IFoS 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.

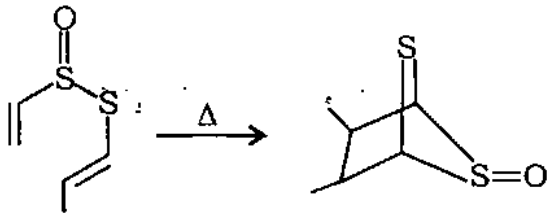
Section—A

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

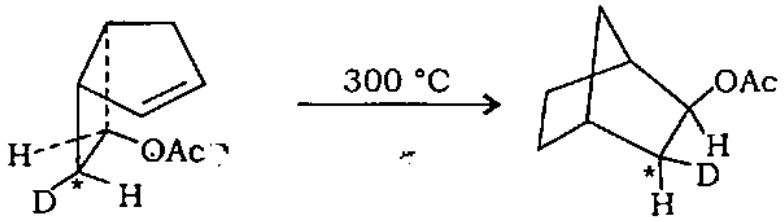
(a) Explain why the hydrocarbon with an acceptable Hückel number of $10(n-2)$ is not aromatic.

(b) Explain alternant and non-alternant hydrocarbons.

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



(d) Explain the following transformation :

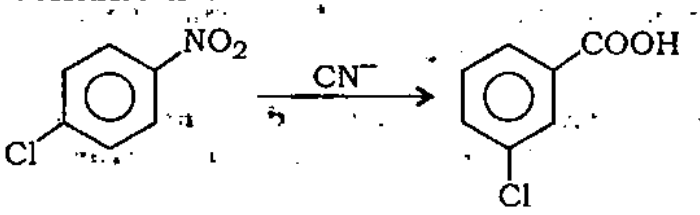


Deuterated bicyclo[3.2.0]heptene Exo-norbornal

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

$$\text{Benzaldehyde} + \text{Acetone} \xrightarrow[60\,^{\circ}C-70\,^{\circ}C]{\text{Base}} ?$$

(f) Complete the following reaction with mechanism :



(g) Explain the difference between the radicals formed by the pyrolysis of $PhN{=}N{-}C(Ph)_3$.

(h) State the product with the mechanism of furan and diazomethane condensation.

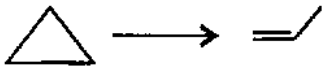
(i) Mention the physical processes in photochemical reaction.

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

(i) $H_2 + CH_3CH{=}CH_2 \rightarrow CH_3CH_2CH_3$

(ii) 

(c) A reaction vessel containing 0·192 mole of RBr undergoes the first-order reaction ($t_{½}$ = 53 s)

$$RBr + H_2O \rightarrow ROH + HBr$$

(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

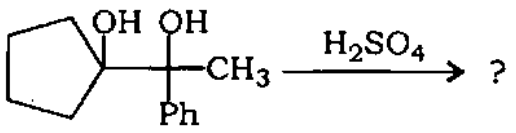
(d) Explain 'molecularity' of a reaction. Describe its types and experimental method of determination. 10

3. *(a)* Account for the rapid rate of ethanolysis of $ClCH_2OCH_2CH_3$, 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

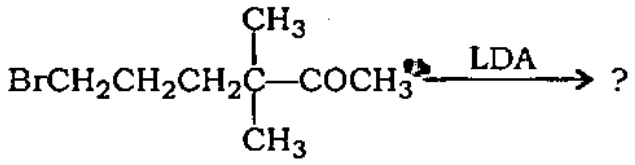
(c) Illustrate the mechanism of bromination of *cis*- and *trans*-2-butenes. 10

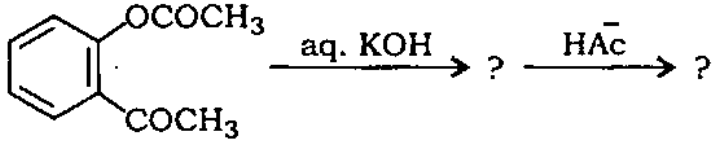
(d) Complete the following reaction and write its mechanism : 10



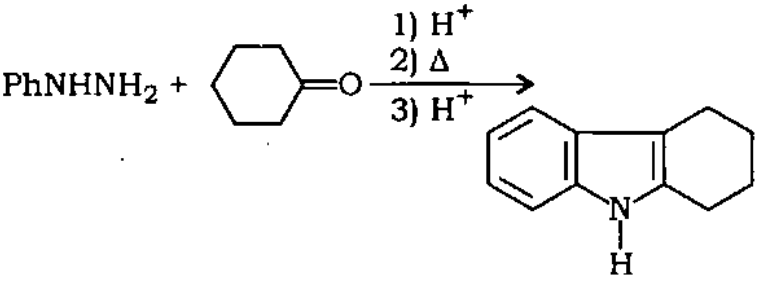
4. (a) What is ketene? How is it prepared industrially? Which products are manufactured from ketene? 10

