

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 no. 1 & 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 chronological 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 answer book must be clearly struck off.

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

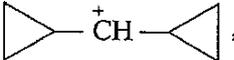
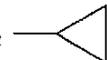
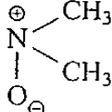
Answers must be written in ENGLISH only.

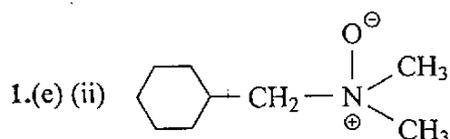
Unless otherwise mentioned, symbols and notations have their usual standard meanings.

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

Neat sketches may be drawn, wherever required.

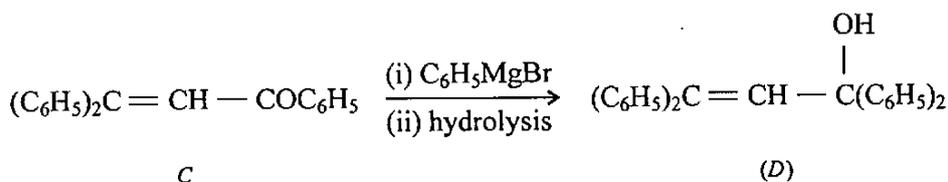
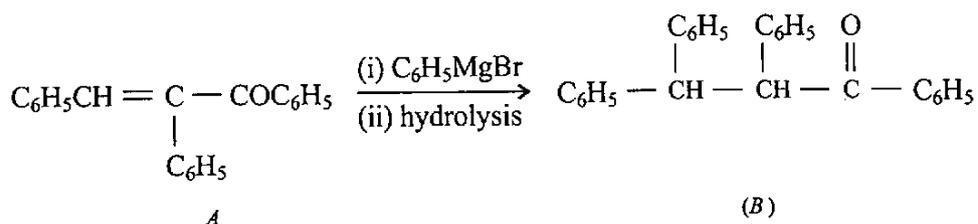
SECTION 'A'

1. Answer the following : 5×8=40
- 1.(a) The base catalysed reaction of pyrrole with formaldehyde gives a compound, $C_{20}H_{14}N_4$.
Is it aromatic ? Explain with its importance in nature. 5
- 1.(b) Amines are more water-soluble than alcohol of similar molecular weights. Offer suitable explanation for this fact. 5
- 1.(c) Arrange the following carbocations in order of their increasing stability with reasoning : 5
- $\overset{+}{C}H_2-CH_2CH_2CH_3$, , $\overset{+}{C}H_2-$ 
- 1.(d) Compare the rates of S_N1 and S_N2 reactions of 1-chlorobicyclo [2:2:2] octane and 9-chloro decalin. 5
- 1.(e) Designate the reaction and products by heating : 5
- 1.(e) (i) $CH_3CH_2CH_2$ 

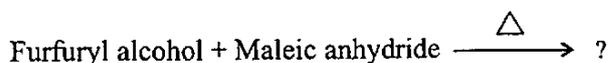


1.(f) Compare the reaction of $\text{H}_2\text{C}=\text{CH}_2$ and $\text{F}_2\text{C}=\text{CF}_2$ with KOEt in ethanol. 5

1.(g) The reactions of Grignard reagent and subsequent hydrolysis with compound A gives (B) whereas compound C gives (D) in 100% yield. Explain with suitable reason. 5



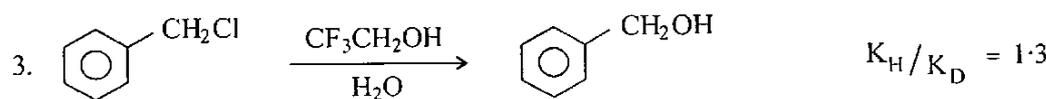
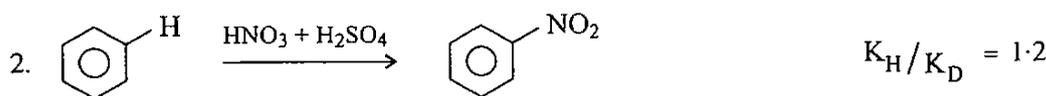
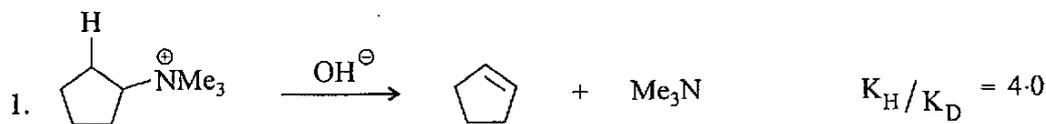
1.(h) Complete the following reaction with designation



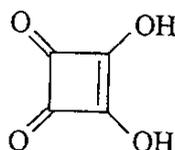
5

2.(a) (i) What is primary and secondary isotope effects ?

