Indian Forest Service
(Main) Exam, 2021

ZCVB-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.*

*Question Nos. **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.

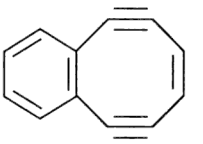
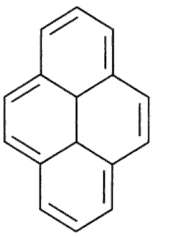
Assume suitable data, if necessary, and indicate the same clearly.

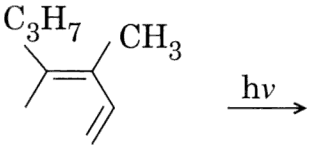
Neat sketches may be drawn, wherever required.

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

SECTION A

Q1. (a) Assign the following compounds as aromatic, antiaromatic and non-aromatic : *5*

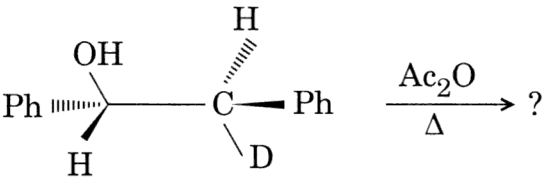
Cyclooctatetraene; cyclobutadiene;  ; 

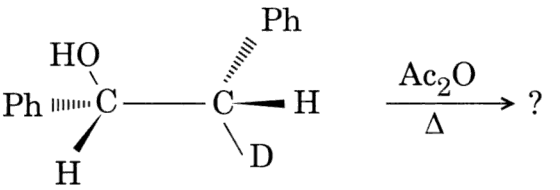
(b) 

(i) Predict the reaction mechanism and configuration of the excited state of the above reaction.

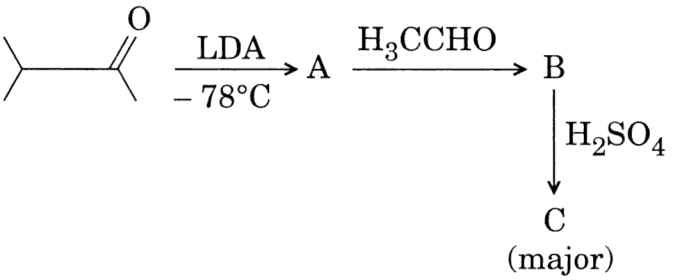
(ii) Using FMO approach, explain the reason for migration of hydrogen. *5*

(c) Complete the following reactions with suitable mechanisms : *5*



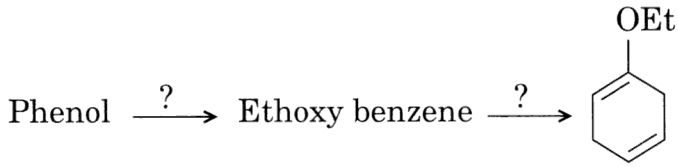


(d) Complete the following reaction sequence and give suitable mechanisms for the formation of the major products : *5*



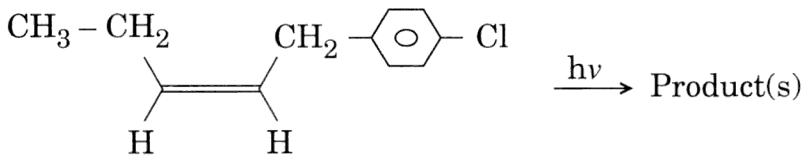
(e) Write the monomer unit of natural rubber. How can natural rubber and polyethene be identified by IR spectroscopy ? *5*

(f) Complete the following reactions and predict their mechanisms : *5*



(g) Complete the following reactions and indicate the intermediates involved in their formation (if any) : *5*

(i) Trans 2,6-dimethylcyclohexanone $\xrightarrow{h\nu}$ Product(s)

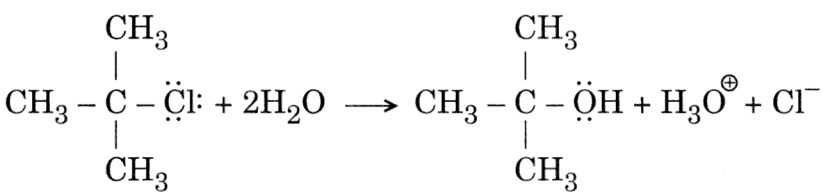
(ii) 

