

1 Feb 2010

Sl. No. 7719

B-JGT-K-DIB

CHEMISTRY**Paper—II**

Time Allowed : Three Hours

Maximum Marks : 200

INSTRUCTIONS

Candidates should attempt Question Nos. 1 and 5 which are compulsory, and any **THREE** of the remaining questions, selecting at least **ONE** question from each Section.

All questions carry equal marks.

Marks for each part/subpart of a question are indicated against each.

Answers must be written in **ENGLISH** only.

Assume suitable data, if considered necessary, and indicate the same clearly.

Unless otherwise indicated, symbols and notations have their usual meanings.

Section—A

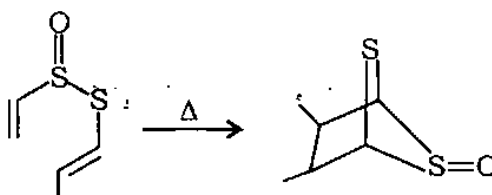
1. Answer the following (any *eight* only) : $5 \times 8 = 40$

- (a) Explain why the hydrocarbon with an acceptable Hückel number of $10(n-2)$ is not aromatic.
- (b) Explain alternant and non-alternant hydrocarbons.

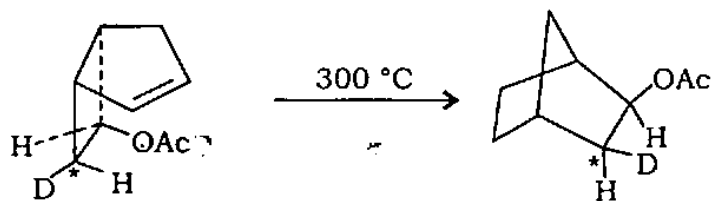
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- (c) Predict the following reaction and illustrate the mechanism :

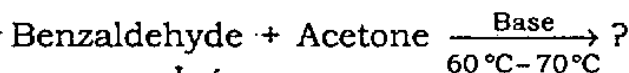


- (d) Explain the following transformation :

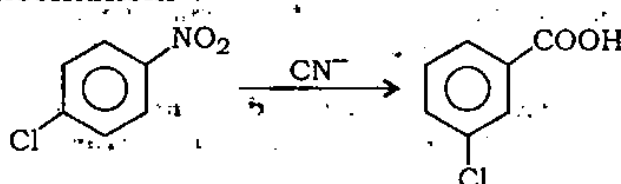


Deuterated bicyclo[3.2.0]heptene Exo-norbornal

- (e) Predict the reaction product and explain the mechanism for



- (f) Complete the following reaction with mechanism :

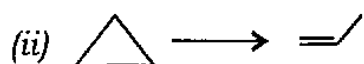
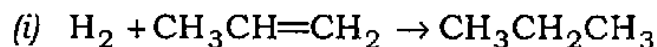


- (g) Explain the difference between the radicals formed by the pyrolysis of $\text{PhN}=\text{N}-\text{C}(\text{Ph})_3$.
- (h) State the product with the mechanism of furan and diazomethane condensation.
- (i) Mention the physical processes in photochemical reaction.

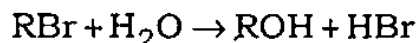
2. Answer the following : 10×4=40

(a) Define the term 'inductive effect'. How does the inductive effect of an alkyl group affect the stability of carbon intermediates? 10

(b) State whether the following reactions have a positive or negative ΔS and explain your choice : 5×2=10



(c) A reaction vessel containing 0.192 mole of RBr undergoes the first-order reaction ($t_{1/2} = 53$ s)



(i) How many moles of RBr will be left after 159 s of the reaction?

