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.

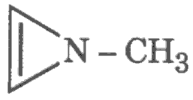
Assume suitable data, if necessary, and indicate the same clearly.

Neat sketches may be drawn, wherever required.

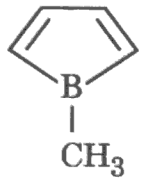
*Answers must be written in **ENGLISH** only.*

SECTION A

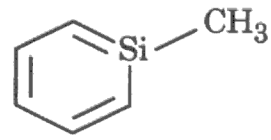
Q1. (a) On the basis of Huckel's Rules of aromaticity, identify the following compounds as aromatic, antiaromatic and non-aromatic : *5*



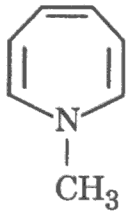
(I)



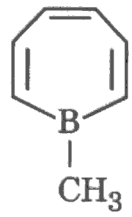
(II)



(III)



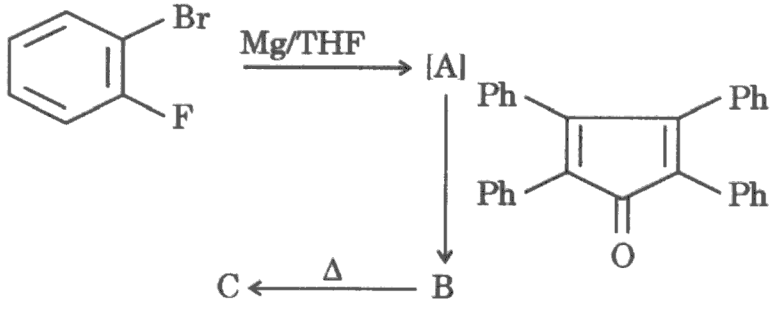
(IV)



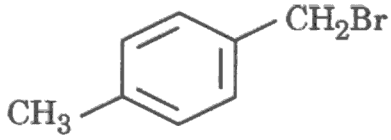
(V)

(b) With the help of the isotopic labelling experiment, how will you establish that $B_{Ac}2$ mechanism of ester hydrolysis involves true intermediate, not a transition state ? *5*

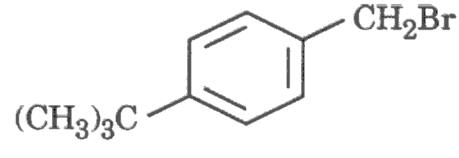
(c) Complete the following reaction and identify the products A, B and C. *5*



(d) Compare with proper explanation, the solvolysis behaviour of the following organic compounds : *5*

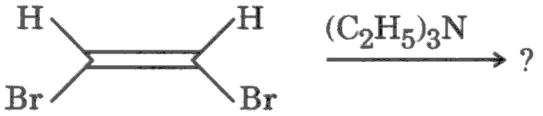


A



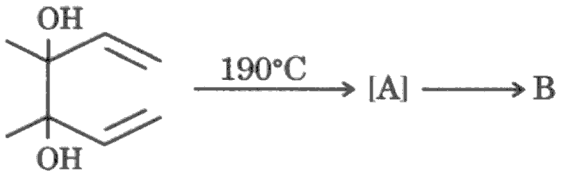
B

(e) Complete the following reaction. Also indicate the name of the mechanism involved in the formation of product(s). *5*

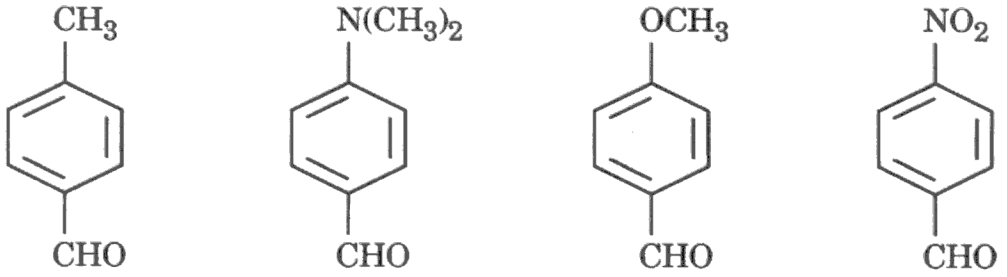


(f) Explain why nucleophilic 1,2 shifts are more common than 1,2 electrophilic or free radical shifts. *5*

