Indian Forest Service
(Main) Exam, 2020

JKLO–B–CHM

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.*

*Questions no. **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.

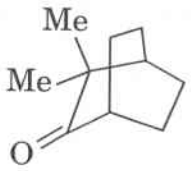
Neat sketches may be drawn, wherever required.

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

SECTION A

Q1. (a) With a suitable cross-over experiment, prove that the Claisen rearrangement proceeds intramolecularly. 5

(b) Which of the following gets enolised more extensively and why ? 5



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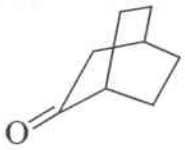
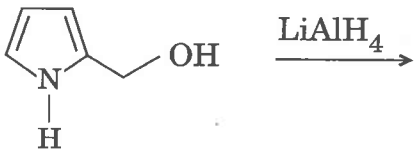


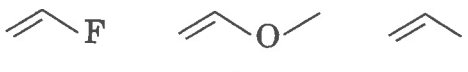
II

(c) Predict the product of the following reaction and write the mechanism. 5



(d) Attempted displacement of iodide ion by fluoride in acetone usually fails. Why ? 5

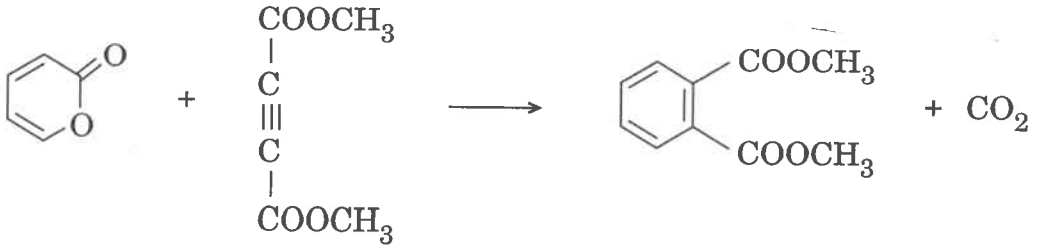
(e) Out of *A*, *B* and *C*, identify the one that would react the fastest and the one that would react the slowest in a typical electrophilic addition reaction. Briefly explain your choice. 5



A *B* *C*

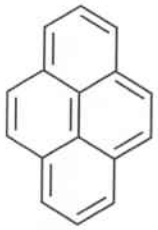
(f) A red colour is formed on reaction of Ph_3CCl with Zn in benzene and it disappears on passing oxygen in the reaction mixture. Account for the observations. 5

(g) The following reaction is known to occur in two thermally allowed steps. Show the structure of the intermediate in the reaction and explain why each step is allowed. 5



(h) Write, why *p*-nitrobenzaldehyde does not react with sodium cyanide but a mixture of *p*-nitrobenzaldehyde and benzaldehyde reacts with this reagent. What is the name of this reaction ? 5

Q2. (a) Comment on the following structures as aromatic/non-aromatic/ anti-aromatic and justify your answer. 5



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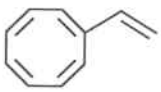


II

(b) Draw the conformational stereostructures of tosylate of *cis*-2-phenylcyclohexanol and tosylate of *trans*-2-phenylcyclohexanol. Which one would react more rapidly with *tert*-butoxide in *tert*-butyl alcohol and why ? Identify the product(s) of elimination reaction of each one of these with *tert*-butoxide in *tert*-butyl alcohol by providing reaction mechanism. 10

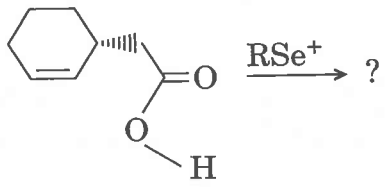
(c) When each of 2-bromocyclohexanone (*A*) and 2-bromocyclobutanone (*B*) is reacted with $EtO^{\ominus}$/EtOD, D is incorporated in the ring of the product/s obtained from *A* but not in that obtained from *B*. Mechanistically justify these observations. 15

