



CHE 517 / CHE 518 / CHE 519

M.Sc. (IIIrd SEMESTER) EXAMINATION, 2023-24,

1547

CHEMISTRY

(CBCS Mode)

Time : Three Hours]

[Maximum Marks : 75

CHE 517

Electrolytics and Electrochemical Phenomena – III-A

Note: There are three sections (A, B and C) and candidate has to attempt all questions. Marks are indicated against each section.

Section-A

1. Answer all questions. 5×3=15
- (a) Define the process of corrosion in metals.
 - (b) What is diffusion phenomenon?
 - (c) Explain the differences among Helmholtz-perrin, Gouy-chapman and stern model of the electrified interface.
 - (d) Why is water a good solvent for ion forming reaction?
 - (e) Explain the effect of solvent on mobility of ions.

Section-B

Note: Answer all questions of the following: 4×5=20

2. (a) Illustrate electropolymerization.

Or

(b) Discuss the various methods for the prevention of corrosion.

3. (a) How is the diffusion coefficient measured experimentally?

Or

(b) Explain the stern model of electrical double layer.

4. (a) Discuss the electrochemical corrosion by hydrogen evolution and oxygen absorption.

Or

(b) Mention characteristics of water as a good solvent.

5. (a) Discuss the concentration polarization.

Or

(b) Discuss Helmholtz-perrin model of electrical double layer.

Section-C

Note: Answer **any two** questions of the following: $2 \times 20 = 40$

6. Derive Butler-Volmer equation. Discuss the condition under which the current is either cathodic or anodic.
7. Discuss the Gouy-chapman theory of electrical double layer.
8. Discuss the various factors affecting the corrosion.
9. Discuss Debye-Huckel-Onsager theory for non-aqueous solutions.

••••

CHE 518

Coordination Chemistry – III-B

Note: There are three sections (A, B and C) and candidate has to attempt all questions. Marks are indicated against each section.

Section-A

Note: Attempt all parts of question. $5 \times 3 = 15$

1. (a) What is “Land interval rule”?
- (b) Explain the “hole formulation”?
- (c) Point out the limitations of crystal field theory?
- (d) Differentiate between magnetically concentrated and dilute systems?
- (e) Write down the selection rules for electronic spectra of transition metal complexes?

Section-B

Note: Attempt all questions from following: $4 \times 5 = 20$

2. (a) Discuss spin-orbit coupling parameters.

Or

- (b) Write a short note on Hund’s rule.

3. (a) Discuss the correlation diagram –pr d^2 system in an octahedral field taking strong and weak field ligands.

Or

- (b) Explain the Tanabe – Sugano diagram for d^2 system.

4. (a) Discuss the electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion

Or

- (b) What do you understand by John–Teller distortion explain with example of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion

5. (a) Discuss the origin of paramagnetism in transition metal complexes with the help of Curie-Vess Law.

Or

- (b) How the magnetic susceptibility vary with temperature for dia, para, Ferro and antiferromagnetic substances ?

Section-C

Note : Attempt **any two** question from following : $2 \times 20 = 40$

6. Discuss the utility of Orgel diagrams, what are their limitations? Draw Orgel diagrams for d^1 and d^2 systems in octahedral field?
7. Discuss the splitting of D and F terms in octahedral weak crystal field using character table for O_h point group as given at the end of the paper?
8. Draw the qualitative molecular orbital energy level diagram for square planar complex and comment on changes with respect to octahedral complex?
9. What do you understand by quenching of orbital angular momentum in applied field, explain the effect of quenching in case of A, E and T term?

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	-1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(R_x, R_y, R_z) (xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	(x, y, z)



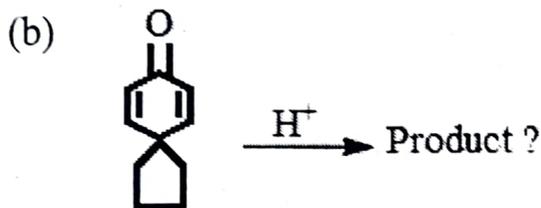
Pericyclic and Rearrangement Reactions – III-C

Note: There are three sections (A, B and C) and candidate has to attempt all questions. Marks are indicated against each section.

Section-A

1. Answer all the questions : 5×3=15

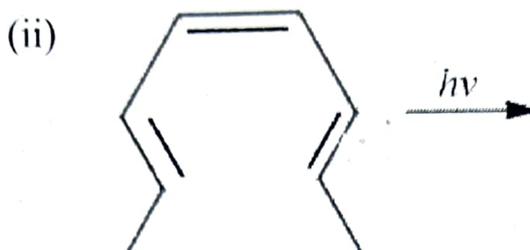
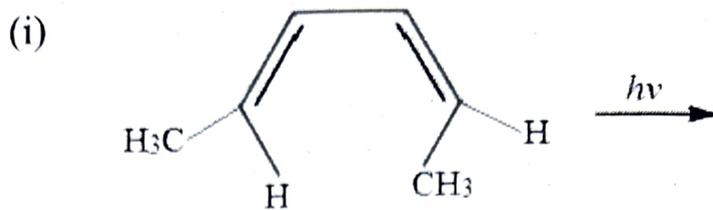
(a) Give an evidence in support of intramolecular nature of sommelet – Hauses rearrangement.



write the structure of product with mechanism.

(c) Give the symmetric properties of HOMO and LUMO of ground state and excited state 1, 3, 5- hexatrienl.

(d) Rationalize the products of the following electrocyclic reactions and write whether the reaction proceeds in a conrotatory or disrotatory fashion.



- (e) What is metalla-ene reaction? What is difference between ene and metalla-ene reaction?