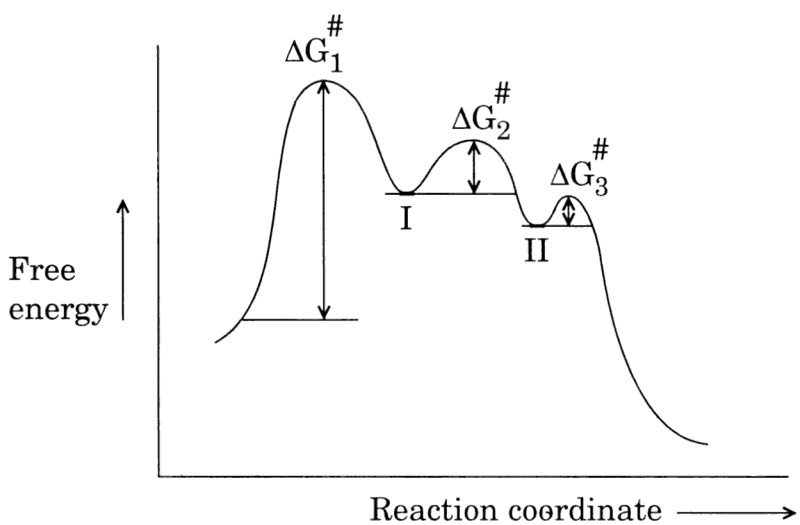
(h) How many lines are possible in the ESR spectrum of $^{13}\dot{C}\ F_2H$? *5*

Q2. (a) 2,4,6-octatriene – [E, E] $\xrightarrow[\text{disrotatory}]{\Delta}$?

Using FMO approach, draw Pi molecular orbitals showing mirror plane symmetry and suggest reaction mechanism and product with stereochemistry. *10*

(b) For the given reaction,



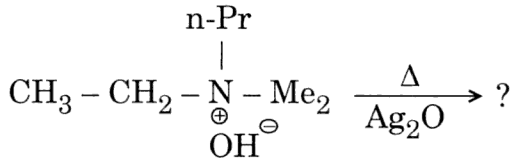


(i) Write the reaction mechanism for the above reaction.

(ii) Give reasons for the formation of I and II as shown in the energy diagram. *10*

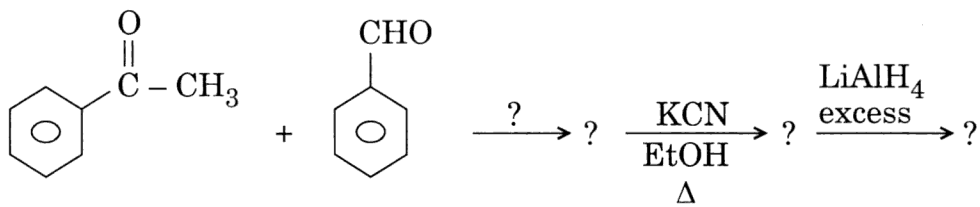
(c) (i) How will you convert p-Toluidine into m-Bromotoluene by using appropriate reagents and conditions ? *5*

(ii) Write the product and explain its formation through Newman projection formula in the given reaction : *5*

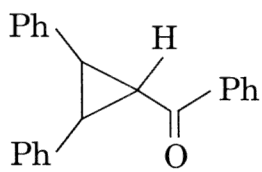


(d) (i) Write the reaction of 2-Bromobutane with alcoholic KOH. Justify the stereochemistry of the major product formed. What is the J (coupling constant) of the olefinic protons ? *5*

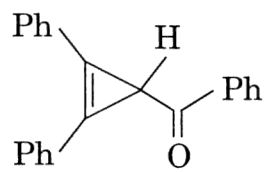
(ii) Write the reaction conditions and products in the following given reactions : *5*



Q3. (a) (i) Hydrogen exchange reaction of the compound A is 6×10^3 times faster than the compound B (given below). Justify your answer. *5*