(ii) How long will it take for 0.18 mole of RBr to react? 5×2=10

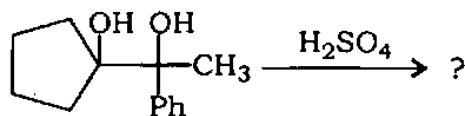
(d) Explain 'molecularity' of a reaction. Describe its types and experimental method of determination. 10

3. (a) Account for the rapid rate of ethanolysis of $\text{ClCH}_2\text{OCH}_2\text{CH}_3$, although the substrate is primary halide. 10

(b) Account that *cis*-(4-*t*-butylcyclohexyl)-trimethyl ammonium hydroxide affords Hofmann elimination while that of *trans*-isomer does not afford. 10

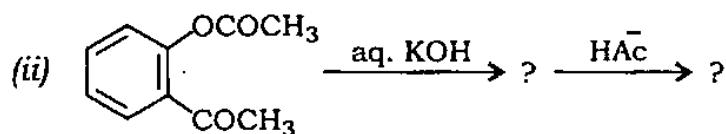
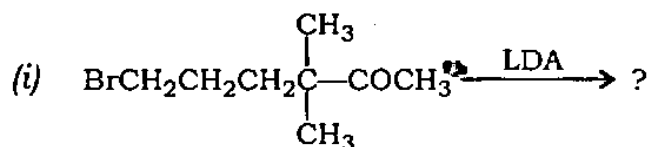
(c) Illustrate the mechanism of bromination of *cis*- and *trans*-2-butenes. 10

(d) Complete the following reaction and write its mechanism : 10

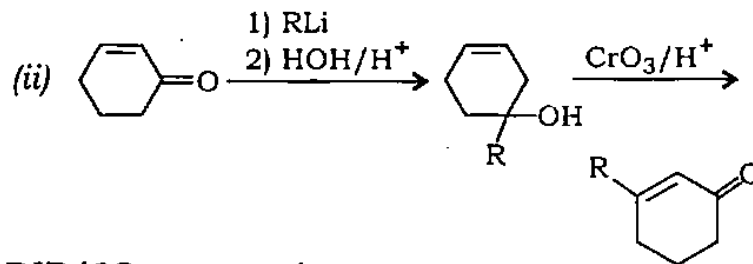
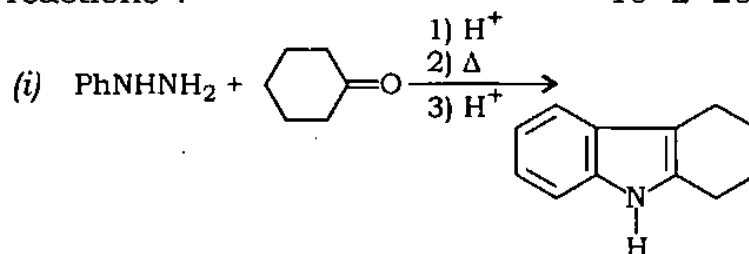


4. (a) What is ketene? How is it prepared industrially? Which products are manufactured from ketene? 10

(b) Complete the following reactions indicating the sequence of events : 10



(c) Give mechanisms of the following conversions and comment on the reactions : $10 \times 2 = 20$



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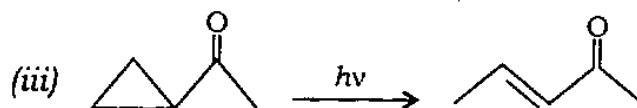
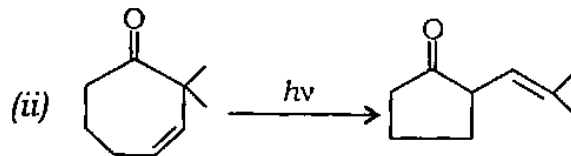
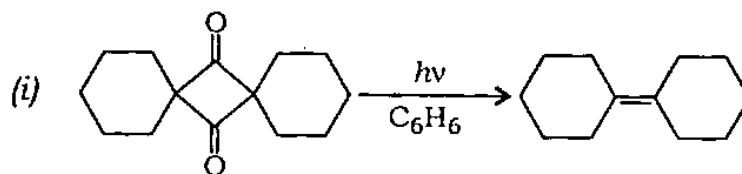
Section—B

