

CHEMISTRY
Paper – III

Time Allowed : **Three Hours**

Maximum Marks : **200**

Question Paper Specific Instructions

Please read each of the following instructions carefully before attempting questions :

*There are **TEN** questions divided under **TWO** sections.*

*Candidate has to attempt **SIX** questions in all.*

*Question No. **1** in Section A and Question No. **6** in Section B are **compulsory**. Of the remaining questions, candidates have to answer **FOUR** questions, choosing **TWO** from each Section.*

The number of marks carried by a question / part is indicated against it.

Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.

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

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

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.

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

- Q1.** (a) From the following data, determine the mass of the sample that should be analyzed to obtain sampling standard deviation of $\pm 5\%$ 5

Given Data

Sample mass (g)	Relative standard deviation (%)
0.1	15
1.5	6
9.2	2.5

- (b) Write the van Deemter equation and briefly discuss its significance. 5
- (c) How can concentration of a non-absorbing analyte be measured by UV-vis spectrophotometry ? 5
- (d) Show the flame absorption profiles for magnesium and silver with respect to flame height. Justify. 5
- (e) What happens in the thermogravimetric analysis for the following conditions ?
- (i) Higher furnace heating rate
 - (ii) Larger particle size of sample
 - (iii) For sample undergoing endothermic reaction 5
- (f) Explain the working principle of quadrupole mass analyzer in ICP-MS. 5
- (g) Briefly outline the gravimetric method for the estimation of nickel content in steel sample. 5
- (h) The powder X-ray diffraction pattern (first order) of a metal is measured with Cu – K_{α} radiation source ($\lambda = 1.539 \text{ \AA}$). Calculate the lattice spacing of the material for diffraction measured at $2\theta = 60^{\circ}$. 5

- Q2.** (a) In an HPLC measurement, a solute has a retention time of 21.0 min and an unretained species is eluted in 1.0 min using a mobile phase comprising 20% (vol by vol) methanol and 80% water. Determine the composition of methanol and water to elute the solute corresponding to retention factor 5.0.

Given :

- (i) Polarity index of water is 10.2, methanol is 5.1;
- (ii) $\log 2 = 0.301$ 10

- (b) Briefly describe the principle involved in ion-exchange chromatography. Arrange the retention time of Li^+ , Ag^+ , Zn^{2+} , and Co^{3+} for a strong acid resin in an ion chromatograph. Give reasons for the sequence of retention of these species. 9+6=15

- (c) The Fe content in an iron ore sample is analyzed at five different laboratories using the same analytical method. The Fe contents are given below as wt% :

60.5%, 61.5%, 68.5%, 52.0% and 62.5%

Using the Q-test, find if any of the above data is due to accidental error and can be rejected. 5

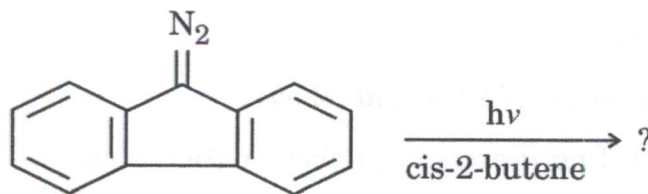
Given : Q_{95} for five analysis is 0.710.

- Q3.** (a) (i) Why does AAS analysis of calcium in a phosphate buffer solution give poor result ? Suggest a method to improve the determination of calcium by AAS in the above solution. 10+5=15
- (ii) Take an example to describe how protective agents improve AAS analysis. 5
- (b) What is a two line correction method in AAS measurement ? 10
- (c) What is a Globar and how does it act as an IR source ? What is the advantage of Globar as compared to Nernst Glower ? 10
- Q4.** (a) Thermogravimetric analysis of a mixture of anhydrous CaCO_3 and CaO recorded between 500°C and 900°C indicates a weight loss from 290.60 mg to 230.80 mg. Determine the percentage of CaCO_3 in the mixture. 10
- Given : Molecular weight of CaCO_3 is 100.1 mol g^{-1} and CaO is 56.1 mol g^{-1} .
- (b) What are the interferences in inductively coupled plasma mass spectrometry ? How are they eliminated ? 10
- (c) Write the significance of ultimate analysis of coal. Describe the method for estimation of ash content in coal sample. 10
- Q5.** (a) Briefly outline the basic theory and instrumentation of energy dispersive X-ray fluorescence spectroscopy. 6+9=15
- (b) How are aniline point, cloud point and pour point relevant in the analysis of petroleum products ? 10
- (c) Describe the method for estimation of TiO_2 in bauxite. 5