(g) Identify A and B in the following reaction : *5*



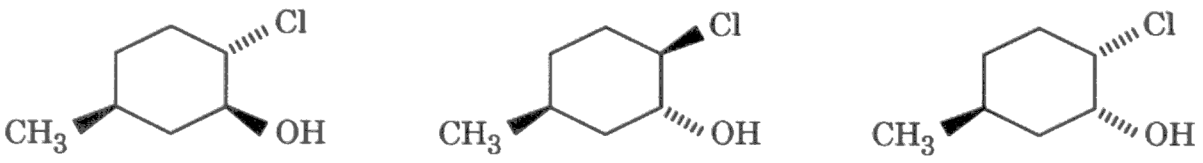
(h) Arrange the following aldehydes towards their ease of reactivity in Cannizzaro's reaction in the decreasing order : *5*



I II III IV

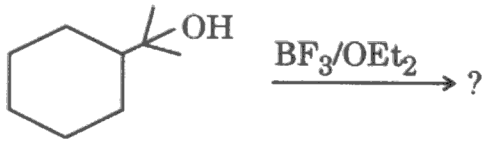
Q2. (a) Cannizzaro's reaction exhibits third order kinetic at low base concentration and fourth order kinetic at higher base concentration. Explain the mechanism of Cannizzaro in the light of above kinetic data. *10*

(b) Arrange the following molecules in the decreasing order of their epoxidation tendency with reason(s) : *10*



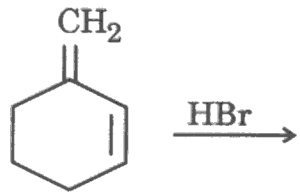
I II III

(c) Complete the following reaction with mechanism, giving the plausible reasons for product spread : *10*

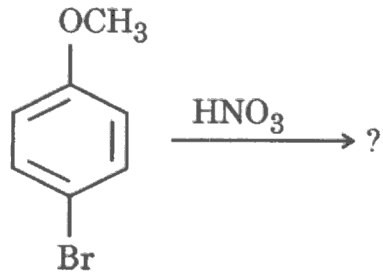


(d) Give the product(s) of the condensation reaction of 2-butanone with phenylhydrazine along with the mechanism. *10*

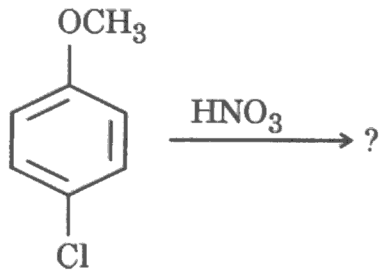
Q3. (a) Predict the product(s) of the following reaction. Which product will be major and why ? *5*



(b) Complete the following reactions :

(i) 

3

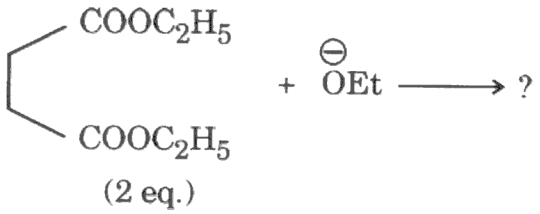
(ii) 

2

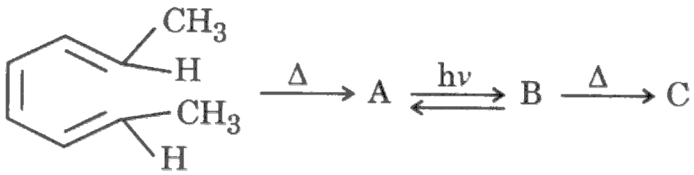
(c) Compare the rate of solvolysis in separate reactions of (i) iodocyclopentane and (ii) 1-iodo-2,4-cyclopentadiene with silver perchlorate in propionic acid. *5*

