DJSM-B-CHMY

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.

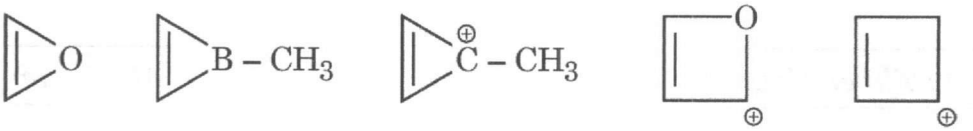
Assume suitable data, if necessary, and indicate the same clearly.

Neat sketches may be drawn, wherever required.

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

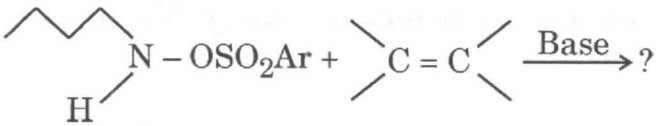
SECTION A

Q1. (a) Based on Huckel's rule of aromaticity, identify the following species as aromatic, antiaromatic, and nonaromatic : 5



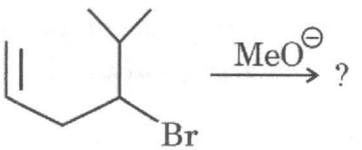
(I) (II) (III) (IV) (V)

(b) Write the major product of the following reaction and give mechanism : 5

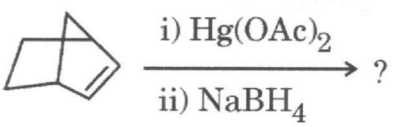


(c) Giving appropriate explanation, compare the order of reactivity of pyrrole and thiophene towards an electrophile. 5

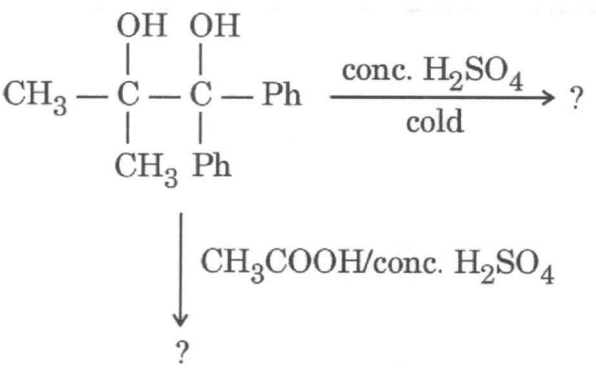
(d) Write the products (major/minor) in the following reaction sequence : 5



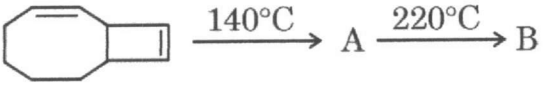
(e) Write the products of the following reaction and justify the stereochemical outcome with an appropriate mechanism : 5



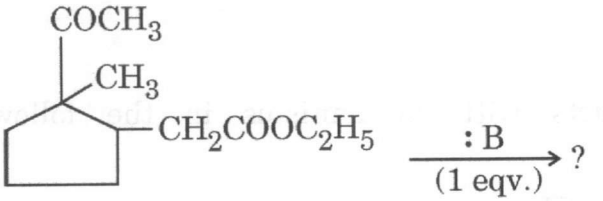
(f) Write the products in the following transformations : 5



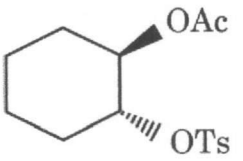
(g) Indicate the products in the following sequence of reactions : 5



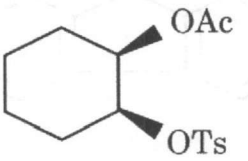
(h) Giving the most plausible mechanism, complete the following reaction : 5



Q2. (a) Compare the rate of acetolysis of A and B giving suitable justification. Also give the product(s) of acetolysis in each case with mechanisms : 10

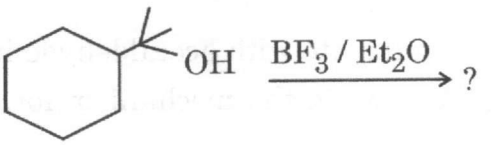


(A)



