

SECOND EXAMINATION IN SCIENCE 1994/ 95 (AUGUST/SEPT 1997)/ REPEAT

ORGANIC SPECTROSCOPY, REACTION MECHANISM AND AROMATICITY (CH202)

Time : 02 Hours

Answer **FOUR** questions only .

1.) Answer **All** the parts.

a.) Write the definitions of the following terms

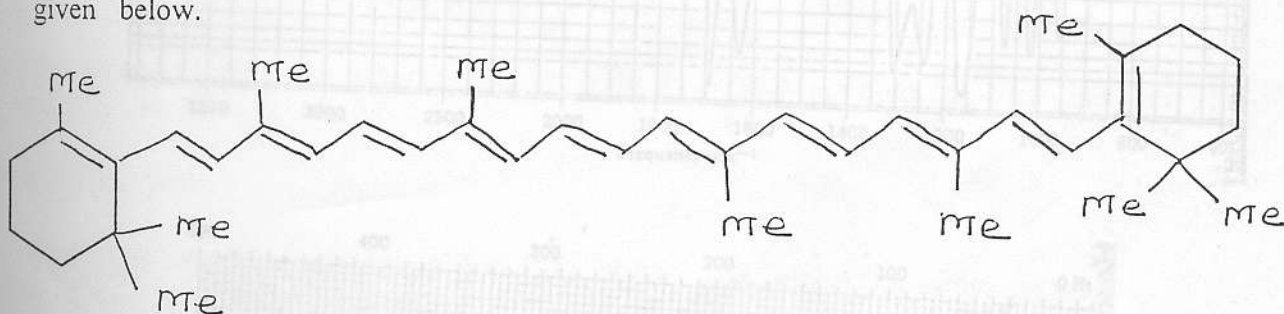
- i.) Coupling Constant
- ii.) Base Peak
- iii.) Auxochrome
- iv.) Symmetric stretching vibration

b.) i.) The Fieser-Kuhn equation for calculating the λ_{max} values of polyenes in hexane solution is given below

$$\lambda_{max} = 114 + 5M + n(48.0 - 1.7n) - 16.5R_{endo} - 10R_{exo}$$

Explain all the terms in the above equation.

Calculate the longest wavelength λ_{max} value of β -carotene whose structure is given below.



ii.) Using the Woodward-Fieser-Scott Rules calculate the λ_{max} value in the UV spectrum of the compounds given below.

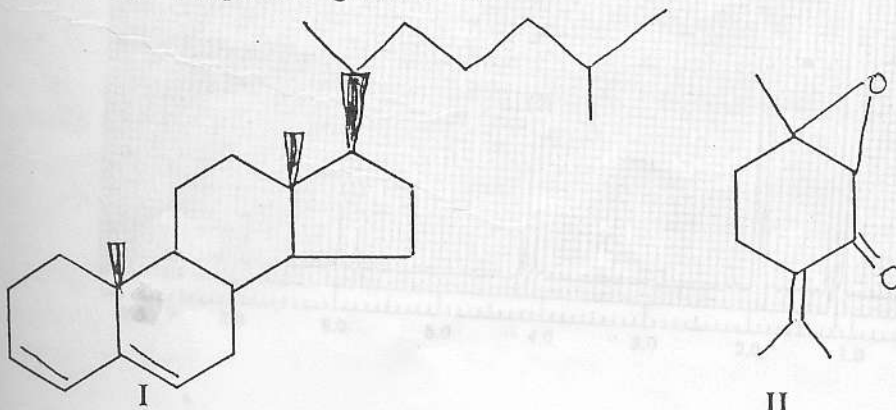


FIGURE - I

- c.) When dissolved in CDCl_3 , a compound **K** with the molecular formula $\text{C}_4\text{H}_8\text{O}_2$ gives a ^1H NMR spectrum that consists of a doublet at δ 1.35, a singlet at δ 2.15, a broad singlet at δ 3.75 (1H) and a quartet at δ 4.25 (1H). When dissolved in D_2O , the compound gives a similar proton NMR spectrum with the exception that the signal at δ 3.75 has disappeared. The I.R. spectrum of the compound shows a strong absorption peak near 1720cm^{-1} .
- i.) Propose a structure for compound **K** and explain why the NMR signal at δ 3.75 disappeared when D_2O is used as the solvent.

2.) Answer all the parts.

