

Roll No.

CHE-551

Reaction Mechanisms, Pericyclic Reactions, Photochemistry and Stereochemistry

M. Sc. CHEMISTRY(MSCCH-12/13/16)

Second Year, Examination, 2017

Time : 3 Hours

Max. Marks : 60

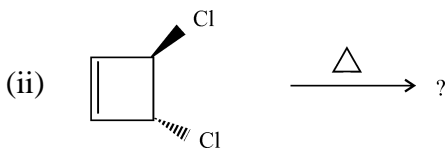
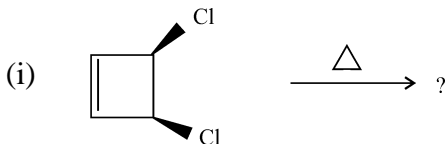
Note : This paper is of **sixty (60)** marks containing **three (03)** sections A, B and C. Attempt the questions contained in these sections according to the detailed instructions given therein.

Section-A

(Long Answer Type Questions)

Note : Section 'A' contains four (04) long answer type questions of fifteen (15) marks each. Learners are required to answer *two* (02) questions only.

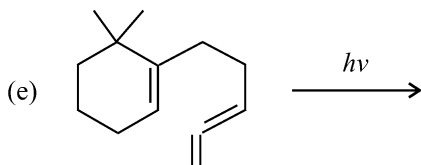
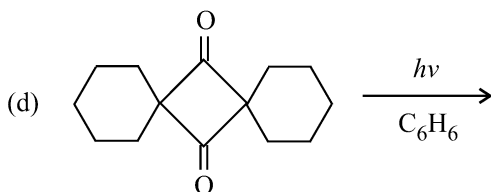
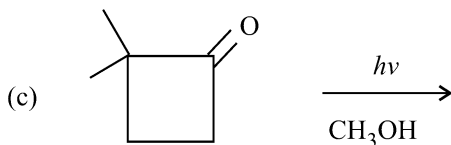
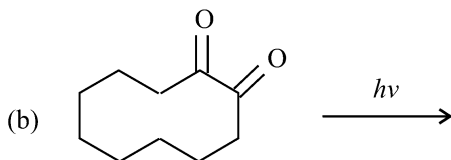
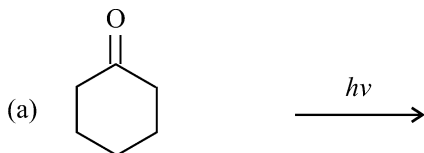
1. (a) Write the product of the following thermal reactions. Show the stereochemistry : 5

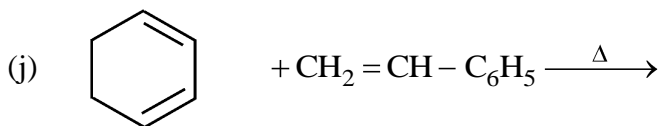
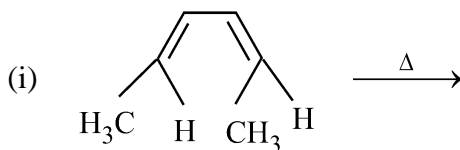
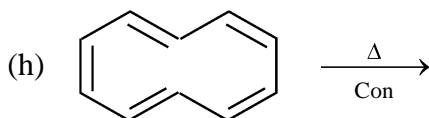
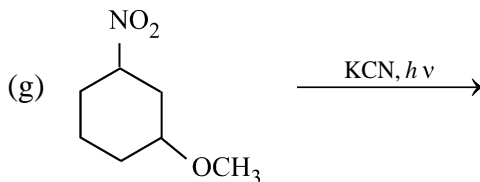
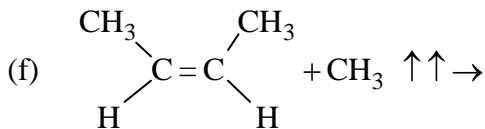


- (b) What are Chelotropic reaction and how is it related to Diel-Adler's additions. 5
- (c) How is Claisen rearrangement related to Cope rearrangement ? Give some examples of Claisen rearrangement. 5

2. Complete the following photochemical reactions :

$1\frac{1}{2}$ each





3. (a) State Curtin-Hammett principle and explain with suitable examples. 5
- (b) Define cycloaddition reactions. What are $(m + n)$ cycloadditions ? 5
- (c) Discuss the boat conformation of cyclohexane. Why is the boat conformation of cyclohexane less stable than the chair conformation ? 5

4. (a) Discuss the stability of carbocation. Formulate the mechanism of an addition reaction of a carbocation. 5
- (b) Discuss the stereospecificity of E_2 reactions with suitable examples. 5
- (c) Discuss the photochemical reactions of diazo compounds.