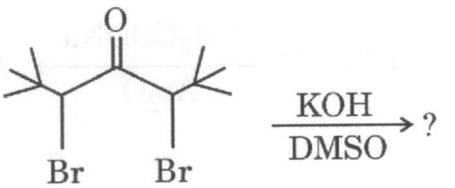
(B)

(b) Complete the following reaction along with the mechanism. Also indicate the product spread with suitable reasons : 10

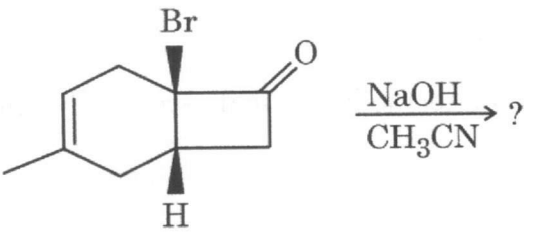


(c) Giving the products, complete the following reactions along with their mechanisms : 10

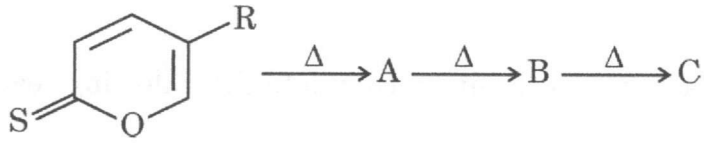
(i)



(ii)

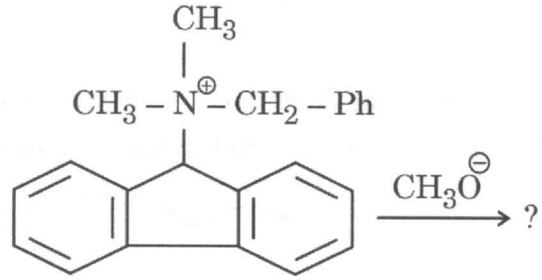


(d) Write the products A, B and C in the following transformation indicating the processes involved and electron flow : *10*

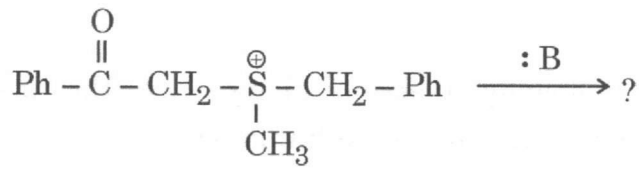


Q3. (a) Write the products with mechanisms in the following reaction sequences : *10*

(i)

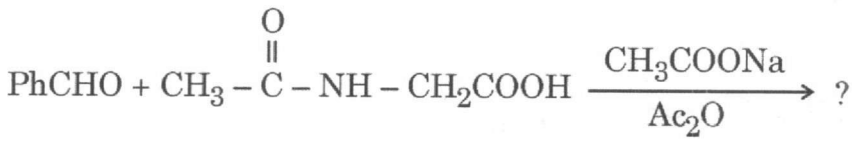


(ii)

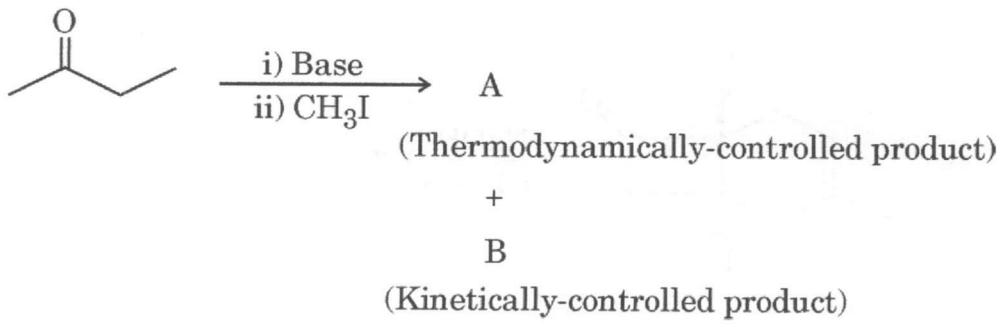


(b) Write the reaction of diethyl malonate with acetaldehyde in the presence of piperidine (as catalyst). Also write the mechanism for the product(s) formation. *10*

(c) Giving mechanism, complete the following reaction : *10*



(d) In the following reaction :



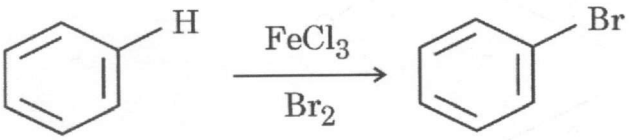
(i) Identify A and B.