SECTION B

- Q6.** (a) Carbenes exist in singlet and triplet states. Which of the two states of carbenes is non-stereospecific in its reaction with alkenes? Explain why. Predict the product/s formed in the following reaction :

4



- (b) The rate of addition of bromine to styrene ($\text{Ph} - \text{CH} = \text{CH}_2$) is greater than propene ($\text{CH}_3 - \text{CH} = \text{CH}_2$). Provide a suitable explanation with mechanisms for both.

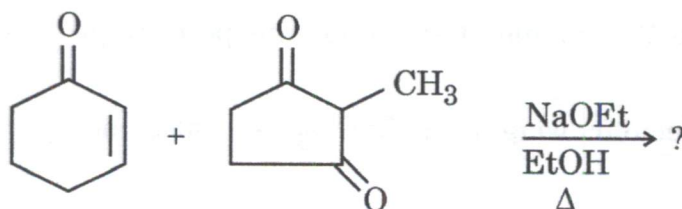
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- (c) The reaction of propanoic acid with HCl can form two possible products, but only one is formed in major quantity. Write the structure of the two products and give suitable explanation.

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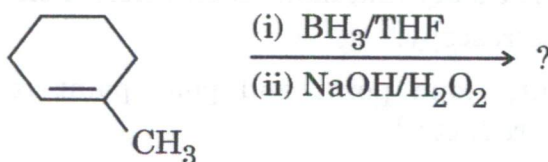
- (d) Predict the product in the following reaction and propose mechanism for the formation of the product

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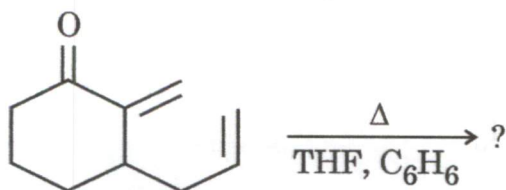
- (e) Predict the product in the following reaction with correct relative stereochemistry. Also provide mechanism for the formation of the product.

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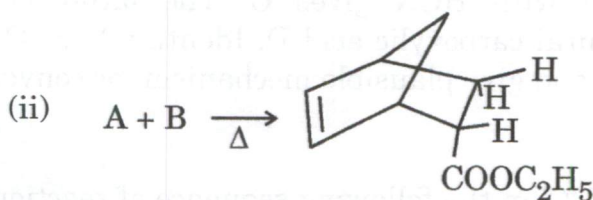
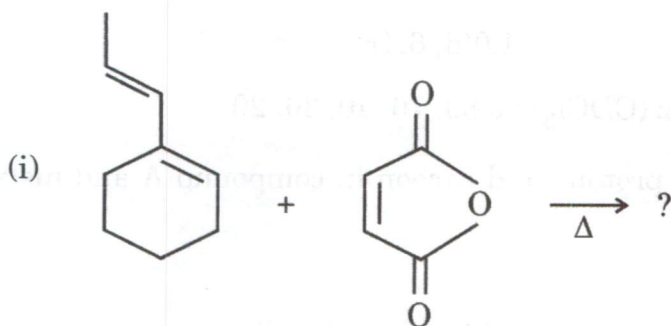


- (f) Predict the structure of the product and name the reaction.