(d) Base catalysed bromination of optically active ketone results in racemization of product. How will you account for this observation ? *5*

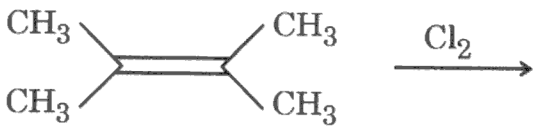
(e) Complete the following reaction with mechanism : *10*



(f) Complete the following reaction sequence by writing the structures of A, B and C. Also write the name of the process involved. *10*



Q4. (a) Complete the following reactions : *5*

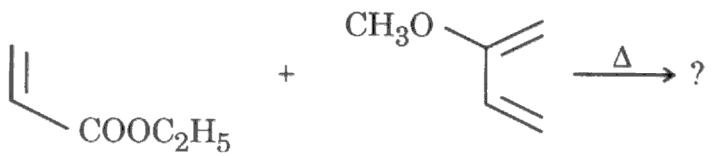
(i) 

(ii) $Ph - CH = C = CH_2 \xrightarrow{HCl/AcOH}$

(b) The following compounds undergo elimination reaction in the presence of C_2H_5ONa/C_2H_5OH at 55°C. Arrange them in decreasing order of elimination behaviour rate. *5*

CH_3CH_2Br	$(CH_3)_3CBr$	$CH_3CHBrCH_3$	$CH_3CH_2CH_2Br$
I	II	III	IV

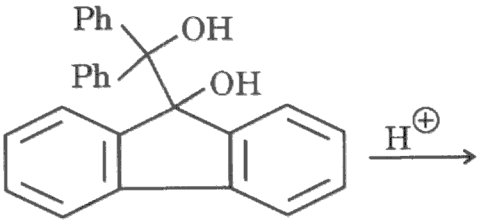
(c) Indicating the product spread, complete the following pericyclic reaction : *5*



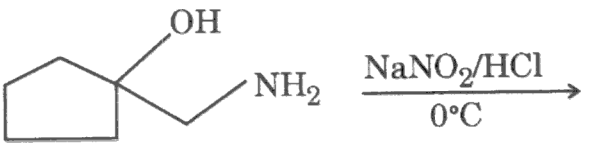
(d) Butanal reacts with ethyl cyanoacetate in the presence of base. Give the product(s) of this reaction along with mechanism. *5*

(e) Write the product(s) of the following reactions : *5*

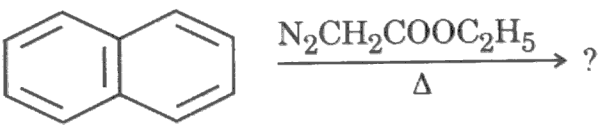
(i)



(ii)



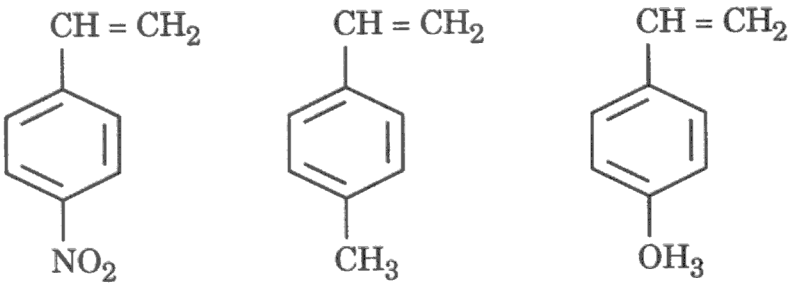
(f) Predict the product(s) of the following reaction : *5*