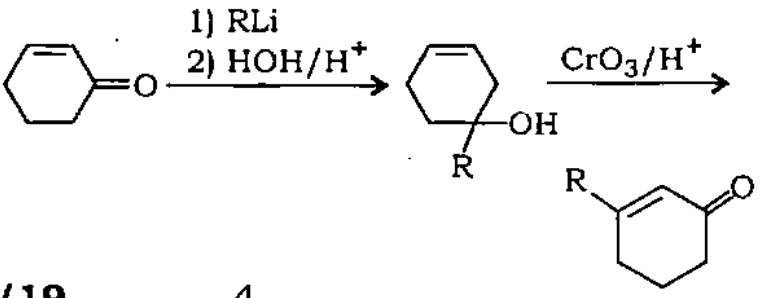
(b) Complete the following reactions indicating the sequence of events : 10

(i) 

(ii) 

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

(i) 

(ii) 

Section—B

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

(a) PVC cannot be heat moulded.

(b) $(BNH_2)_3$ 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 ($\overline{M}_n$) of polymers. Describe the experimental and calculation procedure for the determination of $\overline{M}_n$ 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

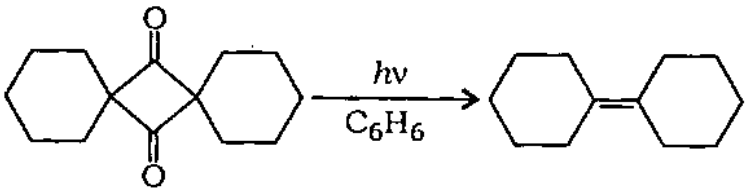
(i) High density polyethylene (HDPE)

(ii) Silicones

(iii) $(NPCl_2)_3$

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

(i)



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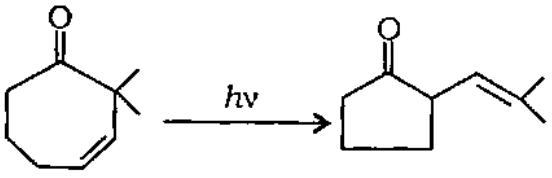
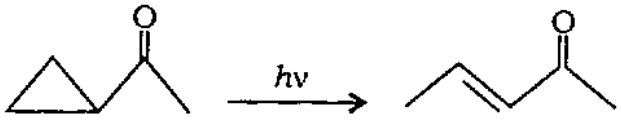
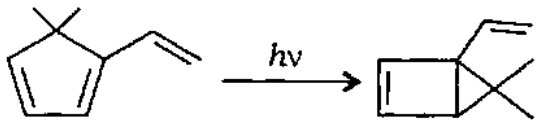
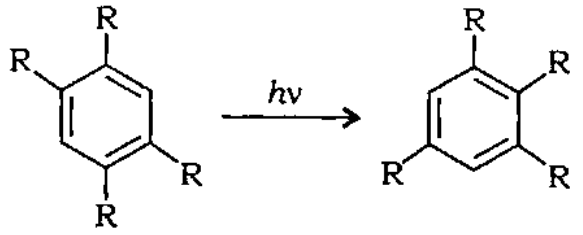


(iii)



(iv) 

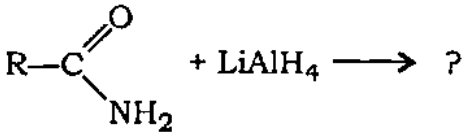
(v) 

1,2,4,5-Tetra-alkyl benzene

1,2,3,5-Tetra-alkyl benzene

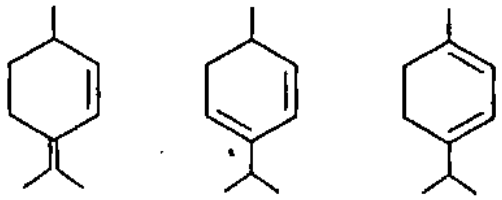
(b) Explain the mechanism of polymerization of vinyl monomer in presence of *n*-butyl lithium. 10

(c) Predict the reaction product of



5

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



(b) A compound having molecular formula $C_4H_{11}N$ exhibits the following spectral features :

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

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

$\delta = 0 \cdot 92$ (3*H*, Triplet)

$\delta = 1 \cdot 16$ (2*H*, Singlet)

$\delta = 1 \cdot 3 - 1 \cdot 5$ (4*H*, Multiplet)

$\delta = 2 \cdot 7$ (2*H*, 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}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

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