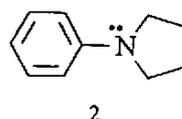
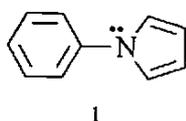
2.(a) (ii) Identify which of the reactions display primary isotope effect and which the secondary effect 10



- 2.(b) Discuss the molecular structure and physical properties of graphite. 10
- 2.(c) Triphenylmethyl radical is not so stabilized by delocalization of the unpaired electron as expected. Comment on this observation. 10
- 2.(d) (i) Why the following cyclic diol (squaric acid) is almost strong an acid as H_2SO_4 ? 5



- 2.(d) (ii) The rotational energy barrier around the C-N bond of compound 2 is higher than compound 1. 5



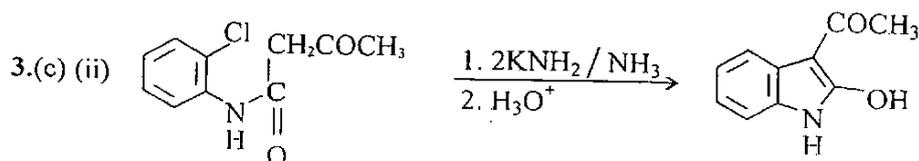
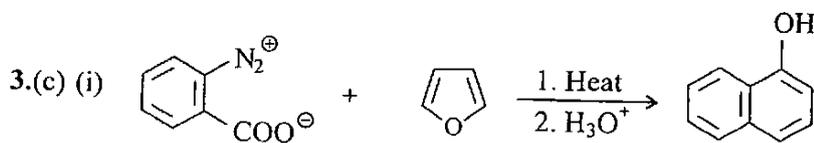
- 3.(a) When (R)-2-bromopropanoate ion is treated with concentrated NaOH, (S)-2-hydroxypropanoate ion is obtained. However, when the same reaction is carried out with a low concentration of hydroxide ion in the presence of Ag_2O , (R)-2-hydroxypropanoate ion is obtained. Account for this observation. 10

- 3.(b) Give the stereochemistry of products formed when

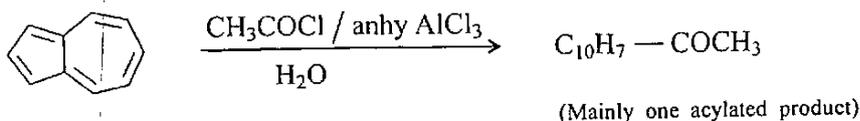
- 3.(b) (i) cis, trans-2,4-hexadiene reacts thermally

- 3.(b) (ii) trans, cis, trans-2,4,6-octatriene reacts photochemically 10

- 3.(c) Suggest a mechanism for the following reactions $5 \times 2 = 10$



3.(d) Friedel-Crafts acylation of azulene gives mainly one acylated product



Which ring of azulene does undergo attack by CH_3CO^+ preferentially and why? Give the mechanism of the reaction. 10

4.(a) What is Steven's rearrangement? Bring out the different mechanisms that have been proposed for this rearrangement by giving the supporting evidences for each of them (including CIDNP studies). 20

4.(b) Outline the synthesis of the following as indicated showing the reagents used and mechanism. 5×2=10

4.(b) (i) $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_2\text{COOC}_2\text{H}_5$ from ethyl benzoate using Reformatsky reaction

4.(b) (ii) Cyclopentanone by Dickman condensation

4.(c) Using Skraup synthesis how would you prepare 5×2=10

4.(c) (i) 4-Methyl quinoline

4.(c) (ii) 3-Ethyl quinoline

SECTION 'B'

5. Attempt the following : 8×5=40

5.(a) Natural rubber and Gutta percha rubber, two polymers, have the same composition of monomers, their properties are radically different. Account for this. 8

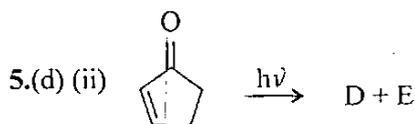
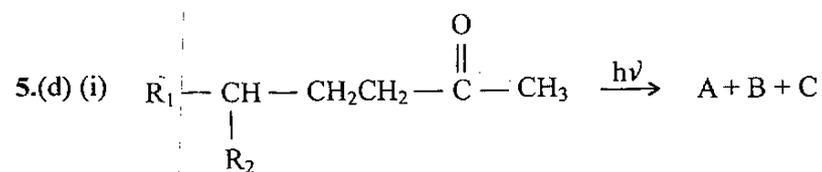
5.(b) Write the name and structure of the bases present in RNA and DNA. 8

5.(c) The compound with molecular formula $\text{C}_6\text{H}_{10}\text{O}$ shows the following IR and ^1H NMR spectra. Write the most probable structure of the compound.

