CHEMISTRY

PAPER—II

Time Allowed : Three Hours | Maximum Marks : 200

QUESTION PAPER SPECIFIC INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions

There are **EIGHT** questions in all, out of which **FIVE** are to be attempted.

Question Nos. **1** and **5** are compulsory. Out of the remaining **SIX** questions, **THREE** are to be attempted selecting at least **ONE** question from each of the two Sections **A** and **B**.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly. Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

All questions carry equal marks. The number of marks carried by a question/part is indicated against it.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

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

Neat sketches may be drawn, wherever required.

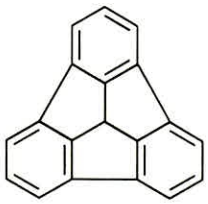
Answers must be written in **ENGLISH** only.

SECTION—A

1. Answer the following questions : 5×8=40

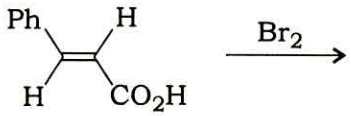
(a) Explain why the dipole moment of naphthalene is 0·00 D and that of azulene is 1·08 D.

(b) Which one of the following compounds is more acidic? Justify your answer :

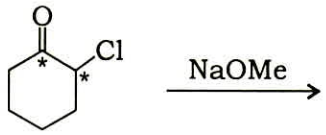


and Ph_3CH

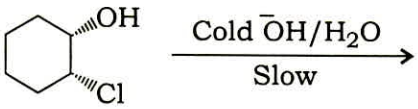
(c) Write the structure of the product(s) with proper stereochemical outcome of the following reaction and also the corresponding mechanistic pathway :

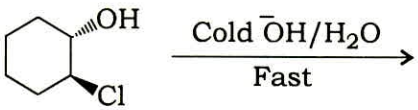


(d) Predict the products of the following reaction showing distribution of the labelled carbon (* = ^{14}C) and the mechanism :



(e) Account for the difference in reactivity of the following two reactions based on diastereomeric chlorohydrins. Write the product in each case :





(f) The initial product formed from the reaction of 2-methylcyclohexadiene and dimethylacetylene dicarboxylate on heating is transformed to another product with elimination of a small molecule. Write the structure of each product (initial and final). Also write how these are formed.

(g) Acetylation of methanol using acetyl chloride and pyridine is proposed to proceed through the following two pathways :

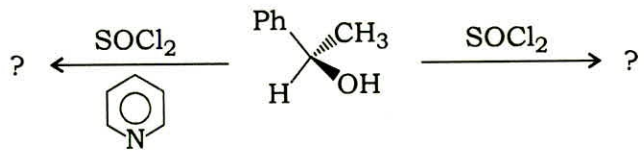
(i) Via formation of pyridinium acetate

(ii) Via formation of ketene

Can you devise an experiment to prove through which pathway the reaction actually proceeds?

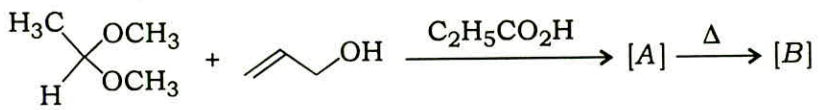
(h) When irradiated, tetrafluoroethene undergoes a cycloaddition reaction with 1-buten-3-yne to yield two products in almost equal amounts. What are the structures of these products?