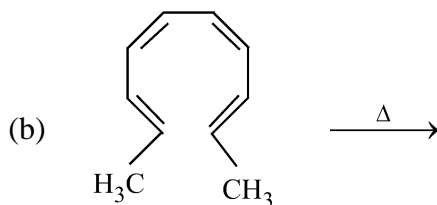
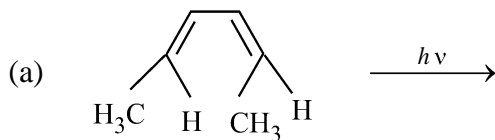
Section-B

(Short Answer Type Questions)

Note : Section 'B' contains eight (08) short answer type questions of five (05) marks each. Learners are required to answer *four* (04) questions only.

1. Discuss the photochemical reaction of α , β -Unsaturated carbonyl compounds.
2. Write short notes on the following :
 - (a) Quantum field
 - (b) Flash Photolysis
3. Discuss the photochemistry of the following :
 - (a) Diazo compounds
 - (b) Azides
4. What is Paterno-Buchi reaction ? Discuss its mechanism along with the stereochemical consequences.
5. Write the product of the following electrocyclic reaction and write whether the reaction proceeds in a

conrotatory or disrotatory fashion. Also give the stereo- chemistry of the products :



6. What are nitrenes ? How are they generated ? Discuss their structure, stability and character.
7. Discuss the mechanism of the following :
 - (a) Lossen rearrangement
 - (b) Di- π methane rearrangement
7. Discuss briefly the conformations of the following :
 - (a) Methyl cyclohexane
 - (b) Disubstituted cyclopentanes

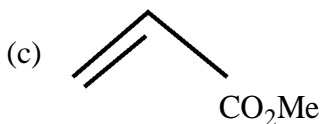
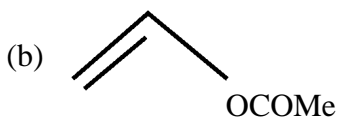
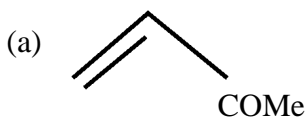
Section-C

(Objective Type Questions)

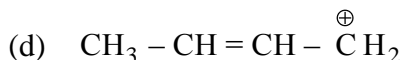
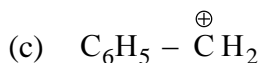
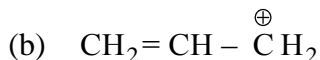
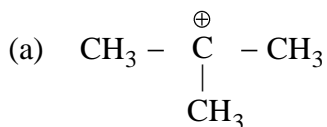
Note : Section 'C' contains ten (10) objective type questions of one (01) mark each. All the questions of this section are compulsory.

1. A molecule with an even number of π -bonds will undergo what type of electrocyclic reaction :
 - (a) Conrotatory, thermal
 - (b) Conrotatory, photochemical
 - (c) Disrotatory, thermal
 - (d) Disrotatory, photochemical

2. Which of the following reacts by the E_1 mechanism in ethanol most readily ?
- (a) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Br}$
- (b) $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$
- (c) $(\text{CH}_3)_3\text{C}-\text{Br}$
- (d) $\text{CH}_3 - \text{CH}_2 - \text{CHBr} - \text{CH}_3$
3. Which of the following dienophiles is the most reactive in normal Diels-Alder's reaction ?



4. Which of the following carbocations is most stable in gaseous state ?



5. The order of stability of the different conformation of cyclohexane is :

(a) Chair form > boat form > twist boat form

(b) Chair form > twist boat form > boat form

(c) Twist boat form > boat form > chair form

(d) Boat form > chair form > twist boat form

6. The Hofmann rearrangement has an intermediate that is electronically similar to that in the :

(a) Pinnacol rearrangement

(b) Claisen rearrangement

(c) Cope rearrangement

(d) Bekmann rearrangement

7. The conversion of acetophenone to acetanilide is best accomplished by using :

(a) Beckmann rearrangement

- (b) Curtius rearrangement
 - (c) Lossen rearrangement
 - (d) Hofmann rearrangement
8. Benzoyl peroxide when heated to about 80°C gives a :
- (a) Free radical
 - (b) Carbonium ion
 - (c) Carbenium ion
 - (d) Carbanion
9. Which of the following carbenes are not electrophilic in character ?
- (a) $\ddot{\text{C}}\text{H}_2$
 - (b) $\ddot{\text{C}}\text{Br}_2$
 - (c) $\ddot{\text{C}}\text{Cl}_2$
 - (d) $\ddot{\text{C}}\text{H} - \text{OCH}_3$
10. The reaction intermediate of E, Cb reaction is :
- (a) Carbocation
 - (b) Carbanion
 - (c) Six membered cyclic TS
 - (d) Benzyne