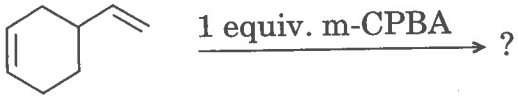
(d) Write the structure of the products (*A* – *E*) in the following set of reactions : 10

$$EtOC \equiv CH + CH_3CH = CHCHO \xrightarrow{Li} A \xrightarrow[(mild)]{[O]} B$$

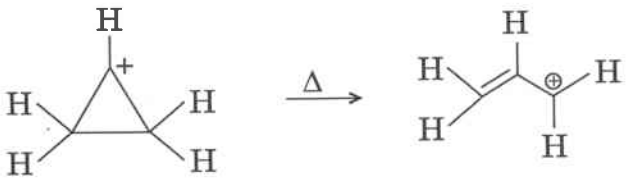
$$\xrightarrow[CH(CO_2Et)_2]{NaOEt} C \xrightarrow[\text{hydrolysis}]{\text{acid}} D \xrightarrow[\text{heat}]{\text{strong}} E$$

Q3. (a) Outlining the mechanism involved, write the product(s) of each of the following reactions and offer a suitable explanation for the choice of your product(s). *10*

(i) 

(ii) 

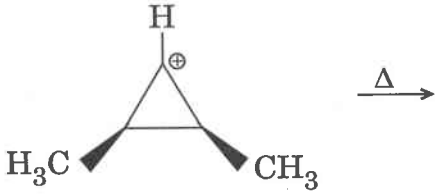
(b) Cyclopropyl carbocations react rapidly to form allyl carbocations.



What kind of pericyclic reaction is this ?

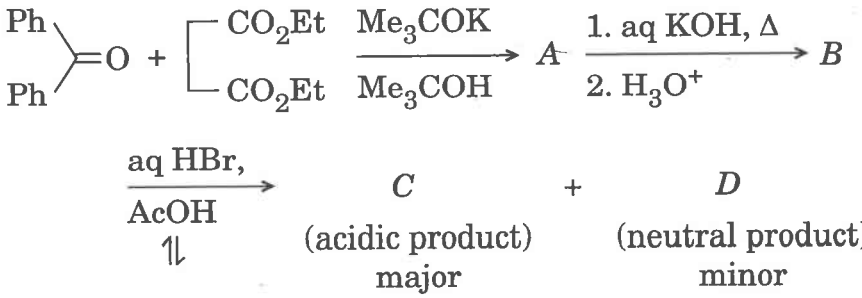
Explain why the allyl carbocation is more stable than the cyclopropyl carbocation.

Predict the stereochemistry of the allyl carbocation that is formed from the following *cis*-dimethylcyclopropyl carbocation : *10*

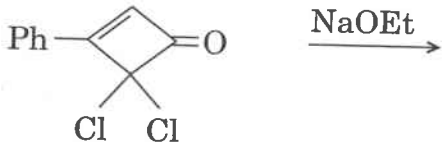


(c) Hex-5-enyl bromide on reaction with BuSnH at 60°C produces a mixture of products. Write the structure of each product, mention the highest yielding product and account for its formation. *5*

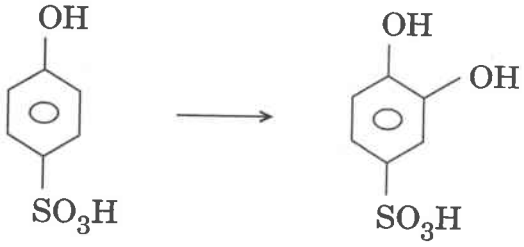
(d) Predict the products (*A* to *D*) for the following reaction steps and name the reaction of the first step. *10*



(e) (i) Predict the product showing mechanism of the following reaction :