2. (a) Predict the product(s) of the following reactions with proper stereochemical outcome and denote the corresponding pathways (abbreviated) : 5



(b) Explain why methyl alkyl ketones (RCH_2COCH_3) undergo aldol condensation via attack at the methyl group in the presence of base catalyst, but via attack at the methylene group in the presence of acid catalyst. 5

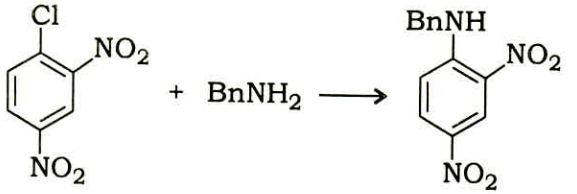
(c) Write the structures of [*A*] and [*B*] of the following sequence of reactions. Write the mechanism of their formation. What type of rearrangement and electronic shift are involved in the second step? 10

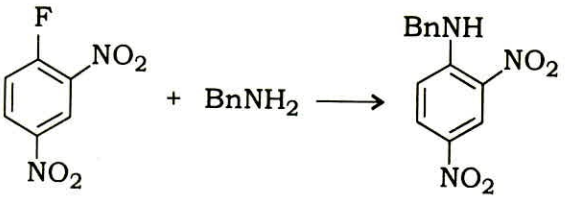


(d) What type of mechanistic pathway is involved in each case of hydrolysis of *S*, *S*- and *S*, *R*-2-acetoxycyclohexyl tosylate, separately? Which one reacts at a faster rate and why? Write the structure of the product(s) with proper stereochemical outcome and mention *R*/*S* to the chiral carbons. Write the structure of the intermediate also (where applicable). 10

(e) Account for the formation of product(s) from a reaction of 3-bromoanisole with $\bar{N}H_2$/liq. NH_3. 5

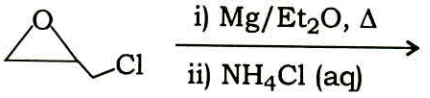
(f) Using the same coordinate system, draw two separate energy diagrams for the following two reactions. How can you denote (abbreviated form) such reactions? 5

(i) 

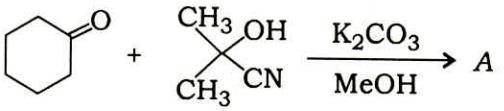
(ii) 

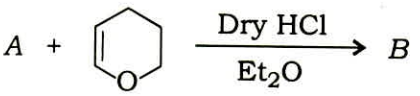
3. (a) Discuss why *p*-dimethylaminobenzaldehyde does not undergo any reaction with KCN, but a mixture of this and benzaldehyde does, giving a condensation product. Name the reaction also. 5

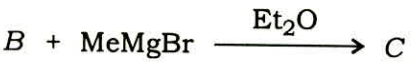
(b) Predict the product and draw the probable mechanistic pathway of the following reaction : 5

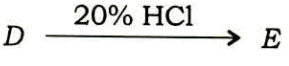


(c) Write the structures (*A* to *E*) for the following sequence of reactions : 10

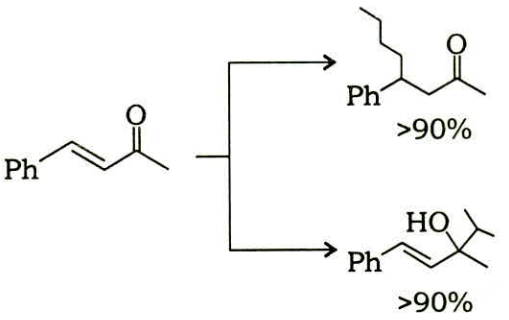




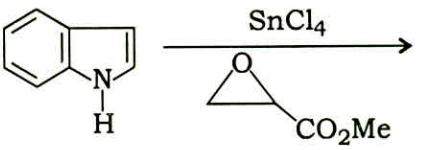




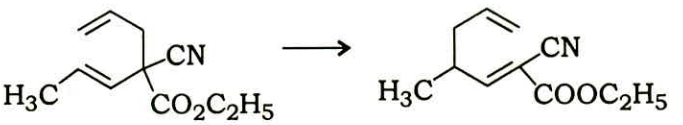
(d) Write the appropriate reagent necessary for the following two conversions and account for their formation : 10



(e) Write the structure of the product of the following reaction and the corresponding mechanistic pathway : 5