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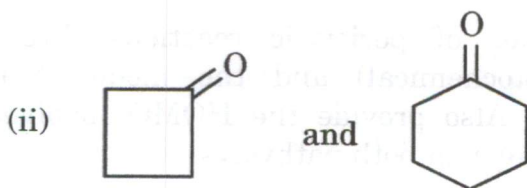
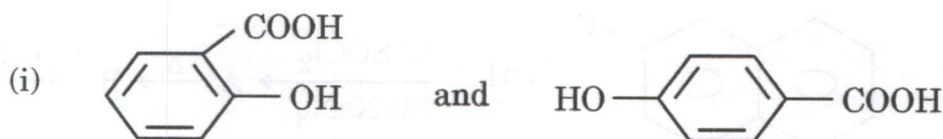


- (g) Given below are two examples of Diels-Alder reaction. Provide the product in the first reaction and the reactants in the second reaction :



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- (h) How can you distinguish between the following pairs on the basis of their IR spectra ?

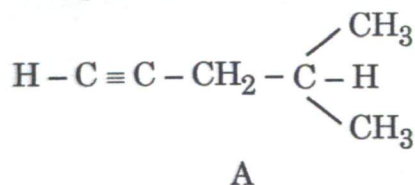


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- (i) 2-Pentanone and 3-Pentanone are structural isomers. Only one of these compounds exhibits McLafferty rearrangement in Mass spectrometry. Identify the same and provide the McLafferty fragmentation for the compound.

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- (j) Compound A exhibits the following spectral data :



^1H NMR – 400 MHz (CDCl_3) : δ 2.5(s, 1H);

2.0(d, 2H);

1.7(m, 1H);

1.0(d, 6H);

^{13}C NMR – 400 MHz (CDCl_3) : δ 80, 70, 40, 30, 20

Assign the peaks of protons and carbon in compound A and justify your answer.

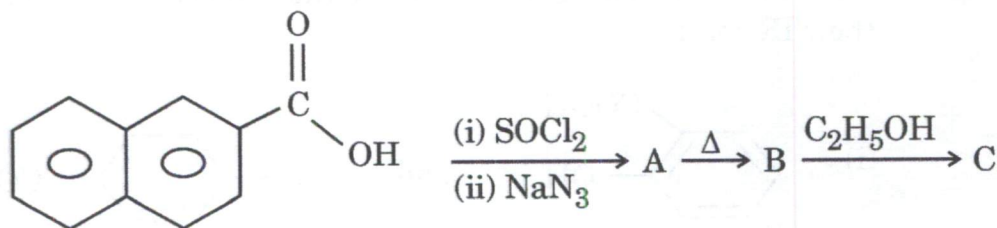
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- Q7.** (a) (i) p-cresol (A) reacts with chloroform in alkaline medium to give B which on addition with HCN gives C. The latter on acidic hydrolysis gives chiral carboxylic acid D. Identify A, B, C and D. Name the reaction and give plausible mechanism for conversion of A $\rightarrow$ B.

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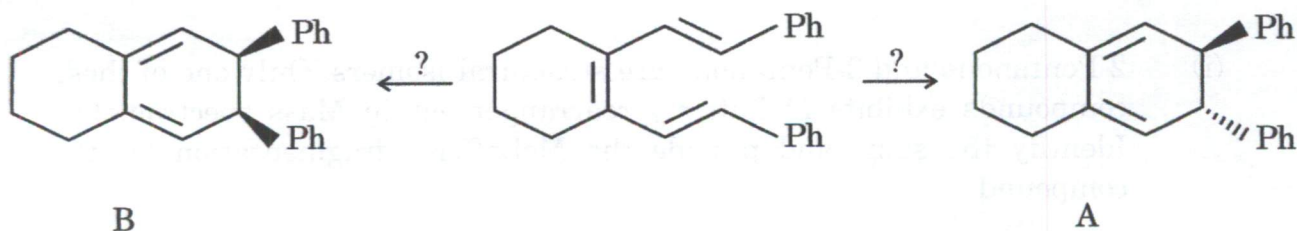
- (ii) Identify 'A', 'B' and 'C' in the following sequence of reactions. Also provide mechanism for conversion of 'A' to 'B'.