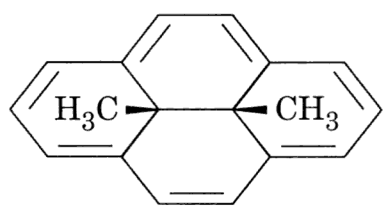


(A)

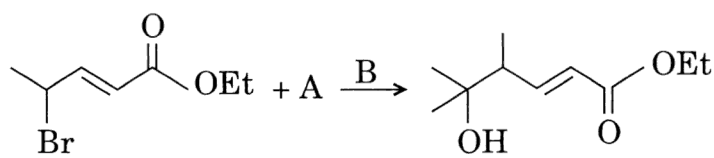


(B)

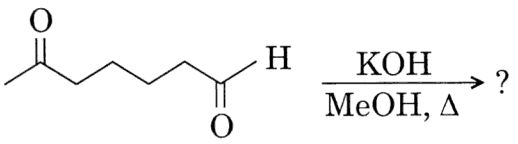
(ii) Give reason why methyl groups are observed at – 4·2 δ ppm in the PMR spectrum of the following compound : *5*



(b) (i) Complete the following reaction and give suitable mechanism : *5*

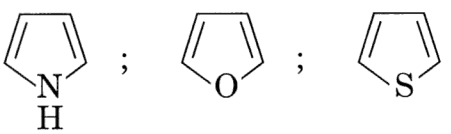


(ii) Complete the following reaction and provide suitable mechanism : 5

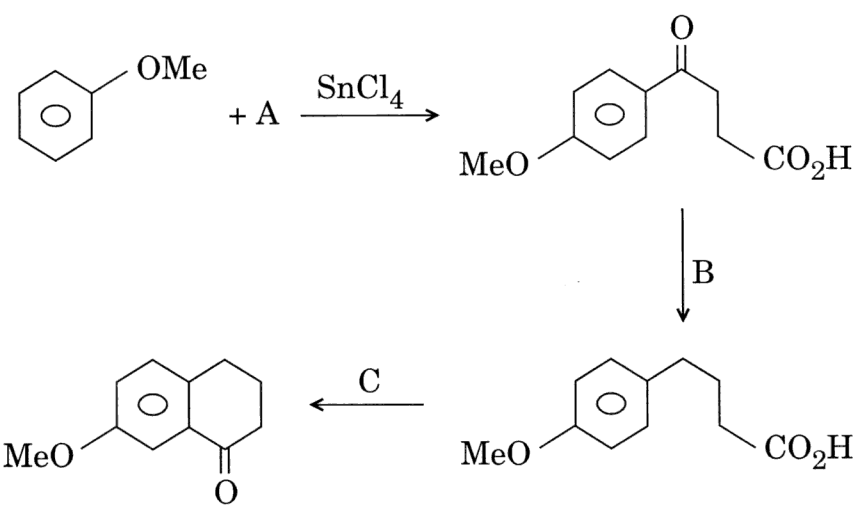


(c) (i) ESR is observed for hydrogen atom with an instrument operating at 9·5 GHz. If G value for electron in hydrogen atom is 2·0026, what is the magnetic field applied ? ($\mu_B = 9{\cdot}274 \times 10^{-24}$ JT^{-1}) 5

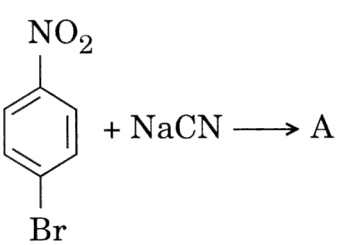
(ii) Arrange the following in increasing order of their degree of aromaticity and justify your answer. 5



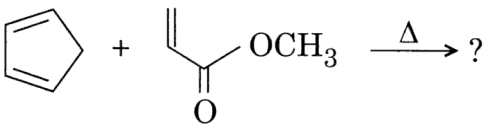
(d) (i) Complete the following reactions sequence : 5



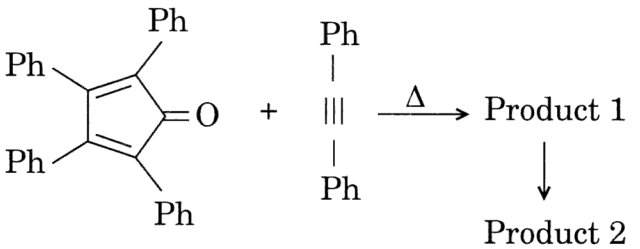
(ii) Complete the following reaction and give appropriate mechanism : 5