- a.) Suggest a structure for the compound $\text{C}_6\text{H}_{10}\text{O}_2$, Whose IR and NMR spectra are reproduced in Figure I

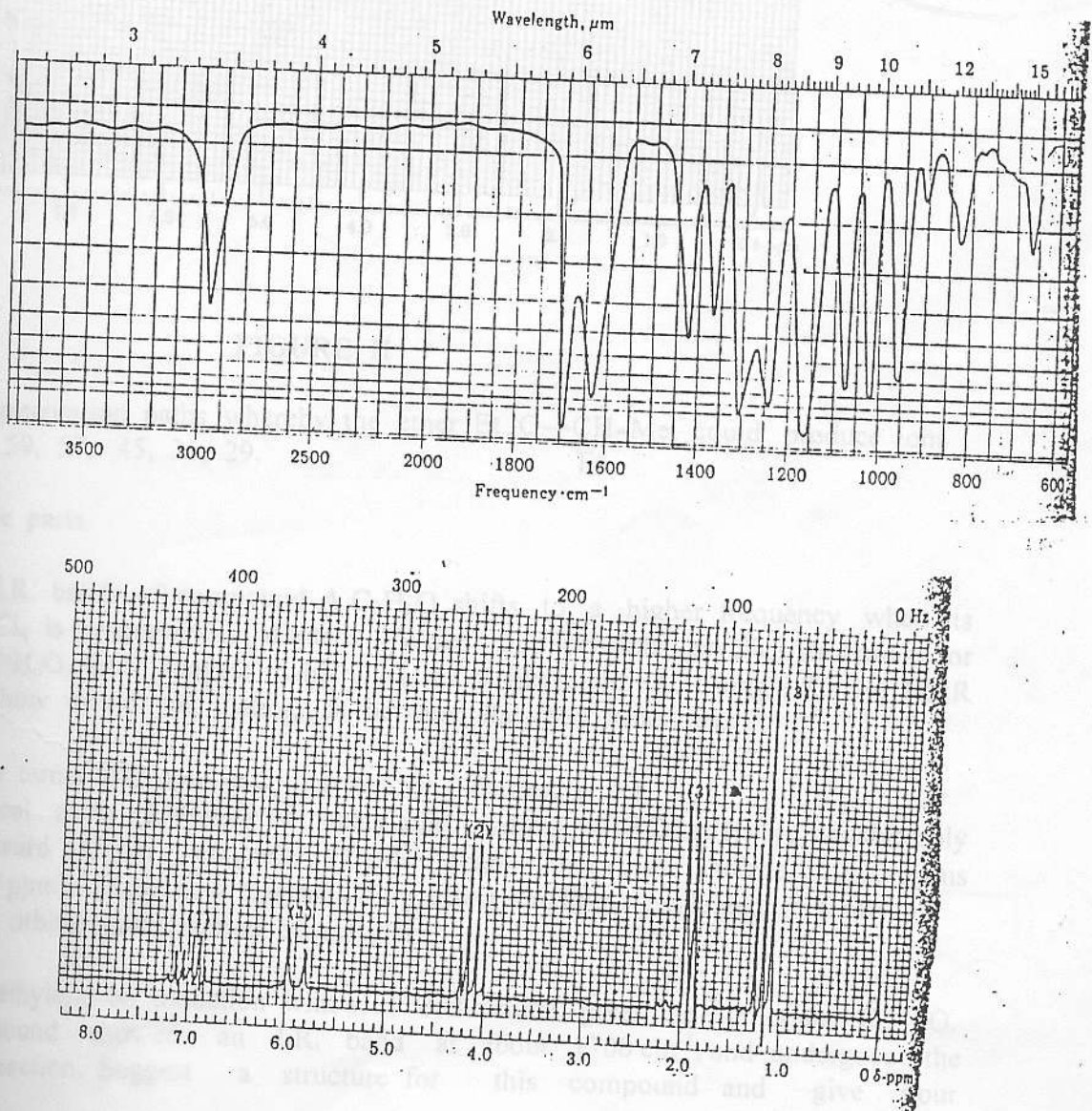


FIGURE - I

- b.) A high-boiling organohalogen compound shows mass spectral ion peaks at m/z 154 and 156 with relative intensities of 3:1. The IR spectrum has a characteristic absorption at 1695cm^{-1} . Figure II reproduces the NMR spectrum. Suggest a structure for the compound.