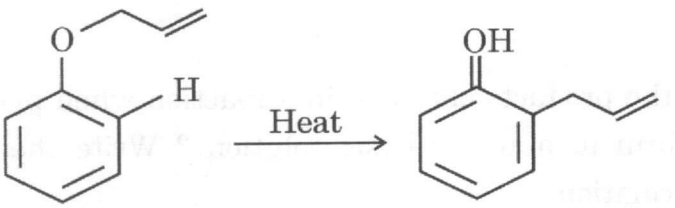
(ii) Write a name of a base in each case to form A and B regioselectively.

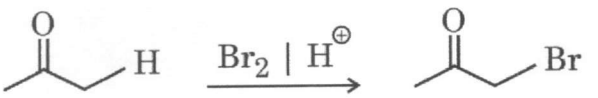
(iii) Write the nature of solvent and the reaction temperature required for regioselective formation of A and B.

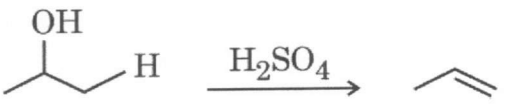
(iv) Give the mechanism of formation of A and B. *10*

Q4. (a) Identify the reaction from the following reactions (i – iv) that shows primary kinetic isotope effect for the H-atom (C – H) and show the mechanism of the reaction to identify the rate limiting step : *10*

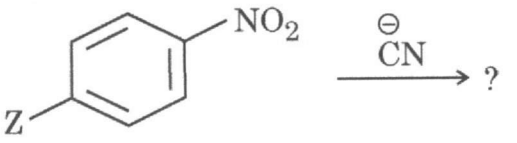
(i) 

(ii) 

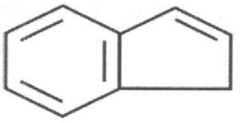
(iii) 

(iv) 

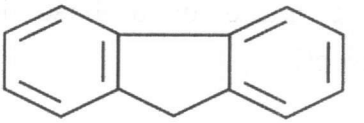
(b) Complete the following reaction with mechanism : *10*



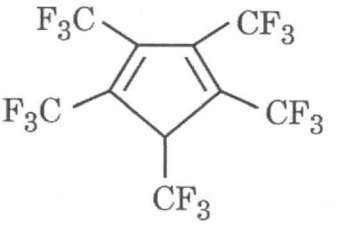
(c) (i) Arrange the following compounds in order of their decreasing acidity and give suitable justification : 5



I

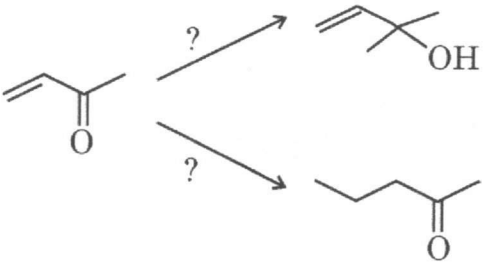


II



III

(ii) Complete the following reactions and give suitable explanation for the formation of the major products : 5



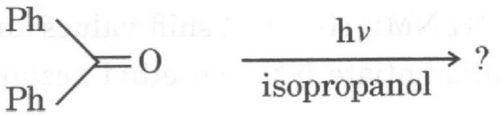
(d) What is/are the products obtained in a reaction when pyrrole is reacted with chloroform in aqueous basic solution ? Write the mechanism of product(s) formation. 10

SECTION B

Q5. (a) Derive the structure of the monomeric product that is identifiable by HPLC in Edman degradation of a peptide. *5*