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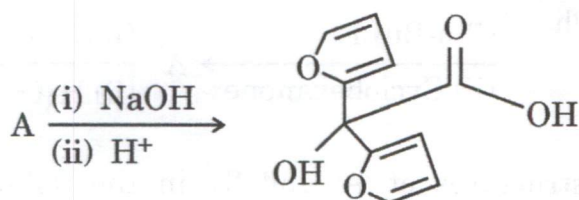
- (b) (i) Following are examples of pericyclic reactions. Predict the pathway (thermal/photochemical) and the mode of rotation involved in each case. Also provide the HOMO involved, with correct phase relationships, in both pathways.

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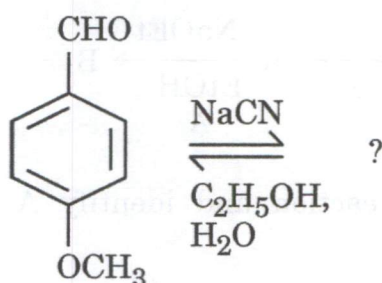
- (ii) Study the following chemical transformation and propose structure of A. Give the possible mechanism for the formation of the product in the reaction.

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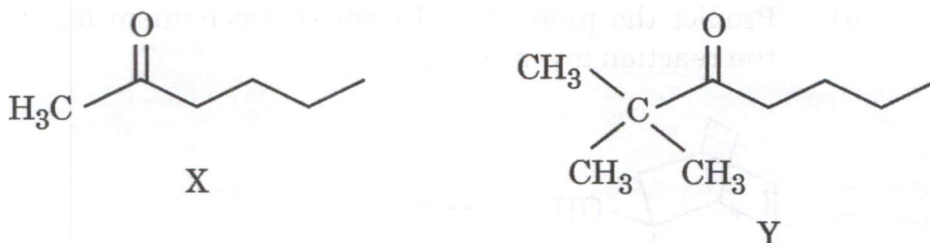
- (c) (i) Predict the product and give mechanism for the formation of the same in the reaction given below :

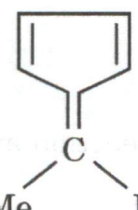
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- (ii) Which of the following two Ketones X and Y will be more prone to Norrish Type II reaction ? Give plausible mechanism and justify your answer about the reactivity of X and Y.

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- Q8. (a) (i) Rationalise that  reacts with LiAlH_4 but $\text{E}_2\text{C} = \text{CMe}_2$



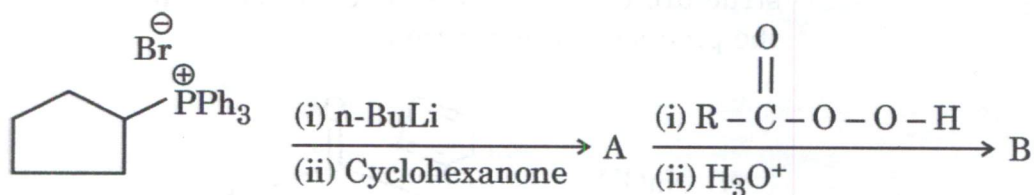
does not. Justify the statement.

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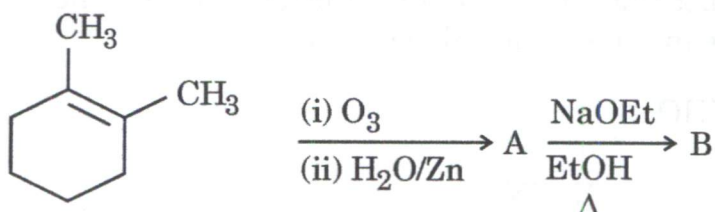
- (ii) What are 'doped' and 'non-doped' conducting polymers ? Provide representative structures of "all-cis-polyacetylene" and "all-trans-polyacetylene" polymers.