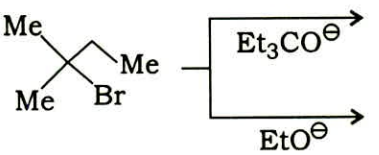


(f) Classify the following sigmatropic rearrangement and suggest if it would proceed readily or slowly. Explain your answer : 5

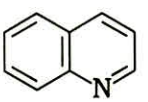


4. (a) When 4-bromonitrobenzene is reacted with cyanide ion, the product is devoid of any nitrogen. Write the structure of the product, name the reaction and write the corresponding mechanism. 5

(b) Write the structure of the major product in the following two reactions and justify their formation : 5

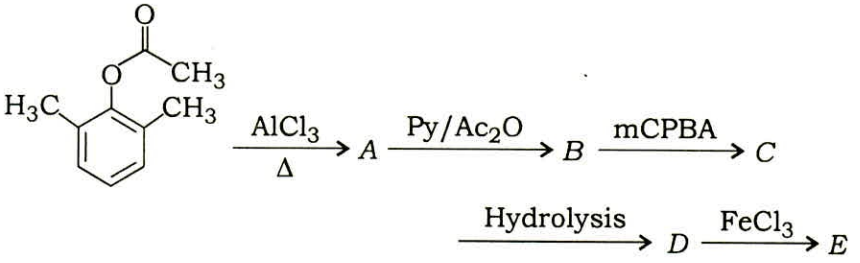


(c) Carry out the following transformations : 5×2=10

(i) Glycerol ⟶ 

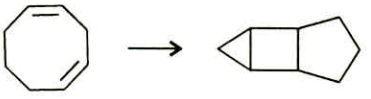
(ii) $HCHO \longrightarrow C(CH_2OH)_4$

(d) Write the structure of the products (A to E) in each step of the following sequence of reactions : 10



(e) What happens when salicylic acid is reacted with bromine in acetic acid? Justify your answer. 5

(f) Would you require the following conversion to require heat or light? Explain. 5



SECTION—B

5. Answer the following questions : 5×8=40

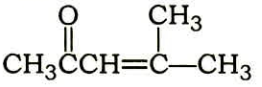
(a) Calculate $\overline{M}_n$ of a polymer consisting of three fractions with molecular weights 1×10^5, 2×10^5 and 3×10^5. The mole fractions are found to be 0·1, 0·5 and 0·4 respectively.

(b) Zimmer plot constructed from light scattering results on polymer solutions, provides useful information. Justify your answer.

(c) Determine the molecular weight of a polystyrene sample. Given $a = 0{\cdot}60$, $K = 1{\cdot}6\times10^{-4}$ dL/g and limiting viscosity number $\eta = 0{\cdot}4$ dL/g.

(d) Compound A consisting of carbon, hydrogen and oxygen shows in ^{1}H-NMR (100 MHz) a singlet (9H) in the upfield region, another singlet (2H) in downfield compared to the previous protons and a third broad singlet (1H) that appears in the most downfield region. A on heating with H_2SO_4 produces B, which again on catalytic hydrogenation produces 2-methylbutane. Write the structures of A and B, and account for the ^{1}H-NMR.

(e) 4-Methyl-3-penten-2-one has two absorption bands in its UV spectrum—one at 236 nm and one at 314 nm.

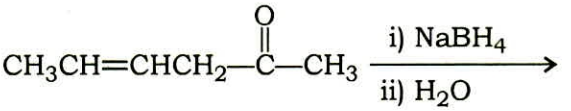


(i) Why are there two absorption bands?

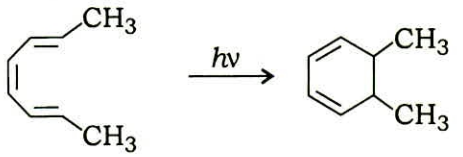
(ii) Which band shows the greater absorbance?