(b) Write the complementary base pairs in RNA and show their H-bondings by drawing the structure of the bases. *5*

(c) Complete the following reaction and identify the electronic states involved in the reaction by showing the proper mechanism for formation of the product(s). *5*



(d) Write the ^1H NMR spectral data of pure ethanol in anhydrous $CDCl_3$ indicating approximate chemical shift values of each signal and their spin multiplicity and integration. *5*

(e) A compound having molecular formula $C_4H_6O_3$ gives the following mass fragments. Deduce the fragmentation pattern to identify the mass peaks and the base peak. *5*

m/z = 102, 60, 43, 42, 15.

(f) An organic compound with molecular formula $C_{10}H_{12}O_2$ exhibits the following spectral data :

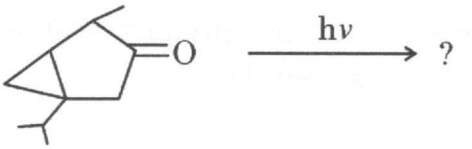
IR (cm^{-1}) : 3100, 2944, 2856, 1690, 1100 cm^{-1}

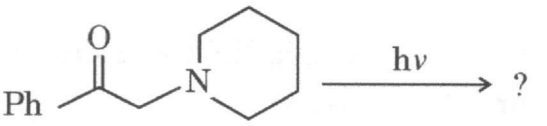
^1H NMR ($CDCl_3$) : δ 7·80 (2H, d, J = 8 Hz), 6·80 (2H, d, J = 8 Hz), 4·10 (2H, q, J = 7·2 Hz), 2·4 (3H, s), 1·25 (3H, t, J = 7·2 Hz)

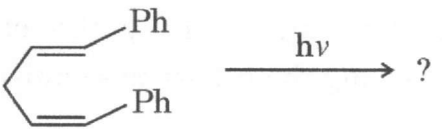
Mass : m/z 164, 121, 43, 15.

Derive the structure of the compound and assign all the data. *15*

Q6. (a) Write the products formed in the following reactions and give suitable mechanism/explanation. *5×3=15*

(i) 

(ii) 

(iii) 

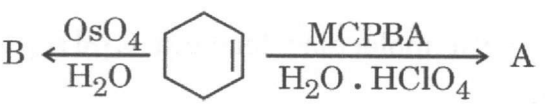
(b) (i) Write approximate ^1H NMR chemical shift values and multiplicity of each signal to differentiate between ethyl acetate and methyl propionate. *5*

(ii) A compound having molecular formula $C_{11}H_{20}O_4$ gives the following ^1H NMR data. Identify the compound and assign the protons. *5*

^1H NMR ($CDCl_3$, 300 MHz) : δ 4·18 (q), 1·92 (t), 1·24 (q), 0·82 (t) ppm.

(c) (i) What will be the number average and weight average molecular weight of a sample of propylene oligomer that consists of 5 mol of pentamer and 10 mol of hexamer ? *10*

(ii) Mention the product of the given reactions with proper mechanism : *5*

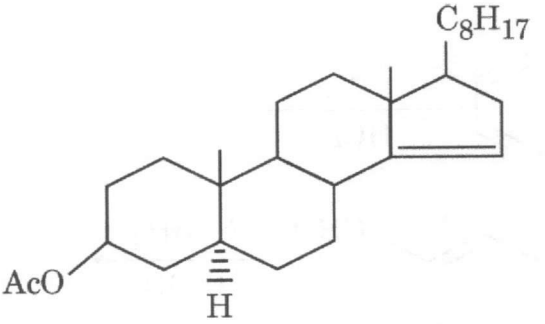


Q7. (a) (i) Propose the chemical reaction for synthesis of polyphosphonitrilic chloride. The freshly prepared polyphosphonitric chlorides are soluble in chloroform but insoluble in petroleum. Why ? *10*