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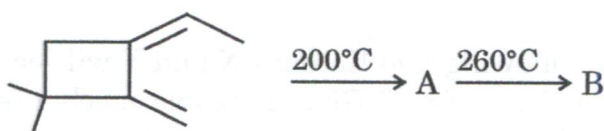
- (b) (i) In the following sequence of reactions, two compounds are formed, 'A' and 'B'. Predict the structures of A and B. Also give possible mechanism for the formation of 'A' from the starting material. 5



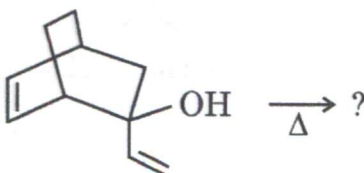
- (ii) Predict the structures of 'A' and 'B' in the following reaction sequence and give mechanism for formation of 'B' from 'A'. 5



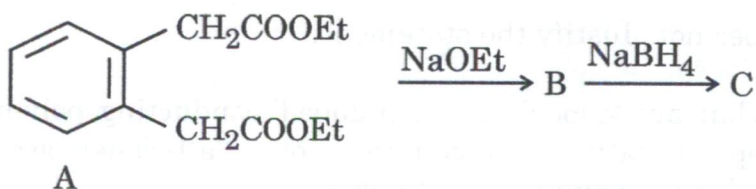
- (c) (i) Complete the following reaction and identify A and B. Give justification. 5



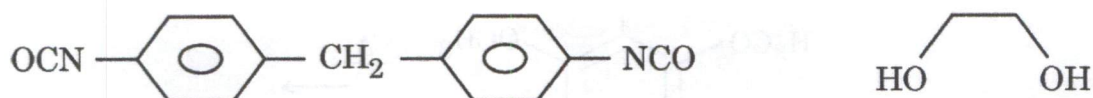
- (ii) Predict the product and propose mechanism for the formation of the reaction given below : 5



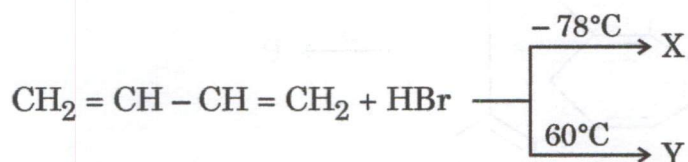
- Q9.** (a) (i) Complete the following reaction and sketch a suitable mechanism for conversion of A $\rightarrow$ B. 5



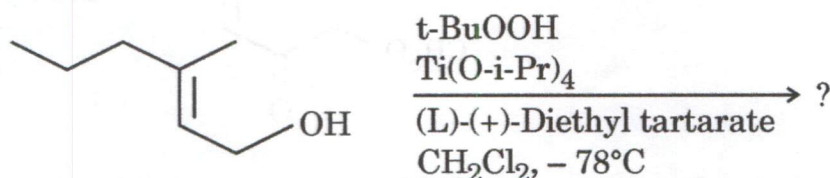
- (ii) What is the characteristic application of polyurethane polymers ?
Provide repeating unit formed by reaction between the following monomers. 5



- (b) (i) Complete the following reaction with suitable mechanism and explanation for the products formed X and Y. 5



- (ii) Predict the major product formed with correct stereochemistry in the reaction given below. What is the role of t-butyl hydroperoxide and Titanium tetraisopropoxide in the given reaction ? 5



- (c) Giving proper explanation, deduce the structure of the organic compound with molecular formula $\text{C}_{10}\text{H}_{13}\text{NO}_2$ having the following spectral data : 10

IR, cm^{-1} : 3300, 1600

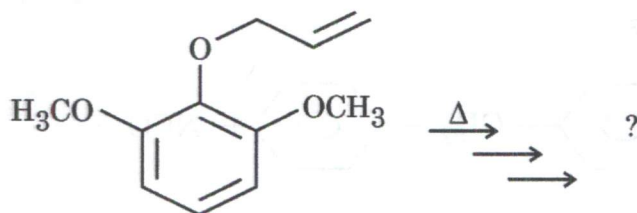
^1H NMR, δ : 1.32 (t, 3H), 2.10 (s, 3H), 4.02 (q, $J = 6$ Hz, 2H), 6.8 (d, $J = 8$ Hz, 2H), 7.4 (d, $J = 8$ Hz, 2H), 7.9 (brs, 1H)