(f) The mass spectra of two different cycloalkanes both show a molecular ion peak at $m/z = 98$. One spectrum shows a base peak at $m/z = 69$ and the other shows a base peak at $m/z = 83$. Identify the cycloalkanes.

(g) Give the product of the following reaction :



(h) Predict the stereochemistry of the product in the following reaction :



6. (a) Give reasons for the following : 5×4=20

(i) Teflon is an inert polymer, while LDPE is a branched polymer.

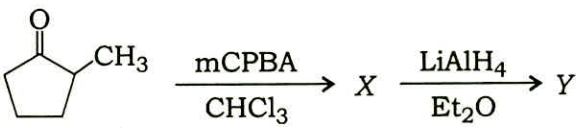
(ii) Natural rubber on masticating with about 30% sulphur becomes a hard plastic.

(iii) Proteins are considered as monodispersed polymers.

(iv) Threshold molecular weight of polyethylene is higher than that for nylons.

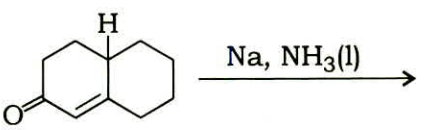
(b) Ethylbenzene shows a characteristic peak at $m/z = 91$, while *n*-propylbenzene shows strong peak at $m/z = 92$. Explain with the help of fragmentation pattern. 10

(c) Identify the compounds *X* and *Y* in the following transformation : 5



(d) Which will show an oxygen-hydrogen stretch at a greater wave number—ethanol dissolved in carbon disulfide or an undiluted sample of ethanol? Justify your answer briefly. 5

7. (a) Write the structure of the major and minor products formed in the following reaction and give a suitable explanation : 10



(b) Justify your answers for the following statements : 5×4=20

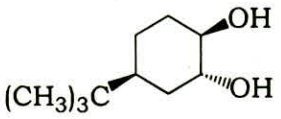
(i) Light scattering is a highly useful technique for the determination of molecular weight of a polymer.

(ii) The determination of molecular weight by end-group analysis of a polymer is carried out only if the number of determinable groups of molecules is known.

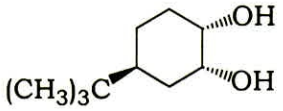
(iii) Osmometric method is preferred over viscosity method for the determination of molecular weight of a polymer.

(iv) Softening temperature of nylon 6,6 is higher than that of nylon 6,10.

(c) Of the following two compounds *A* and *B*, one cannot be oxidized by periodic acid. Identify it and justify your answer : 10



A



B

8. (a) 2,2-Dimethylcyclopropanone undergoes ring-opening when attacked by methoxide ion. The product (b.p. 101 °C) has the following spectral properties :

IR : 1740 cm^{-1} (s), 1160 cm^{-1} (no absorption near 1600 cm^{-1} or 3100 cm^{-1})

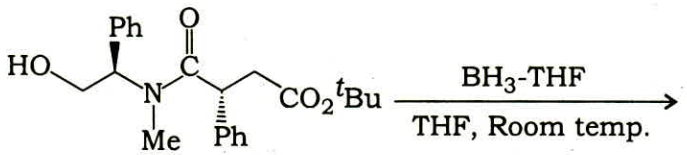
^{1}H-NMR : δ 3·6 (3H, singlet), δ 1·2 (9H, singlet)

UV : Transparent above 200 nm

Mass : *m/z* 116, 85, 59, 31

Deduce the structure of the product and assign the spectral data. From the mechanism, an alternative product might have arisen. What is it? 15

(b) (i) Write the structure of the product in the following reaction :



How many moles of BH_3 are needed to react with 2 moles of the starting material? 5

(ii) What stereoisomer would be formed from the reaction of cyclopentene with OsO_4 followed by hydrolysis? Explain. 5

(iii) Draw the ESR spectrum of $CH_3\dot{C}HOCH_2CH_3$. 5

(c) Sketch the chemical reactions in the preparation of polystyrene starting from benzene and list a few important properties. 10

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