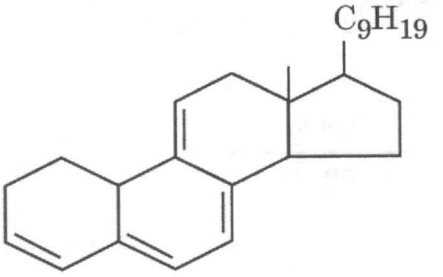
(ii) Propose the mechanism for synthesis of silicones from dialkyl dichlorosilane. How is chain branching introduced in silicones ? *10*

(b) (i) Calculate the ultraviolet absorption maxima of substituted dienes using Woodward-Fieser rules : 5

(I)

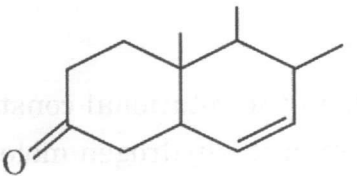


(II)

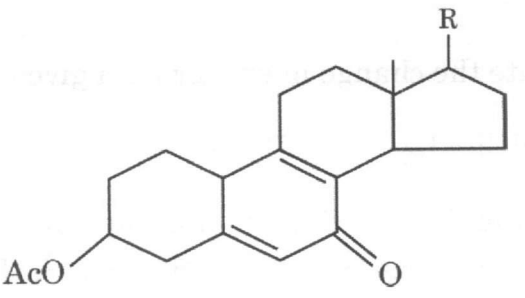


(ii) Deduce the λ_{max} values in given α-β-unsaturated carbonyl compounds using Woodward-Fieser rules : 5

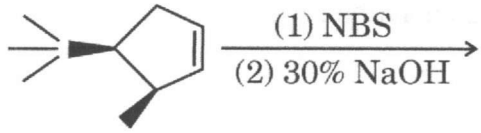
(I)

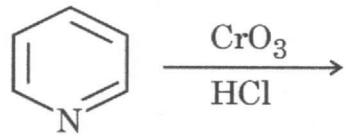


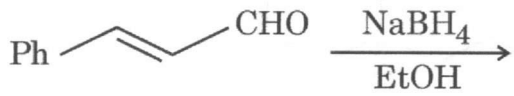
(II)

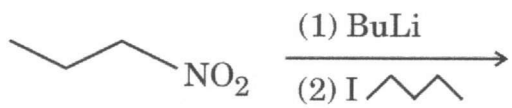


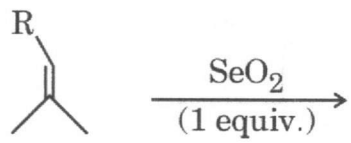
(c) Write down the major product of the following reactions : *10*

(I) 

(II) 

(III) 

(IV) 

(V) 

Q8. (a) (i) Deduce the rotational constant and C – O bond length in carbon monoxide when the first line in the rotational spectrum has a frequency of 3·8424 cm^{-1}.

Given : Avogadro number = $6{\cdot}022 \times 10^{23}$

$h = 6{\cdot}625 \times 10^{-27}$ cm^2 g/s; $c = 3 \times 10^{10}$ cm/s *10*

(ii) Calculate the change in the rotational constant, when hydrogen is replaced by deuterium in the hydrogen molecule. *5*

(b) (i) Calculate the change in energy for a given reaction :

$$HCl + D_2 \longrightarrow DCl + HD$$

Given the frequencies of vibration of the molecules at $v = 0$, HCl = 2885 cm^{-1}, D_2 = 2990 cm^{-1}, DCl = 1990 cm^{-1} and HD = 3627 cm^{-1}, $h = 6{\cdot}625 \times 10^{-34}$ m^2 kg/s, $c = 3 \times 10^8$ m/s. *10*

(ii) What will be the intensity of the hot band

$v = 1 \rightarrow v = 2$ relative to the fundamental

$v = 0 \rightarrow v = 1$ in Iodine molecule at temperature 300 K ?

Given : Equilibrium vibration frequency of Iodine molecule = 215 cm^{-1}

Anharmonicity constant $x_e = 0{\cdot}003$.

$c = 3 \times 10^8$ m/s; $h = 6{\cdot}625 \times 10^{-34}$ m^2 kg/s *10*

(c) Despite the lower electronegativity of sulphur, thiophene metallates as readily as furan. Why ? *5*