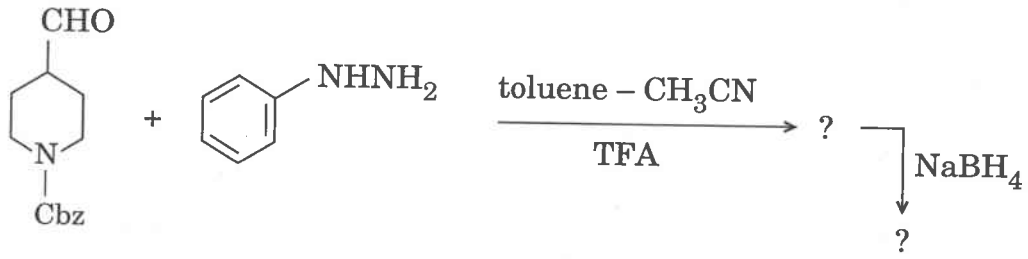
(ii) Write the appropriate reagent to be used for the following one-step conversion :



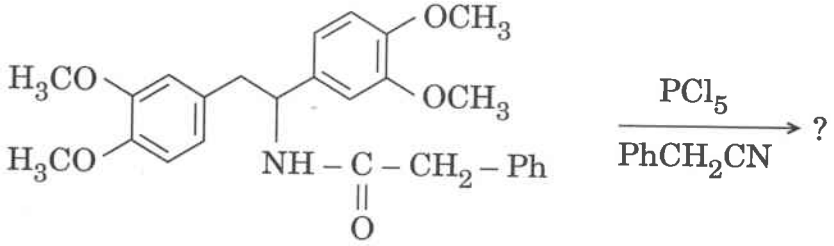
5

Q4. (a) Formulate the product(s) and mechanism of the following reactions : 15

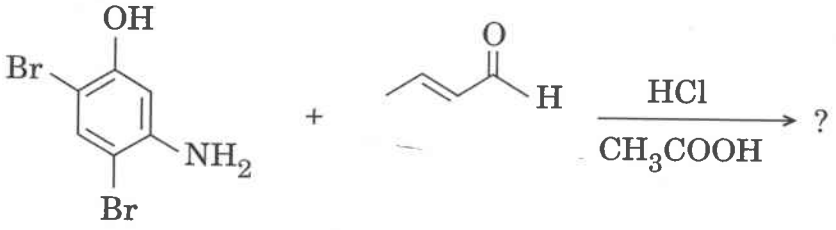
(i)



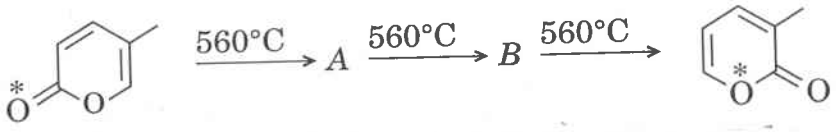
(ii)



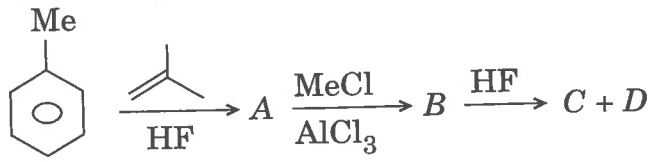
(iii)



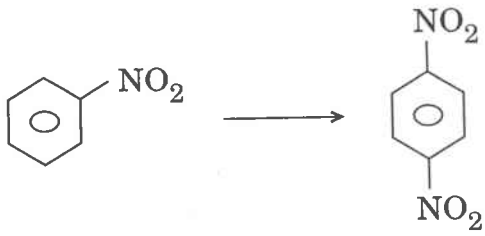
(b) Explain the following transformation by identifying the intermediates *A* and *B*. Also identify the types of pericyclic reactions involved along with their stereochemical modes. 5



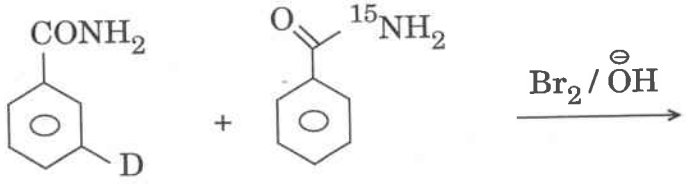
(c) Write the structure of the product (major) in each step and account for their formation in the following reactions : 10



(d) Carry out the following transformation : 6



(e) Predict the products of the following reaction showing proper distribution of D and ^{15}N in each of these. 4

