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(CBCS)

(6th Semester)

CHEMISTRY

TENTH PAPER

(Organic Chemistry—III)

Full Marks : 75

Time : 3 hours

The figures in the margin indicate full marks for the questions

(SECTION : A—OBJECTIVE)

(Marks : 10)

Tick (✓) the correct answer in the brackets provided :

1×10=10

1. The absorption of UV-radiation by a molecule causes

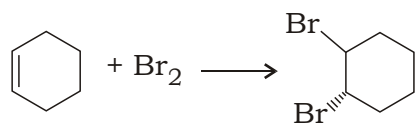
- (a) only vibrational excitation ()
- (b) only rotational excitation ()
- (c) only electronic excitation ()
- (d) vibrational, rotational and electronic excitation ()

2. In carbonyl compounds, the absorption of UV-light at 285 nm causes

- (a) $n \rightarrow \pi^*$ transition ()
- (b) $\pi \rightarrow \pi^*$ transition ()
- (c) $n \rightarrow n$ transition ()
- (d) $\pi \rightarrow n$ transition ()

3. Which of the following statements is wrong for pericyclic reaction?
- (a) It is stereospecific. ()
 - (b) It is initiated by heat or light. ()
 - (c) It is stereoselective. ()
 - (d) It is a concerted reaction. ()
4. The ground-state HOMO of 1,3-butadiene is having
- (a) m -symmetry ()
 - (b) C_2 -symmetry ()
 - (c) three nodes ()
 - (d) two nodes ()
5. Alkyl magnesium halide reacts with ketone to give
- (a) carboxylic acid ()
 - (b) primary alcohol ()
 - (c) secondary alcohol ()
 - (d) tertiary alcohol ()
6. When sulphonic acids are heated with dilute mineral acids at about $150\text{ }^\circ\text{C}$ in the presence of superheated steam, the $-\text{SO}_3\text{H}$ group is replaced by
- (a) $-\text{OH}$ ()
 - (b) H_2O ()
 - (c) $-\text{H}$ ()
 - (d) $-\text{SO}_2$ ()
7. Cyclohexanone oxygenase enzyme is typically used as
- (a) oxidizing agent ()
 - (b) reducing agent ()
 - (c) hydroxylating agent ()
 - (d) hydrating agent ()

8. The % atom economy in the reaction



is

- (a) 1 ()
 - (b) greater than 100 ()
 - (c) 100 ()
 - (d) less than 100 ()
9. The number of signals produced by 2,2-dimethyl propane is
- (a) 4 ()
 - (b) 2 ()
 - (c) 3 ()
 - (d) 1 ()
10. The NMR spectroscopy is useful for the detection of
- (a) aromaticity ()
 - (b) geometrical isomers ()
 - (c) hydrogen bonding ()
 - (d) All of the above ()

(SECTION : B—SHORT ANSWER)

(Marks : 15)

Answer the following questions :

3×5=15

UNIT—I

1. Explain singlet and triplet states of an electron.

OR

2. Write a note on quenching in photochemical reaction.

UNIT—II

3. Explain conrotatory and disrotatory motions of π - or σ -MO in an electrocyclic reaction by taking suitable examples.

OR

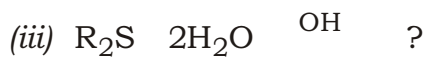
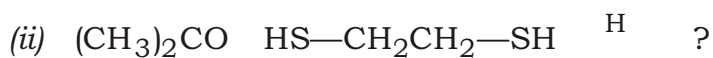
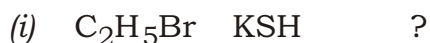
4. "The $[\frac{s}{2} \frac{s}{2}]$ cycloaddition reaction is photochemically allowed but thermally forbidden." Explain.

UNIT—III

5. Grignard's reagent reacts with CO_2 to give carboxylic acid but organolithium with CO_2 gives ketone as the major product. Explain with suitable example.

OR

6. Write the products of the following reactions :



UNIT—IV

7. Explain % yield and % atom economy of a chemical reaction.

OR

8. Describe green method of Michael addition reaction taking suitable example.

UNIT—V

9. Explain base peak and molecular ion peak in mass spectrometry.

OR

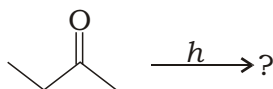
10. Explain shielding and deshielding of protons in $^1\text{H}_{\text{NMR}}$ spectra.