Q4. (a) (i) Write the product of the following reaction and justify the stereospecificity of the reaction with the help of formation of proper transition state : *5*

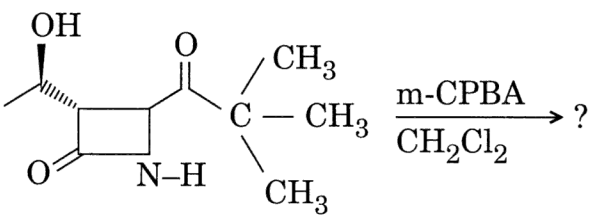


(ii) Identify the products 1 and 2 from the following reaction : *5*

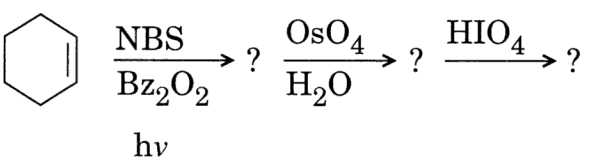


(b) Complete the following reactions : *5*

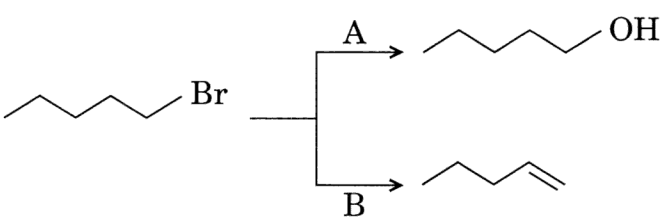
(i)



(ii)

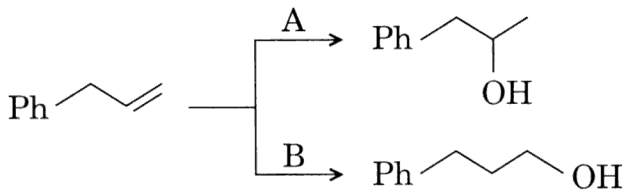


(c) (i) Write the reagents for following conversions and give suitable justification to support your answer. *5*



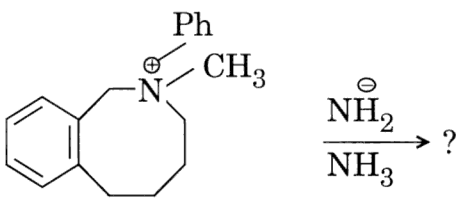
(ii) Write a reaction for the conversion of 2° alcohol into 2° alkyl chloride with retention of configuration and formation of intimate ion pair. *5*

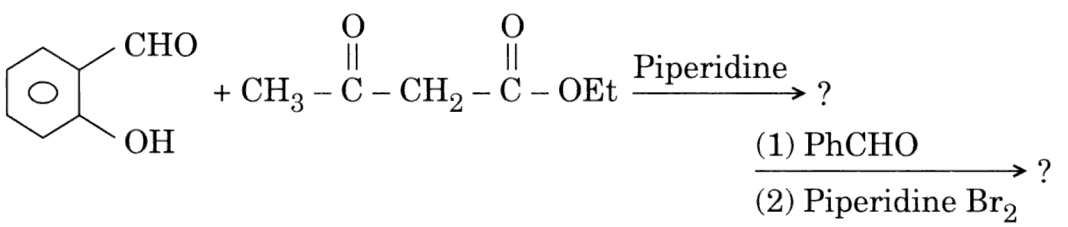
(d) (i) Write the reagents of the following conversions and give appropriate mechanism : 5