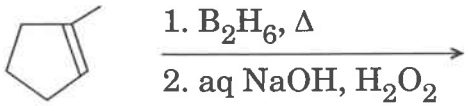


SECTION B

Q5. (a) What is the need for average molecular weight of polymer ? Describe different types of average molecular weights. What is Z-average molar mass ? 5

(b) How can cyclohexane-1,2-dione be obtained from cyclohexanone ? Give its mechanism. 5

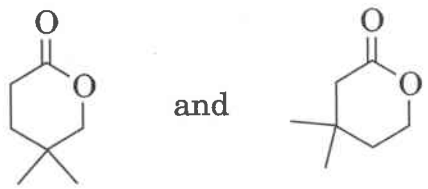
(c) Write the structure of the intermediate and also the final product showing relative stereochemistry of the ring attached groups in each, and write the mechanism of the second step. 5



(d) The Norrish type-I process is not important for the photolysis of diaryl ketones. Suggest a reason. 5

(e) Write all the isomers possible with the molecular formula C_4H_6O whose UV spectra exhibit a high intensity peak at λ_{max} = 187 nm and a very low intensity peak at λ_{max} = 280 nm. 5

(f) How would you use ^1H NMR spectroscopy to distinguish between the following compounds ? 5



(g) Why are majority of mass spectra run with a 70 eV beam ? Also explain why does fragmentation occur in mass spectrometry. 5

(h) Draw the ESR hyperfine structure of radicals containing (a) one ^{14}N and having two equivalent protons, and (b) having three equivalent ^{14}N nuclei. *5*

Q6. (a) A protein has a sedimentation coefficient value of $3{\cdot}12 \times 10^{-13}$ sec in water. Its diffusion coefficient is found to be $8{\cdot}2 \times 10^{-7}$ cm^2/sec. Both the values have been corrected for 20°C in water. The partial specific volume of protein is 0·735 and density of water at 20°C is 0·9982. Determine the molecular weight of the protein. *10*

(b) An unknown organic compound gave the following spectral data :

(i) IR (ν_{max}, cm^{-1}) : 1743, 1229, 751, 698

(ii) ^1H NMR (δ, ppm) : 2·06 (s, 3H), 5·08 (s, 2H) and 7·33 (m, 5H)

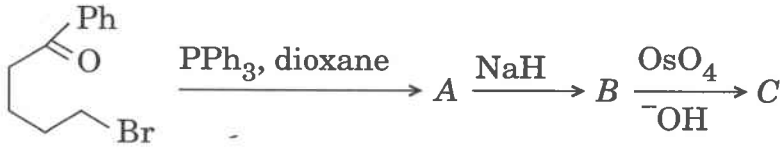
(iii) Mass [m/z (relative intensity %)] : 150 (34·1), 151 (3·5), 152 (0·32), 108 (100), 91 (50), 79 (26), 77 (13·6), 43 (40·3)

Identify the unknown organic compound and explain all observed spectral data. *10*

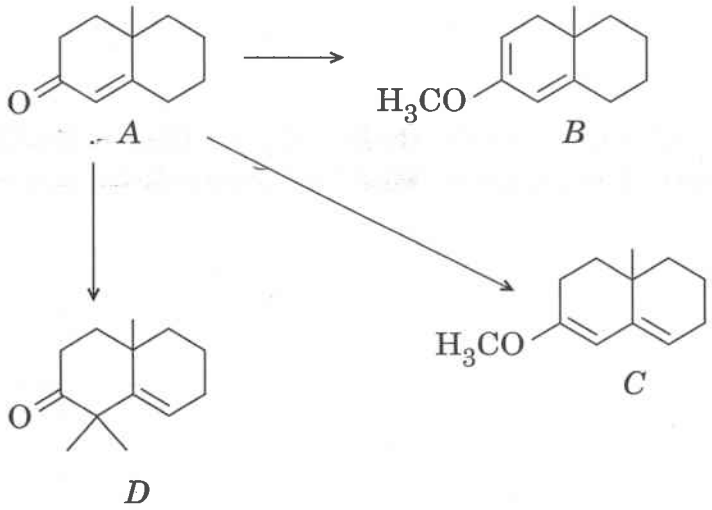
(c) Calculate the value of I and r of CO. *5*