(SECTION : C—DESCRIPTIVE)

(Marks : 50)

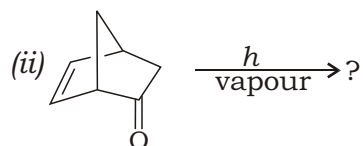
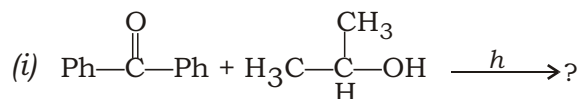
UNIT—I

1. (a) Draw Jablonski diagram and explain the following : 6
- (i) Vibrational relaxation
 - (ii) Internal conversion
 - (iii) Intersystem crossing
 - (iv) Fluorescence
 - (v) Phosphorescence
- (b) Explain Norrish type-I reaction. Write the Norrish type-I product of the given reaction : 1+3=4



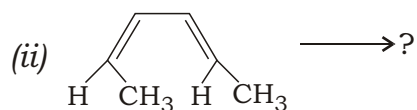
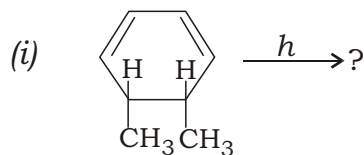
OR

2. (a) Explain Paterno-Buchi reaction taking suitable example. 4
- (b) Complete the following reactions with suitable mechanism : 3×2=6



UNIT—II

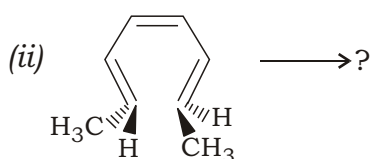
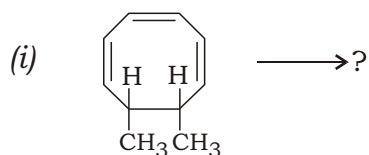
3. (a) Based on FMO approach, predict the product and stereochemistry of the following reactions : 3×2=6



- (b) Based on Woodward-Hoffmann rule, explain the electrocyclic interconversion of cyclobutene to 1,3-butadiene system. 4

OR

4. (a) Based on FMO approach, predict the product and stereochemistry of the following reactions : 3×2=6



- (b) Based on Woodward-Hoffmann rule, explain the [4+2] cycloaddition reaction. 2
- (c) Explain Norrish type-II reaction taking suitable example. 2

UNIT—III

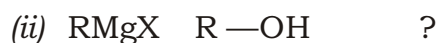
5. (a) Write the preparation of organolithium compounds and complete the following reaction : 1+2=3



- (b) Complete the following reaction with suitable mechanism : 3

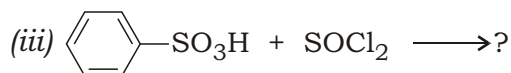
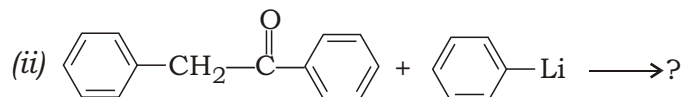
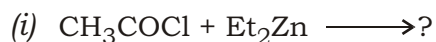


- (c) Complete the following reactions : 2×2=4



OR

6. (a) Complete the following reactions : 2×3=6



(b) Write one preparation of each of the following : 2×2=4

(i) Benzenesulphonamide

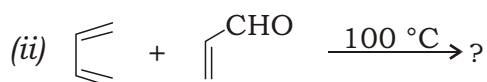
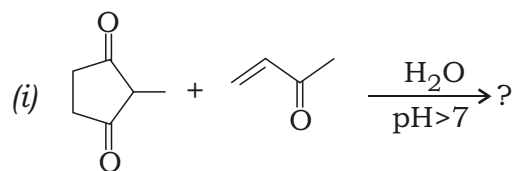
(ii) Sulphaguanidine

UNIT—IV

7. (a) What is aldol condensation reaction? Write an example of green method for aldol condensation reaction. 1+2=3

(b) Write the preparation of butyraldehyde by sonication method. 3

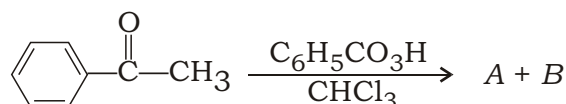
(c) Complete the following reactions : 2×2=4



OR

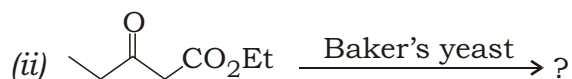
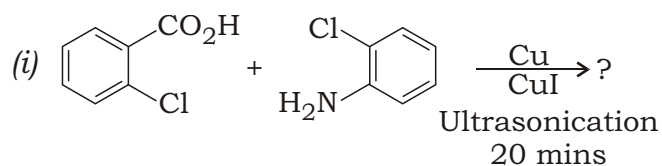
8. (a) Briefly explain microwave-assisted Hoffmann elimination reaction. 3

(b) Predict the major and minor products based on relative migratory aptitude for the given reaction : 3



(c) Write the products of the following reactions :

2×2=4



UNIT—V

9. (a) A compound (C_8H_{10}) shows a prominent peak of m/z value at 106, 91, 65 in its mass spectra. Show the entire fragmentation pattern and determine its molecular structure. 4
- (b) Distinguish between *cis*- and *trans*-stilbene on the basis of $^1H_{NMR}$ spectroscopy. 3
- (c) Acetylenic protons are more shielded than ethylenic protons although the former are attached to a more electronegative *sp*-carbon. Explain. 3

OR

10. (a) Write the possible fragmentation and related m/z value of benzene molecule in mass spectrometry. 3
- (b) Explain McLafferty rearrangement in mass spectrometry taking suitable example. 3
- (c) Draw the high resolution $^1H_{NMR}$ spectra of the following : 2×2=4
- (i) Anhydrous ethanol
- (ii) Toluene

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