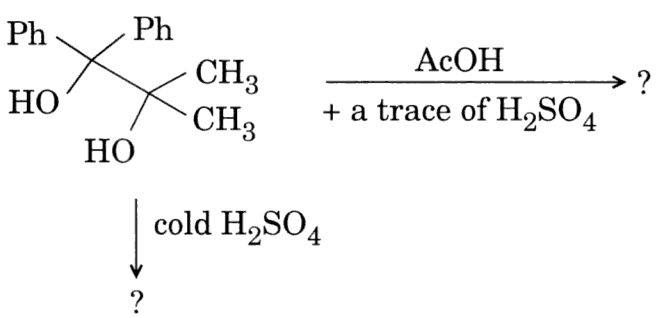


(ii) Draw the structure of a nucleoside and nucleotide clearly by drawing the structure of each individual component. 5

(e) Complete the following reactions : 5

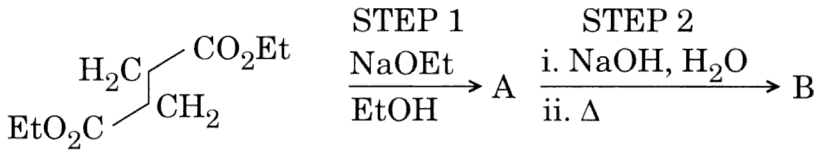
(i) 

(ii) 

(iii) 

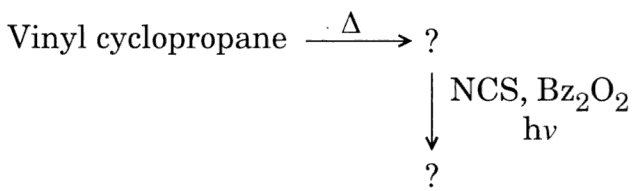
SECTION B

Q5. (a) Complete the following reactions sequence and give the mechanism of the STEP 1. *5*

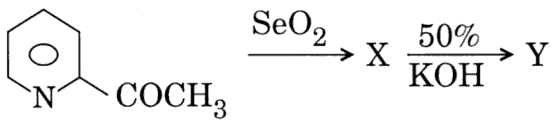


(b) Write the structure of the four bases of DNA and show the H-bonding between the base pairs. *5*

(c) Identify the products in the following reaction : *5*



(d) Identify the products X and Y in the following reactions and propose suitable mechanism for their formation : *5*



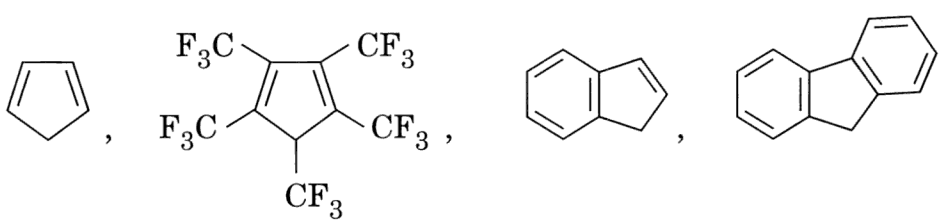
(e) Suggest a suitable explanation by using UV-visible spectroscopy for the following statement :

Azobenzene is a deep orange-red compound while hydra 30 benzene is colourless. *5*

(f) Can indole be nitrated using conc. HNO_3 and conc. H_2SO_4 mixture ? If yes, then what are the products ?

If no, then how can indole be nitrated ? Give the reaction with appropriate example. *5*

(g) Arrange the following compounds in increasing order of their acidity : *5*



(h) Identify the following photo products A to F in the given reactions : 5

(i) 2-pentanone $\xrightarrow{h\nu}$ A + B + C

A + D + E

(ii) Benzophenone + Isobutylene $\xrightarrow{h\nu}$ F (major) products

Q6. (a) (i) Complete the following reaction and give appropriate mechanism (with proper arrows and charges) : 5

$$H_2C(CO_2Et)_2 + Br\text{-}(CH_2)_3\text{-}Br \xrightarrow[\text{(ii) Hydrolysis, } \Delta]{\text{(i) NaOEt}} ?$$