(g) Write the product(s) of reaction of 1-chloro-3-phenyl-2-propanone and 1-chloro-1-phenyl-2-propanone CH_3ONa/CH_3OH separately. Explain the mechanism involved. *10*

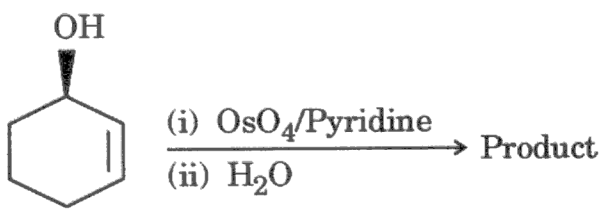
SECTION B

Q5. (a) List the following groups of monomers in order of decreasing ability to undergo anionic polymerization and give suitable justification. *5*

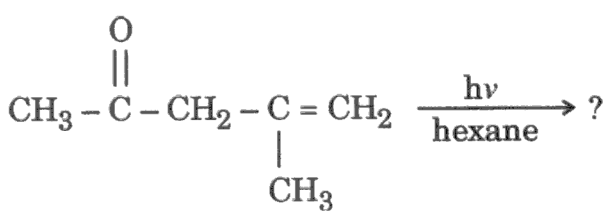


(I) (II) (III)

(b) Write the product for the following reaction and offer a suitable explanation for your answer. *5*



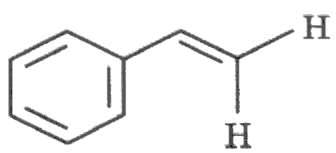
(c) Giving the mechanism complete the following reaction : *5*



(d) Calculate λ_{max} values of 2-methoxy-pent-3-en-2-one (A) and 3-methoxy-2-methyl-but-2-enal (B). *5*

(e) Differentiate between o-xylene and p-xylene using IR spectroscopy. *5*

(f) Identify the chemically equivalent protons and magnetically equivalent protons in the following compound : *5*



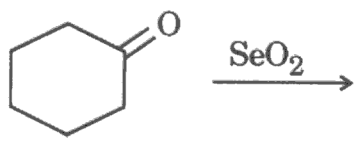
(g) From the data given below, calculate the mass of the parent peak (P) whose daughter peak is 65. *5*

MS (m/z) : 106, P, 65, 46·42, 29, 15

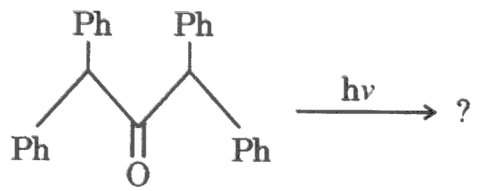
(h) Write the structure of the complementary base pairs of DNA and show their bonding interactions. *5*

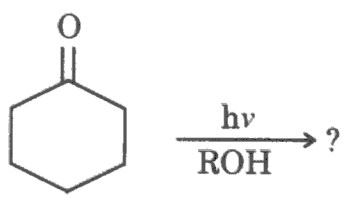
Q6. (a) Complete the following reactions and give their mechanism : *10*

(i) $C_6H_5 - CH = CH - CHO + LiAlH_4 \xrightarrow{Et_2O/RT}$

(ii) 

(b) Write the products in the following reactions with their mechanisms : *10*

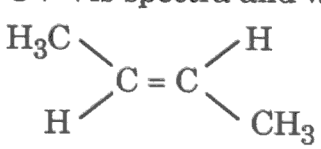
(i) 

(ii) 

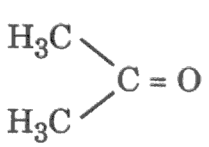
(c) Two compounds having molecular formula C_3H_6O react separately with 2,4-dinitrophenyl hydrazine to give blood red precipitates. Using IR spectroscopy, how would you ascertain the functional group(s) present in the compounds ? *5*

(d) What is coupling constant in ^1H NMR spectroscopy ? How does external magnetic field affect coupling constant values ? For two vicinal protons, do we observe same or different coupling constant values and why ? *5*