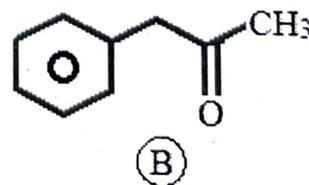
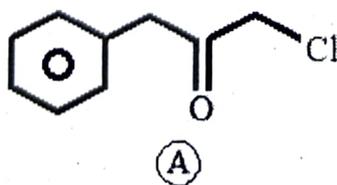
Section-B

Note: Answer all the question of the following: $4 \times 5 = 20$

2. (a) What are homo and Quasi Favorskii rearrangement. Discuss their mechanism.

Or

- (b) Two isomers (A) and (B) when treated separately with NaOH. Give the same product. Give the explanation.

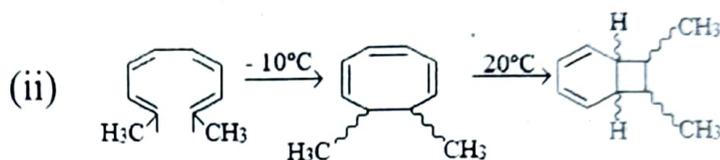
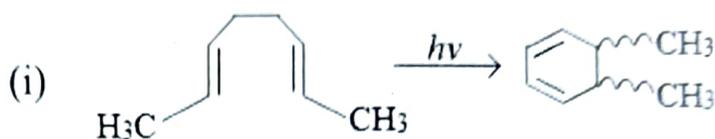


3. (a) Discuss the mechanism of Curtius Rearrangement.

Or

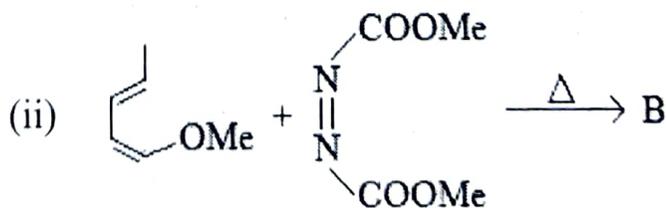
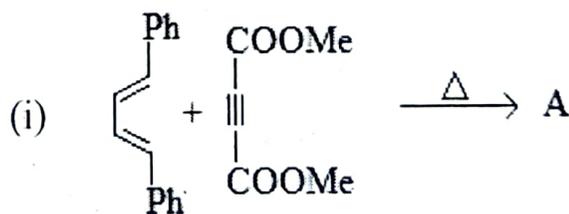
- (b) Discuss the mechanism of Stevens Rearrangement.

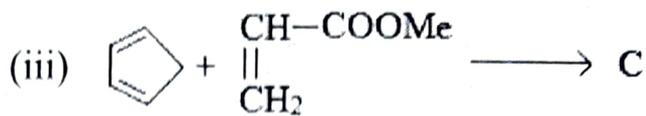
4. (a) Predict the stereochemistry of the following reaction products with explanation :



Or

- (b) Considering Diels-Alder reaction, give the stereo structure of the major products A to C in the following reactions :





5. (a) [2+2] cycloaddition reactions of Ketene with alkenes are thermally allowed reactions explain the fact with FMO treatment.

Or

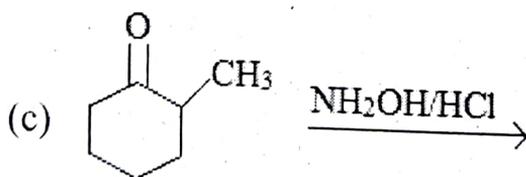
- (b) Give an account of Cope's re-arrangement of 1,2 – divinyl cyclopropane.

Section-C

Note: Attempt any two question from following: $2 \times 20 = 40$

6. Describe Beckmann rearrangement in light of its :

- (a) Mechanism in cyclic compound
(b) Stereochemistry



- (d) Application

7. Write the mechanism of **any two** of the following :

- (a) Tiffeneau – Demjanov Rearrangement
- (b) Wagner – Meerwein Rearrangement
- (c) Schmidt Rearrangement

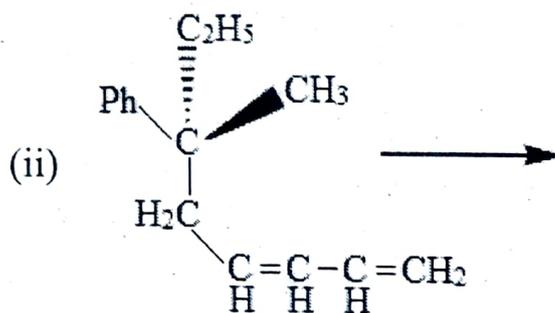
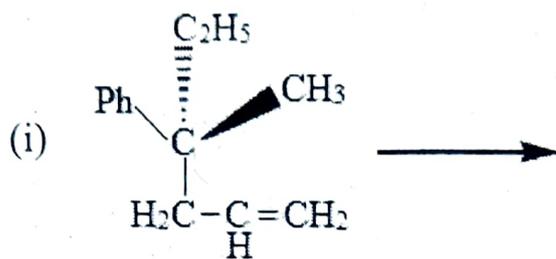
8. (a) Draw correlation diagram to establish that $[\pi^4s + \pi^2s]$ cyclo-addition is a thermally allowed process.

(b) Draw molecular orbital diagrams to rationalize the mechanism of chelotropic cycloaddition reactions of alkenes with.

- (i) Singlet carbene and
- (ii) SO_2

9. (a) Write explanatory note on the [1,3] and [1, 5] sigmatropic shifts of alkyl group under thermal and photochemical conditions.

- (b) On the basis of above derived selection rules for sigmatropic rearrangements, rationalize the following reactions products defining stereochemistry at the chiral centres –



••••