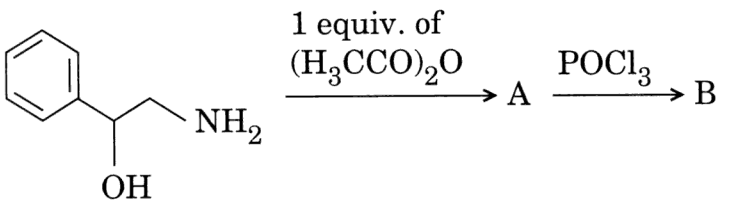
(ii) Complete the following reaction and give suitable mechanism to justify the geometry of the major product : 5

$$PhCHO + \text{-}CH_2\text{-}CH_2\text{-}\overset{\oplus}{P}Ph_3\overset{\ominus}{Cl} \xrightarrow{KOBu^t} ?$$

(b) (i) Write the role of various bonding and non-bonding interactions present in tertiary structure of proteins. 5

(ii) Calculate the end group content (weight fraction) of polystyrene of molecular weight 1,50,000 g mol^{-1} assuming that the phenyl group constitutes both the end groups of an average polymer molecule. 5

(c) (i) Identify the products (A) and (B) in the following reaction sequence and give appropriate mechanism (with proper charges and arrows) : 5

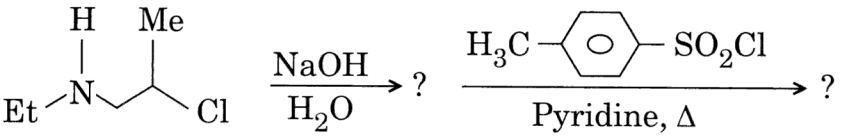


(ii) Write the synthesis of terylene starting from p-xylene. Mention the IR bands of the functional groups having lower percentage of transmittance. 5

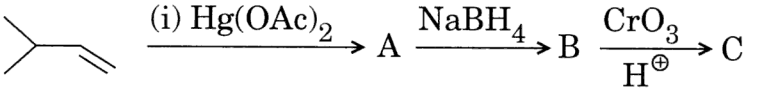
(d) Write a method for synthesis of indole where [3,3]-sigmatropic rearrangement is one of the key steps. 5

(e) Calculate the acid equivalent of nylon-6,6 whose average degree of polymerization is 440. 5

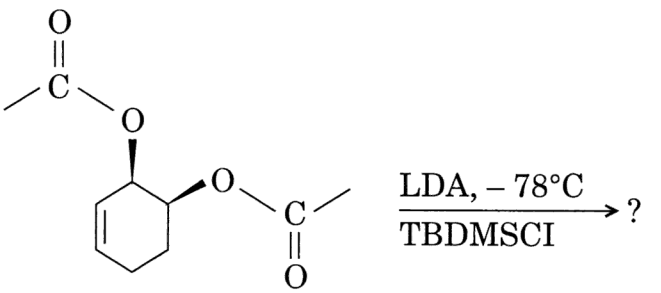
Q7. (a) (i) Suggest the reaction mechanism and product for the given reaction : *5*



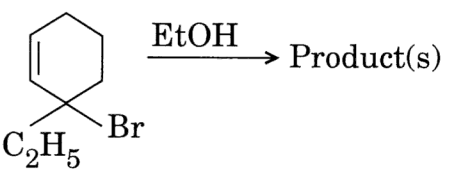
(ii) Complete the following reaction sequence and give suitable mechanism : *5*



(b) Write the product of the following reaction and give suitable mechanism : *10*

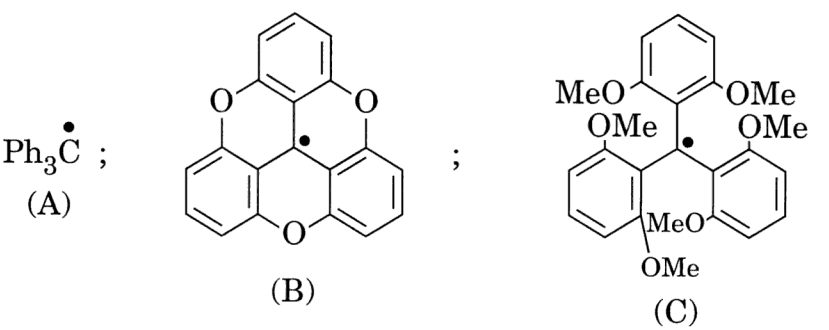


(c) (i) Write the product and give the mechanism of the following reaction : *5*

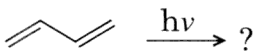


(ii) What will happen when vinyl cyclobutane reacts with methanol in presence of catalytic amount of H_2SO_4 ? Give the product with reaction mechanism. *5*