$B = 1{\cdot}92118\ cm^{-1}$

(d) Draw the structure of the product(s) obtained in each step of the following reactions depicting also the intermediates of the second step. Show the relative stereochemistry of the attached group in the final product. Name the reaction involved in the first two steps. *10*



(e) Enone *A* is a versatile starting material, and can be converted into compounds *B*, *C* or *D*.



(i) Show how one could easily differentiate between the structures using UV spectroscopy.

(ii) Define explicitly how IR spectroscopy can be used to follow the conversion of *A* to *D*. *5*

Q7. (a) Discuss the effect of macromolecules on the viscosity of a solution. Describe the relation between intrinsic viscosity and molecular weight of polymer. *5*

(b) Write down the mechanism of the Claisen rearrangement on photolysis. *10*

(c) Three bottles on the stockroom shelf marked $C_5H_{11}Br$ have their labels fallen off. Having only IR machine at your disposal, you first treat a sample of the contents in each bottle with NaOH in aqueous ethanol, and then you determine the IR spectrum of each product or product mixture. Here are the results :

(i) $C_5H_{11}Br$ isomer in bottle A on treatment with NaOH in aqueous ethanol : IR bands at 1660, 2850 – 3020 and 3350 cm^{-1}.

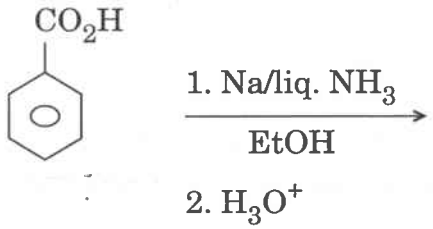
(ii) $C_5H_{11}Br$ isomer in bottle B on treatment with NaOH in aqueous ethanol : IR bands at 1670 and 2850 – 3020 cm^{-1}.

(iii) $C_5H_{11}Br$ isomer in bottle C on treatment with NaOH in aqueous ethanol : IR bands at 2850 – 3020 cm^{-1}.

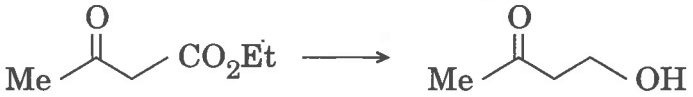
(1) What does the data tell you about each product or product mixture ?

(2) Suggest possible structures for the contents of each bottle. *10*

(d) (i) Write the structure of the product with mechanism, and account for its formation in the following reaction :



(ii) Carry out the following transformation :



10

(e) What is the main difference in absorption of infrared and UV radiation by a molecule ? *5*

Q8. (a) Describe light scattering method for determination of molar mass of macromolecules. Also discuss the significance of Zimm plot. *10*

(b) ESR of $CD_3^{\bullet}$ radical :

CD_3 one odd $e^{\ominus}$, S = 1/2 and I = 1. Then

(i) calculate number of lines.

(ii) draw spike lines.

(iii) calculate intensity pattern.

(iv) draw spectrum. *5*

(c) A compound with molecular formula C_7H_5OBr gave the following data :

(i) IR (ν_{max}, cm^{-1}) : 1700, 1192, 786, 707, 672, 647 and 642.

(ii) ^1H NMR (δ, ppm) : 10·00 (s – 1H)
8·2 (d – 1H)
7·8 (d – 1H)
7·7 (dd – 1H)
7·3 (d – 1H)

(iii) Mass [m/z] : 184 – 186, 183 – 185, 155 – 157, 74 – 77.

Assign the structure of the compound explaining the observed spectral data. *10*

(d) How does the aryl acetate undergo photochemical rearrangement ? Give the products and mechanism. *10*

(e) Assigning the chemical shift value of methyl protons of acetonitrile and chloromethane in ^{1}H NMR spectrum, offer a suitable explanation for the difference. *5*