1. Fis-2009

Sl. No.

7424

B-JGT-J-DIB

CHEMISTRY

Paper II

Time Allowed: Three Hours

Maxinum Marks: 200

INSTRUCTIONS

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

Marks for each question are indicated against each.

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

Answers must be written in ENGLISH only.

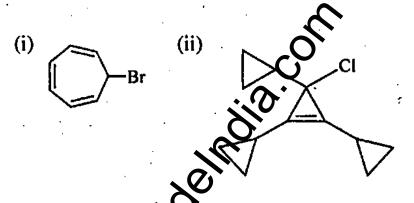
Unless otherwise indicated, symbols and notations have their usual meanings.

Section - A

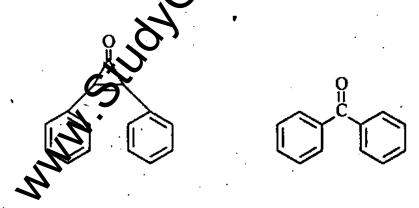
1. Answer any *four* of the following (in about 150 words each): 10×4

Explain the following briefly:

(a) Formation of corresponding stable ions from the following molecules.



(b) Which of the following two compounds will have higher dipole moment and why?



(c) Write the product and outline mechanistic steps for its formation

$$\bigcirc = O \xrightarrow{\text{Mg, ether}}$$

- (d) Will an amide be formed from the reaction of an acyl chloride with an aqueous solution of pyridine?
- (e) Why should cyclopentadiene show acidic properties?
- 2. (a) Write structure of B, C and D. Explain the formation of products.

$$\begin{array}{c|c}
OH & & & & \\
\hline
 & H_2SO_4 \\
\hline
 & 100^{\circ}C
\end{array}$$

$$B \xrightarrow{Br_2} \xrightarrow{H^+} D$$

(b) Predict the product and outline mechanistic steps for following reaction. 5+5

(c) Redict the possible products of following Diels Alder reaction and explain which product is preferentially formed and why?

3+3+4

$$CH_2$$
=CHCH=CHOCH₃ + CH_2 =CHCH \longrightarrow A + B

(d) Write the structure of the product formed in the following reaction. Explain briefly its formation.

5+5

$$CH_3$$
 $+ H_2$ Pd

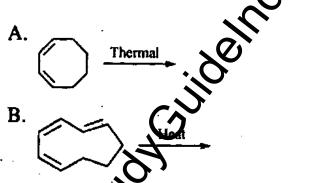
, 3. Give the name of the reaction and explain the mechanism involved in the formation of the products.

(a)
$$\frac{}{}$$
 $\frac{}{}$ $\frac{}{}$

$$(d) \qquad CI \qquad RO^- \qquad \bigcirc COOR$$

4. Explain briefly

- (a) While writing the Diels Alder products for reaction of 2,4,6-cycloheptatrienone with cyclopentadiene and with ethene respectively, why does it use two pi electrons with cyclopentadiene while with ethene it uses four pi electrons?
- (b) Why lycopene and beta carotene appear coloured in nature?
- (c) Predict the product of following electrocyclic reactions. Indicate and comment upon the steric positions of hydrogens in the product.



(d) Draw the structure of [18]-Annulene and show how many types of NMR signals are given by it. Explain.

Section - B

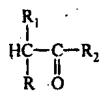
5. Answer any four of the following:

(a) Use aldol condensation to synthesize useful compound from cheap and readily available compounds/reagents, the food preservative sorbic acid,

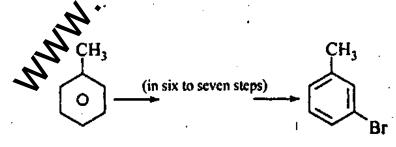
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10

(b) Considering bromination of carbonyl compounds as acid catalysed, suggest a reasonable mechanism in which enol is an intermediate, use the following compound.



- (c) Reaction of 1 mole of semicarbazide with a mixture of 1 mole each of cyclohexanone and benzaldehyde precipitates exclohexanone semicarbazone, but after a few bours the precipitate is benzaldehyde semicarbazone. Explain. 10
- (d) Why attack of GN on benzaldehyde does not bring about Caprizzaro reaction while that of OH- brings about it. Write the mechanistic steps and products in the two cases.
- (e) Effect the following conversion 10



6. (a) Why carboxylic acid group of amino acids is more acidic (pKa = 2) than carboxylic acid group of acetic acid (pKa = 4.76)?

(b) Arrange the following alkenes for their increasing rate of bromination in methanol. Justify in a few lines. 5+5

$$Me$$
 $C = CH_2$

(iii)
$$Me$$
 $C = <_H^{Me}$

$$C = CH_2$$

(c) Write reaction products in the following:

(ii) OH
$$\frac{\text{SbF}_5\text{-HF}}{\text{Br}_2}$$
? 2

$$\begin{array}{ccc}
\text{(v)} & \text{OH} & \\
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$$\begin{array}{c|c}
 & Cl \\
 & & 450^{\circ}C
\end{array}$$
?

(ix)
$$O$$
 NHOH O ?

$$\begin{array}{c|c}
(x) & NO_2 \\
\hline
0 & O & NH_2OH2
\end{array}$$
?

$$(xi)$$

$$CH_2N^+M_3X^-$$

$$NaNH_2$$
?

(xii) HO OH +
$$CH_3CN$$
 $\frac{ZnCl_2}{HCl}$? $\frac{H_2O}{\triangle}$? Ether -10 - 0°C

3

7. (a) A compound with molecular formula C₈H₁₄O shows the following proton NMR, and IR bands.

The singlet at δ 3·1 in the proton NMR disappears when the sample is shaken with D₂O. IR: 3500 cm⁻¹, 3300 cm⁻¹, 2100 cm⁻¹.

¹HNMR : d (6H, δ 1·0), s (3H, δ 1·5), d (2H, δ 1·6), m (1H, δ 1·9), s (1H, δ 3·1).

Determine the structure of the compound, with justification. 15

(b) When 1-butanol is dissolved in superacid at -60° C the ¹H NMR shows signals at δ 9.5 (2H, t), δ 5 (2H, ti). On raising the temperature to above 0°C all the above signals decrease largely and then the ¹H NMR is dominated by a new singlet at δ 4.0.

Explain the results.

10

(c) A hydrocarbon in its mass spectrum showed molecular ion at m/z = 134 and prominent agments at m/z = 119 and 77. The spectral data for this compound are as follows:

¹H NMR δ = 7·0 (s, 4H); 2·82 (heptet, J = 7·0 Hz, 1H), 2·28 (s, 3H) and 1·22 ppm (d, J = 7·0 Hz, 6H); ¹³C {¹H} NMR δ = 21·3, 24·2, 38·9, 126·6, 128·6, 134·8, and 145·7 ppm; IR bands at 3030, 2970, 2880, 1515, 1465 and 815 cm⁻¹; UV λ _{max}(ε) = 265 (450).

What is its structure? Justify your answer. 15

- 8. (a) Explain the following with a suitable simple example for each
 - (i) Co-polymer
 - (ii) Coordination polymerization. 5+5
 - (b) Examine the structures of the following synthetic polymers. Tell what class of compounds it belongs to and give structure of the likely monomers.
 - (i) C(CH₂)₄CNH(CH₂)₆NHCCH₂)₄CNH
 - (ii) CCH₂(CH₂)₄NH₂ NH₂ O
 - (iii) CH2CH2OCH2CH2OCH2CH2CH2

(v) CH₂CCl₂CH₂CCl₂

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