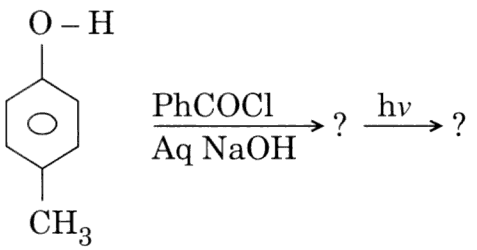
(d) Arrange the following free radicals in order of their stability with proper justification : *5*



(e) (i) Complete the following photochemical reaction and indicate S_1 and T_1 state products :



(ii) Complete the following reactions :



5

Q8. (a) (i) Using mass spectroscopy, how will you distinguish between 3-Methylcyclohexene and 4-Methylcyclohexene ? *5*

(ii) An unknown organic compound with molecular formula $C_9H_{10}O_3$ shows the following spectral data :

IR (ν_{max}, cm^{-1}) : 3400 and 1680

PMR (δ, ppm) : 7·8 (1 H, d, J = 8 cps)

7·0 (1 H, d, J = 8 cps), 6·5 (1 H, s)

5·8 (1 H, s, D_{20} exchangeable), 3·9 (3 H, s)

2·3 (3 H, s)

Identify the structure of the compound and write the reduction product of the compound with Zn – Hg | HCl. *5*

(b) An unknown organic compound with MF $C_{12}H_{14}O_4$ gave the following spectral data :

UV (λ_{max}, nm) : 225 and 265

IR (ν_{max}, cm^{-1}) : 2900, 2800, 1720, 1030 and 860

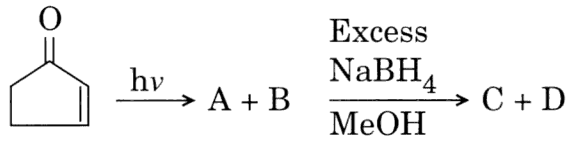
PMR : δ 1·48 (6 H, t, J = 7 cps), 4·4 (4 H, q, J = 7 cps) and 8·1 (4 H, s)

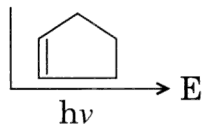
Mass (m/z) : 222, 194, 177 (base peak), and 149.

On the basis of the above spectral data, deduce the structure of the compound. *10*

(c) (i) Acetic anhydride when refluxed with potassium permanganate, gives compound A, $C_4H_4O_3$. The IR spectrum of A shows bands at 1860 cm^{-1} and 1785 cm^{-1}. What is A ? Suggest reactive intermediate formed in its formation and give its hydrolysis product. *5*

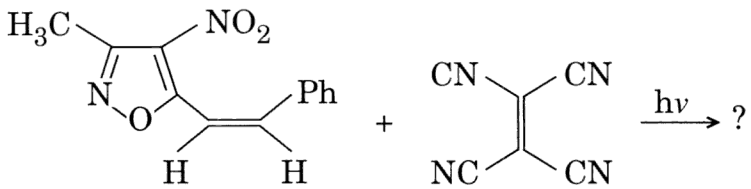
(ii) Complete the following reaction : *5*



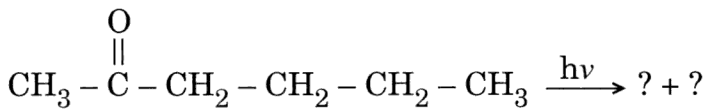


(d) Complete the following reactions : *5*

(i)

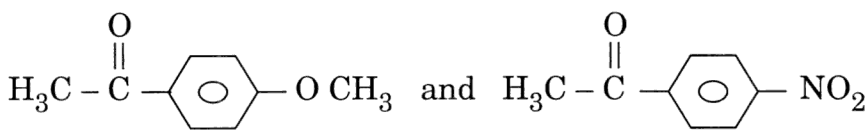


(ii)



(e) How would you distinguish between the following pairs of organic compounds by IR spectroscopy ? *5*

(i)



(ii)