$^1\text{H-NMR}$: δ 3.31 (s, 3H); δ 2.41 (s, 6H); δ 1.43 (s, 1H)

IR ν_{max} : 2110, 3300 cm^{-1} 8

5.(d) Give the mechanism for the following conversion 4×2=8

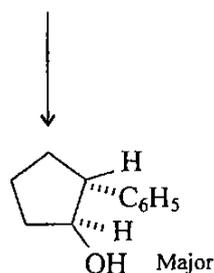
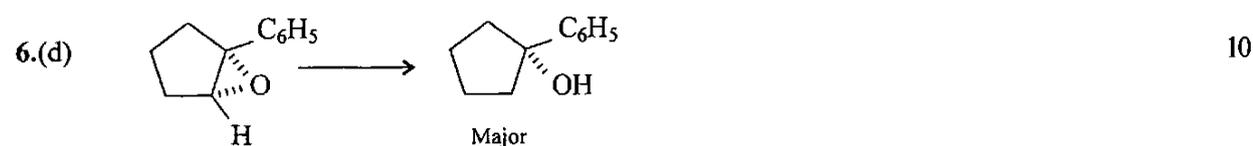
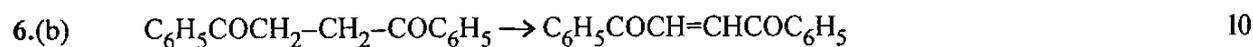
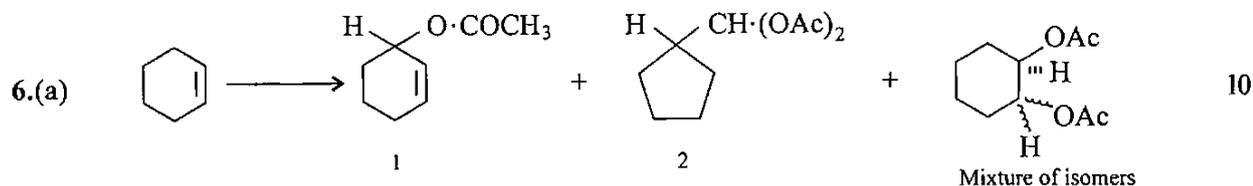


5.(e) Discuss the synthesis of the following polymers showing their chemical reactions 4×2=8

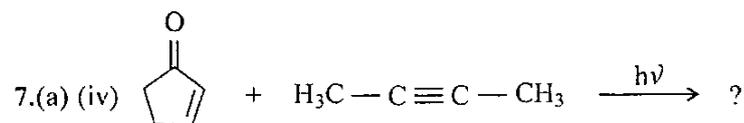
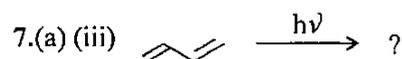
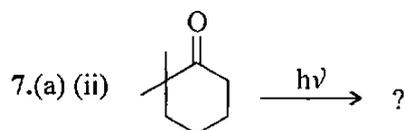
5.(e) (i) Teflon

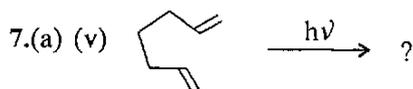
5.(e) (ii) Terylene

6. How would you convert the following ? Propose mechanism.

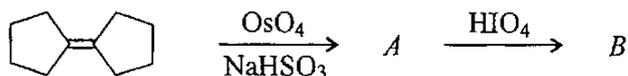


7.(a) Predict the product(s) of the following : 4×5=20





7.(b) Write the products for the following reaction. Propose suitable mechanism for the formation of products 10



7.(c) EPR spectrum of Bis-Salicylaldimine copper (II) showed only eleven peaks instead of fifteen peaks. Account for this. 10

8.(a) Propose a structure consistent with the following spectral data for a compound of molecular formula $C_8H_{18}O_2$

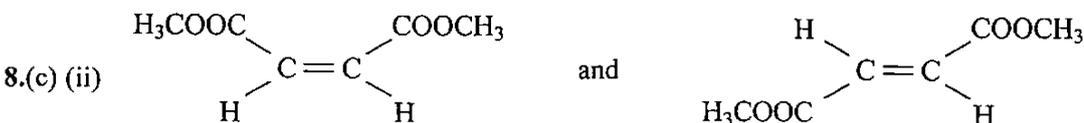
IR ν_{\max} : 3350 cm^{-1}

$^1\text{H-NMR}$: δ 1.24 (s, 12H); δ 1.56 (s, 4H); δ 1.95 (s, 2H) 10

8.(b) Explain why in the mass spectrum of bromobenzene, there will be two peaks at m/z 156 and 158 of approximately equal intensity. 10

8.(c) Which spectroscopic tool or tools (UV, NMR, IR) would you use to distinguish the two members of each of the following pairs of compounds? What features of the spectrum would be most diagnostic of the structure?

8.(c) (i) $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$ and $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}_2$



8.(c) (iii) $\text{CH}_3\text{COOCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CO}\cdot\text{OCH}_3$ 10

8.(d) A compound of m.f. $C_9H_{11}NO_2$ exhibits the following spectral characteristics. Assign a suitable structure and account for the spectral data

UV λ_{\max} : 250 nm

IR ν_{\max} : 1670, 3170 and 3320 cm^{-1}

$^1\text{H-NMR}$: δ 7.8 (d, 2H); 6.7 δ (d, 2H); 4.2 (q, 2H)

δ 4.0 (broad s, exchangeable with D_2O); δ 1.2 (t, 3H)

$^{13}\text{C-NMR}$: δ 165 (s), 151(s), 130 (d), 119 (s), 112 (d), 59 (t), 12 (q) 10