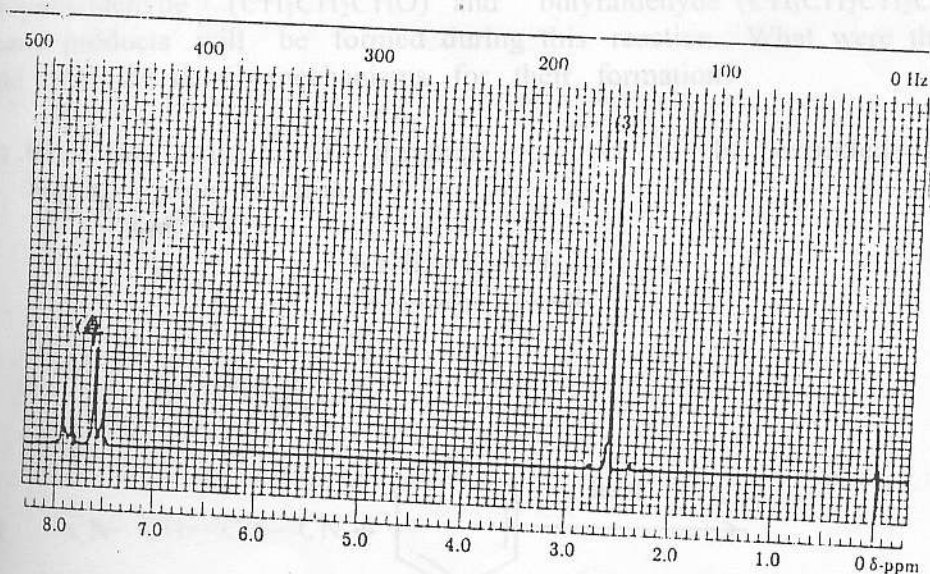


FIGURE II

- .) Show the fragmentation paths whereby the ether $\text{Et}-\text{O}-\underset{\text{Et}}{\text{CH}}-\text{Me}$, could produce ions m/e 102, 87, 59, 57, 45, 31, 29.

.) Answer all the parts.

- .) One of the I.R. bands of compound A $\text{C}_3\text{H}_6\text{O}$ shifts to a higher frequency when its solution in CCl_4 is progressively diluted. Write four possible acyclic structures for the formula $\text{C}_3\text{H}_6\text{O}$, and suggest which is most likely for A. Using I.R. and NMR spectroscopy how would you distinguish between the four structures.

- i.) Explain the terms spin-spin coupling and ring current effect.
 ii.) The chemical shifts (2.4ppm) of acetylenic hydrogens ($\text{RC}\equiv\text{CH}$) are considerably more toward higher magnetic fields than those of alkene hydrogens (4.6 to 6.9 ppm). Show how this shielding effect might be explained in terms of the atomic orbital representation of acetylenes.

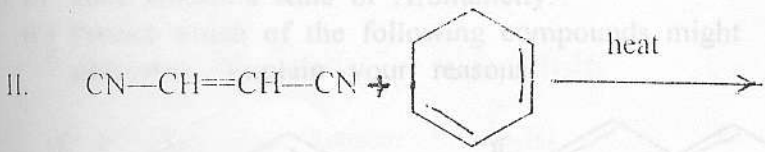
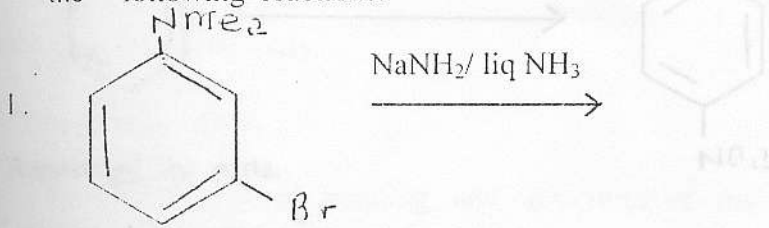
- i.) Tetramethylethylene on oxidation with acid dichromate gives the compound $\text{C}_6\text{H}_{12}\text{O}$. This compound showed an I.R. band at about 1700cm^{-1} , and undergoes the haloform reaction. Suggest a structure for this compound and give your reasons.

ii.) An aliphatic ketone M.W. 86, when converted into its oxime, which is then reduced gives an amine that can be resolved. What is the ketone?
 If more than one is possible, how could they be distinguished by a physical method?

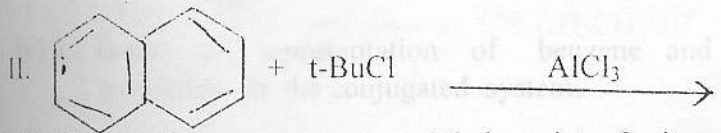
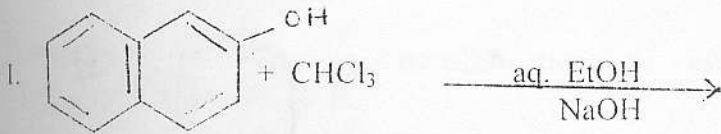
4.) Answer all the parts.

a.) An aldol condensation was carried out on equal amounts of propionaldehyde ($\text{CH}_3\text{CH}_2\text{CHO}$) and butyraldehyde ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$). How many products will be formed during this reaction. What were their structures, and write the detail mechanisms for their formation?

b. i.) Write the structure of the major product to be expected from each of the following reactions.