(e) Which of the following two compounds will give higher intensity in UV-Vis spectra and why ? *5*



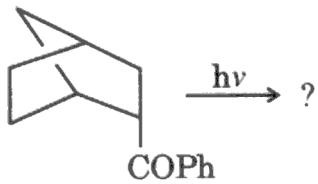
(I)



(II)

(f) Write the effect of isotopic substitution on the rotational spectrum of a diatomic molecule. *5*

Q7. (a) Write the product(s) in the following photochemical reaction : 5



(b) Complete the following reactions sequence : 5

$$Ph - CH = CH_2 \xrightarrow[THF]{\text{n-BuLi}} A \xrightarrow{CH_2 = CH - CH = CH_2} B \xrightarrow{ROH} C$$

(c) Write the structure of neoprene and its monomer precursor which gives the former by use of Zeigler-Natta catalyst. 5

(d) Why is the weight average molecular weight and the number average molecular weight used in polymer chemistry rather than simply measuring molecular weight ? Explain. 5

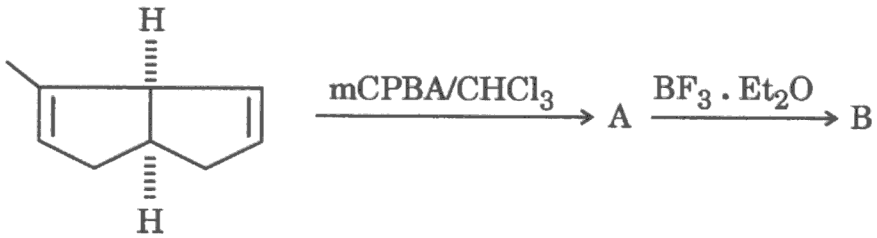
(e) A compound having molecular formula $C_5H_8O_2$ may be either ethyl acrylate or vinyl propionate. How would you identify the correct compound using IR spectroscopy ? 5

(f) Give the mechanism for detection of N-terminal amino acid in a protein with Sanger's reagent. 5

(g) A compound gives two signals at δ 4·3 ppm and δ 5·7 ppm. If the spectrum is recorded in a 400 MHz NMR machine, write their chemical shift difference in Hz (hertz). 5

(h) A compound with molecular formula C_8H_6 gives a product (C_8H_8O) upon treatment with dil. sulphuric acid in the presence of mercurous sulphate. Write approximate ^1H NMR chemical shifts and multiplicity of the protons in the product. 5

Q8. (a) Complete the following reactions and give a suitable mechanism for both the steps : *10*



(b) A compound having molecular formula C_9H_{12} gives the following MS (m/z) data :

m/z 120, 92, 91, 77 and 51

Write the mass fragmentation of the compound to elucidate the structure of the fragment having mass m/z 92. *5*

(c) Answer the following, when benzene is treated with an alkali metal in THF as solvent : *5*

(i) The spectroscopy to be used to identify the product.

(ii) The structure of the product.

(iii) Total spin of the product.

(iv) The number of lines observed.

(v) The intensity distribution of the lines.

(d) A terpolymer is prepared from vinyl monomers A, B and C; the molecular weight of the repeat units are 104, 184 and 128, respectively. A particular polymerisation procedure yields a product with the empirical formula $A_{3\cdot55}\ B_{2\cdot20}\ C_{1\cdot00}$. Calculate the average unit weight of the polymer. *5*

(e) A compound with molecular formula $C_5H_6O_3$ gives the following data : *15*

MS (m/z) 114, 76, 73, 60, 55

IR (cm^{-1}) 2981, 1850, 1758, 1250

^{1}H-NMR ($CDCl_3$) δ 2·43 (t, 4H), 1·96 (pent., 2H)

^{13}C-NMR ($CDCl_3$) δ 177, 33, 19·6

Assign the structure to the compound.