^{13}C NMR, δ : 18, 26, 65, 118, 123, 131, 157, 169

Mass (m/z) : 179 (M^+), 164, 136, 134

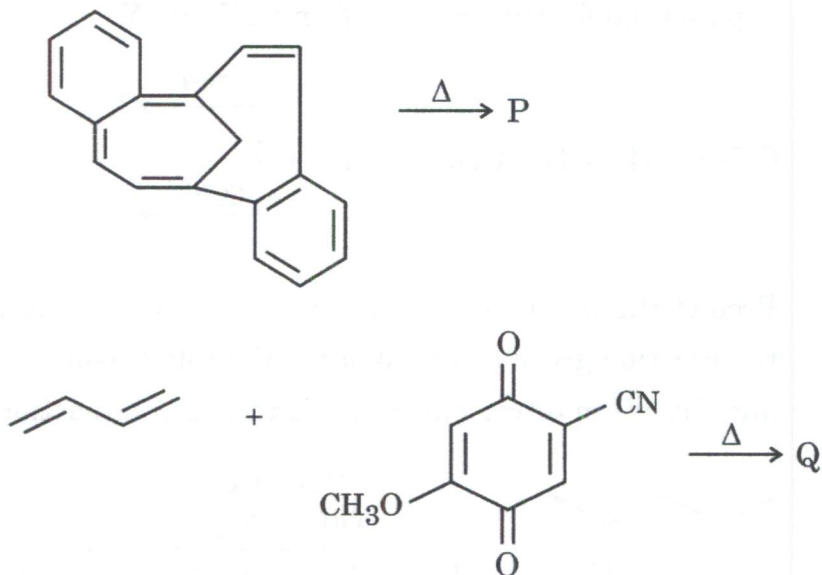
- Q10.** (a) (i) Predict the product formed in the following reaction. Provide the correct description for each step of the overall chemical transformation.

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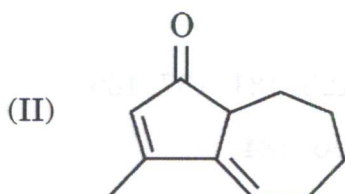
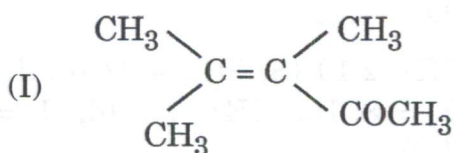
- (ii) Predict the products P and Q and identify the concerted process involved in the following reaction :

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- (b) (i) Two Ketones were filled in two reagent bottles A and B, but their labels got damaged and were removed. Measurement of UV spectra of the contents of the two bottles gave λ_{max} 249 for A and 287 nm for B. Assign the structures with appropriate λ_{max} for A and B by using Woodward-Fieser rule.

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- (ii) Find the structure of an organic compound having C, H and O with molecular weight 108, which exhibited the following peaks in the IR spectrum, cm^{-1} : 3401, 3077 (w), 2899, 1499 (w), and 1456. It can be oxidized with alkaline KMnO_4 and gives negative test with FeCl_3 solution.

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- (c) (i) An organic compound with molecular formula $\text{C}_9\text{H}_8\text{O}_2$ gives following spectral data :

IR : Broad band between 3000 and 2500 cm^{-1} ;
1680 cm^{-1}

^1H NMR : δ 11.0 (s, broad, 1H); 7.8 (d, 1H, $J = 16.1$ Hz);
7.55 – 7.40 (m, 5H); 6.5 (d, 1H, $J = 16.1$ Hz)

^{13}C NMR : 173, 147, 134, 133, 131, 129, 128, 127, 117

Deduce the structure and interpret the spectral data.

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- (ii) Compounds given below have the same molecular formula $\text{C}_9\text{H}_{10}\text{O}_2$. Only one of the two compounds gives m/z ions at 43, 91 and 108 as major ions. Identify the compound and justify your answer by proposing suitable fragmentation ions for the compound.

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