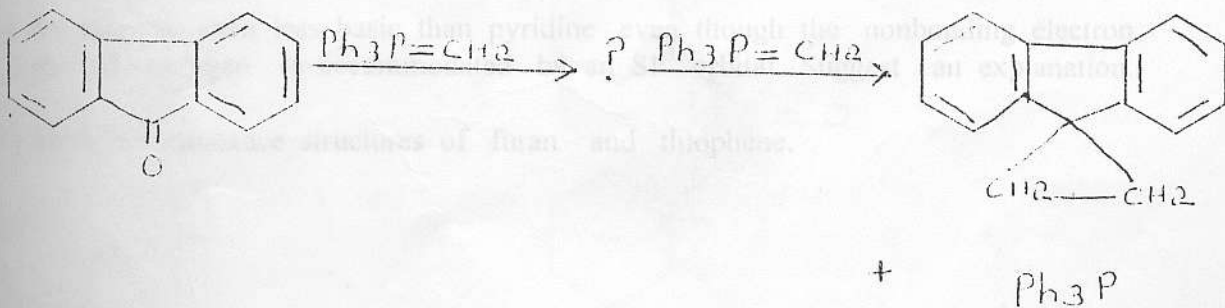


ii.) Complete the following equations.



c. i.) How could you convert naphthalene into 2-nitronaphthalene

ii.) Complete the equation and suggest the mechanism involved in the reaction sequence





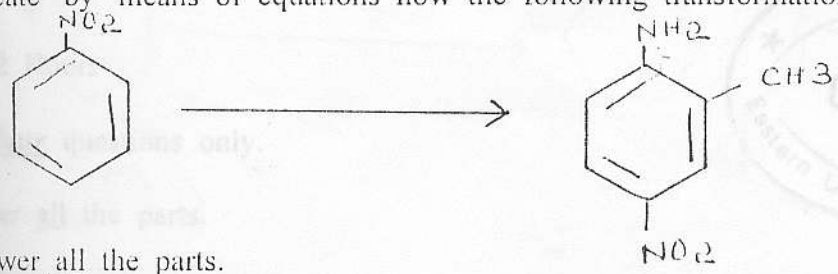
5.) Answer all the parts.

a.) Give the mechanisms of the following reactions.

- i.) Benzoin Condensation.
- ii.) Perkin Reaction.
- iii.) Claisen Condensation.

b.) i.) Starting from benzene, outline the preparation of benzenediazonium chloride and discuss the use of this compound in the preparation of aromatic halides.

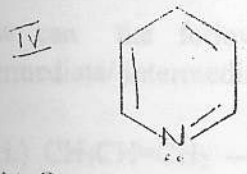
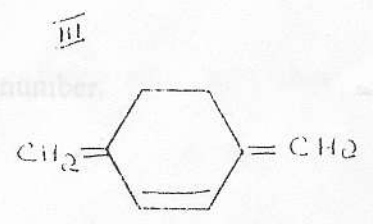
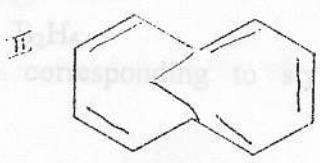
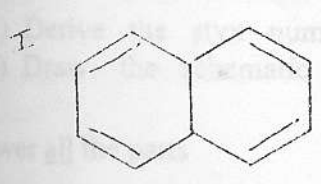
c.) Indicate by means of equations how the following transformation could be effected.



6.) Answer all the parts.

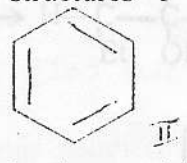
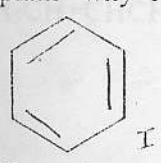
a.) i.) State Huckel's Rule of Aromaticity.

ii.) Predict which of the following compounds might be expected to show aromatic properties. Explain your reasons.



b.) i.) Draw a representation of benzene and pyrrole that shows the interacting p orbitals in the conjugated system.

ii.) Explain why resonance structures I and II are equal in stability.



c.) i.) Aniline is even less basic than pyridine even though the nonbonding electron pair of nitrogen is accommodated by an sp^3 orbital. Suggest an explanation.

ii.) Draw the resonance structures of furan and thiophene.