involvement of nitronium ion in the reaction. (5)
- (c) Discuss the mechanism of the following reactions :
- (i) Chlorination of benzene
- (ii) Reimer-Tiemann reaction
- (iii) Gattermann reaction. (4 + 4 + 4)
3. (a) What are classical and non-classical carbocations? Give examples. (4)
- (b) Predict the products



(iii) Which of the following compounds will react faster in a S_N1 reaction? Why?



(c) Write short notes on :

(i) Ambident nucleophile

(ii) Von Brown reaction

(iii) BAC^2 mechanism of ester hydrolysis.

(3 + 3 + 4)

4. (a) What is chugaev reaction? (3)

(b) What are singlet and triplet carbenes? Give their structure. (5)

(c) Write short notes on :

(i) Hofmann and Saytzeff's rule

(ii) Mechanism of E_2 and E_{1CB} reaction.

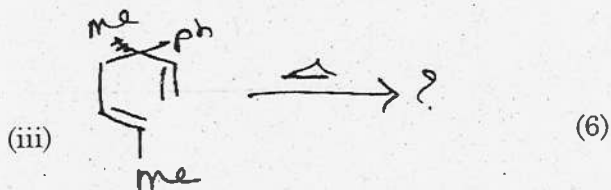
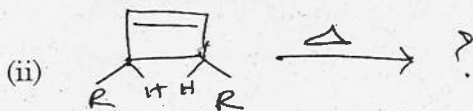
(iii) Hofmann degradation

(iv) Methods of generation of nitrene.

(3 + 3 + 3 + 3)

5. (a) Explain the mechanism of chlorination of methane. (4)
- (b) Write notes on the structure and stability of triphenylmethyl free radical. (6)
- (c) Write briefly on :
- (i) Paneth mirror technique
 - (ii) Sandmeyer and Hunsdicker reactions
 - (iii) Electrolytic methods of generation of free radicals. (3 + 4 + 3)
6. (a) Explain the mechanism and stereochemistry of hydroboration reaction. (4)
- (b) What is Mannich reaction? Write its synthetic utility. (6)
- (c) Outline the mechanism for the following reactions.
- (i) Knoevenagel reaction
 - (ii) Wittig reaction
 - (iii) Dieckmann condensation. (3 + 3 + 4)

7. (a) Predict the products :



(b) Outline the mechanism and applications of Di- π -methane rearrangement. (6)

(c) Write notes on oxy-cope rearrangement. (4)

(d) Explain the FMO analysis of Diels-Alder reaction. (4)

8. (a) Define specific rotation. (3)

(b) Explain the optical isomerism exhibited by nitrogen containing organic compounds. (5)

(c) Write short notes on :

(i) 1,3-diaxial interaction

(ii) Stable conformation of butane

(iii) Conformation of ethane-1,2-diol. (12)

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First Year

Chemistry

INORGANIC CHEMISTRY — I

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

All questions carry equal marks.

(5 × 20 = 100).

1. (a) Explain the terms : (i) Catenation
(ii) Intercalation Chemistry. (10)
- (b) Write a note on dinuclear clusters. Draw the structure of $\text{Re}_2\text{Cl}_8^{2-}$. (10)
2. (a) Write a note on phosphorotric compounds. (10)
- (b) Explain free electron theory. What are its disadvantages? (10)

3. (a) Explain super conductivity of Solids. (10)
(b) Explain the terms (i) Paramagnetism
(ii) Ferro-Magnetism. (10)
4. (a) Explain the liquid drop model of a nucleus.
How it can explain nuclear fission? (10)
(b) Explain the different types of nuclear forces.
(10)
5. (a) What are nuclear isomerism and isomeric
transaction? (10)
(b) Calculate the binding energy and binding
energy per nucleon for helium atom. The
mass of helium nucleus is 4.0028 amu. Mass
of proton = 1.007277 amu ; mass of neutron
= 1.008665. (10)
6. (a) Explain the theory of nuclear fission. (10)
(b) Explain any two applications of radio
isotopes. (10)
7. (a) Explain the GM counter and its working. (10)
(b) What are particle accelerators? Explain
about cyclotron. (10)
8. (a) Explain the principle of TGA and DTA
curves with the help of one compound as the
example. (10)
(b) Write notes on :
(i) XPS.
(ii) Auger electron spectroscopy. (10)

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M.Sc. DEGREE EXAMINATION, MAY 2014.

First Year

Chemistry

PHYSICAL CHEMISTRY — I

Time : Three hours

Maximum : 100 marks

Answer any FIVE questions.

All questions carry equal marks.

(5 × 20 = 100)

1. (a) Explain the following with diagrams

(i) Proper axis of rotation

(ii) Improper axis of rotation

(iii) Centre of symmetry

(iv) Identify element

(v) Plane of symmetry.

(10)

(b) Assign the point groups to the following molecules

(i) Tetrahedral CHCl_3

(ii) T-shaped ClF_3

(iii) Naphthalene

(iv) $[\text{Ni}(\text{CN})_4]^{2-}$

(v) 1, 3, 5 tribromobenzene. (10)

2. (a) Obtain the symmetries of the vibrational modes in H_2O molecules (10)

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

(b) Construct the character table for C_{3v} point group. (10)

3. (a) Explain the terms :

(i) Linear operator

(ii) Hamiltonian operator

(iii) Angular momentum operator. (10)

- (b) Show that commutator $\left[x, \frac{d}{dx} \right] = -1$. (5)
- (c) Discuss the time-dependent Schrodinger wave equation. (5)
4. (a) Derive an expression for the eigen value and eigen function of a simple harmonic oscillator using the Schrodinger wave equation. (10)
- (b) Determine the degree of degeneracy of the energy level $\frac{14h^2}{8ma^2}$ of a particle in a cubical box. (5)
- (c) How can eigen function for a particle in a one dimensional box be normalised? Write expression for the normalised wave equation. (5)
5. (a) Using the variation method solve the Schrodinger wave equation for the ground state energy of helium atom. (10)
- (b) Using the normalized wave function $\psi_{1s} = \left(\frac{1}{\pi a_0^3} \right)^{1/2} \exp\left(\frac{-r}{a_0} \right)$ for the ground state of hydrogen atom, calculate the probability for the electron to be confined in a sphere of radius $r = a_0$, the Bohr radius. (5)
- (c) Derive an expression for energy of a hydrogen atom. (5)

6. (a) Explain the determination of fugacity of gases by using graphical method. (10)
- (b) How will you determine the activity of solvent from boiling points? (5)
- (c) Explain the Nernst heat theorem. (5)
7. (a) Describe the following :
- (i) Microcanonical ensemble
- (ii) Canonical ensemble. (5)
- (b) Derive the Maxwell-Boltzmann distribution law. (10)
- (c) Derive the relationship between entropy and thermodynamic probability. (5)
8. (a) Calculate the translational partition function for 1 mole of oxygen at 1 atm pressure at 25°C, assuming the gas to behave ideally. (5)
- (b) Derive an expression for Fermi-Dirac statistics. (10)
- (c) Discuss the Debye's theories of heat capacity of solids. (5)