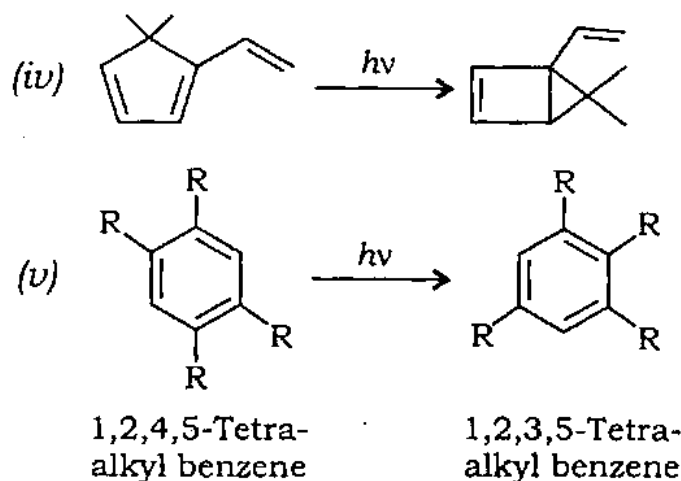
5. Explain any *eight* of the following observations briefly (within 50 words each) with a suitable example wherever necessary : $5 \times 8 = 40$

- (a) PVC cannot be heat moulded.
- (b) $(\text{BNH}_2)_3$ is also called inorganic benzene.
- (c) OsO_4 is less preferred as catalyst for the oxidation of organic compounds. Consider the case of alkenes.
- (d) Phosphorescence is different from fluorescence.
- (e) $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are extremely useful in the interpretation of electronic spectra of organic molecules whereas $\sigma \rightarrow \sigma^*$ transitions are of little use.
- (f) Mass spectrum of CH_3Br shows two peaks of nearly equal intensity at m/e of 94 and 96.
- (g) It is essential to record first or second derivative spectrum in case of esr.
- (h) ^{13}C shows NMR whereas ^{12}C does not.
- (i) Silica has SiO_4^{4-} as structural unit but it is represented as SiO_2 .

6. (a) Define number average molecular weight (\bar{M}_n) of polymers. Describe the experimental and calculation procedure for the determination of \bar{M}_n by osmometry. 15
- (b) What are inorganic polymers? Explain their characteristic properties. In what respects these differ from organic polymers? 15
- (c) Outline the synthesis and properties of any *two* of the following polymers : 5×2=10
- (i) High density polyethylene (HDPE)
 - (ii) Silicones
 - (iii) $(\text{NPCl}_2)_3$

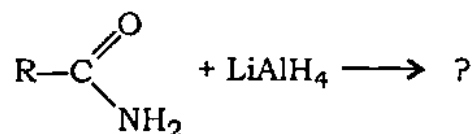
7. (a) Provide mechanistic rationalization for each of the following reactions : 5×5=25





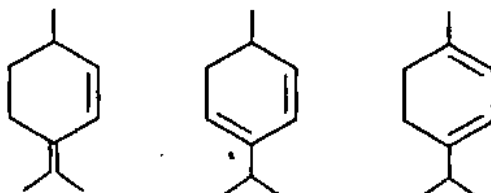
(b) Explain the mechanism of polymerization of vinyl monomer in presence of *n*-butyl lithium. 10

(c) Predict the reaction product of



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8. (a) Predict λ_{max} values for the following structures : 10



(b) A compound having molecular formula $\text{C}_4\text{H}_{11}\text{N}$ exhibits the following spectral features :

(i) IR spectrum : Two bands in the region $3300 \text{ cm}^{-1} - 3500 \text{ cm}^{-1}$, a broad band near 800 cm^{-1} and another band around 1090 cm^{-1} .

(ii) $^1\text{H-NMR}$: Four sets of signals at

$\delta = 0.92$ (3H, Triplet)

$\delta = 1.16$ (2H, Singlet)

$\delta = 1.3 - 1.5$ (4H, Multiplet)

$\delta = 2.7$ (2H, Triplet)

(iii) Mass spectrum shows a base peak at m/e of 30 besides a molecular ion peak at 73.

Identify the compound and give its structure explaining all the spectral characteristics. 15

(c) Name the reference standards used in $^1\text{H-NMR}$ and esr. Discuss their importance in respective measurements. 10

(d) How would you distinguish between *cis*- and *trans*-isomers of 2-butenes by infrared analysis? 5
