No. of Printed Pages : 7

CS-89/06

CHEMISTRY

Paper-II

Time : 3 Hours] **[Full Marks : 300**

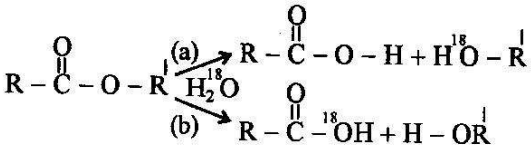
Note : (1) Candidates should attempt Question No. **1** from Section-A and Question No. **5** from Section-B which are compulsory, and any **three** of the remaining questions, selecting at least **one** from each Section.

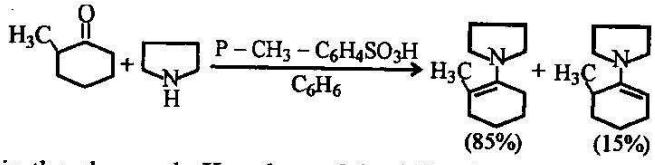
(2) **All** questions carry equal marks.

SECTION – A

1. Answer any **three** of the following : **20 × 3 = 60**

(a) Explain the following and provide the mechanism.

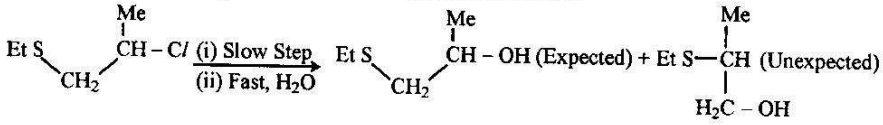
(i) 

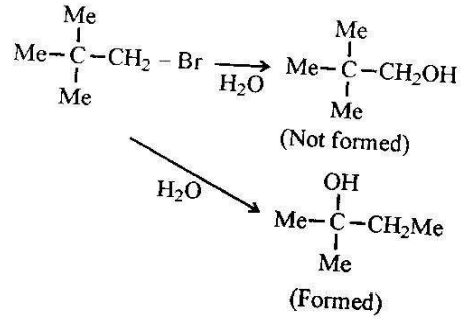
(ii) 

(b) Explain the observed pK_a values of the following compounds :

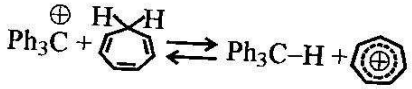
HCO_2H	$HO_2C{\cdot}CO_2H$	$HO_2C{\cdot}CH_2{\cdot}CO_2H$	$C_6H_5{\cdot}CO_2H$	$HO_2C{\cdot}C_6H_4{\cdot}CO_2H$
(i)	(ii)	(iii)	(iv)	(v)
$pK_a = 3.77$	1.23	2.83	4.17	o – 2.98 m – 3.46 p – 3.51

(c) Rationalize the following observation with mechanism :

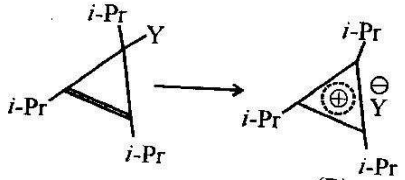
(i) 

(ii) 

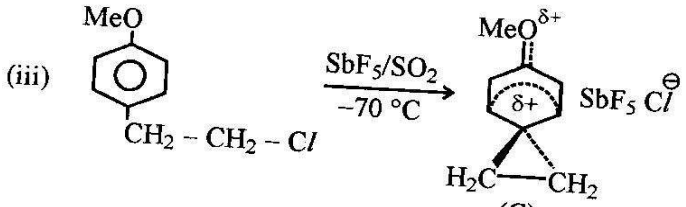
(d) Discuss the stability of carbocations in the following cases :

(i) 

(A)

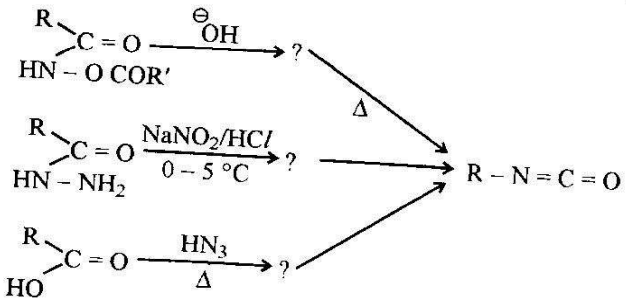
(ii) 

(B)

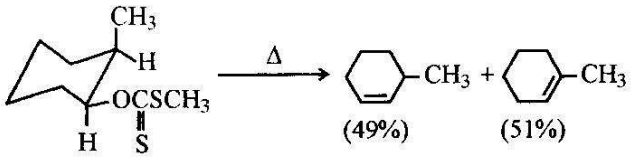
(iii) 

(C)

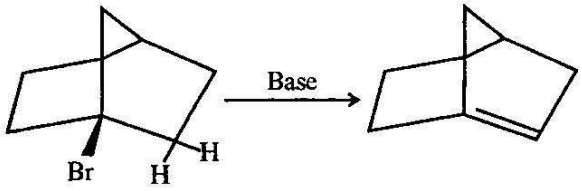
2. (a) Explain and provide the mechanism for the formation of isocyanate : **15**



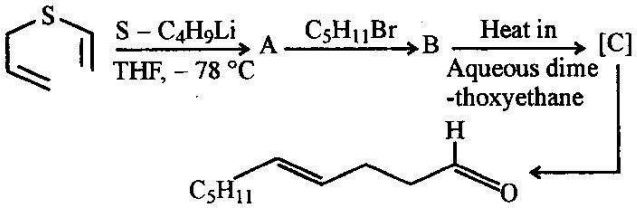
(b) Give the mechanism to rationalize the formation of following percentage of products : **15**



Is the following product possible ? Explain.



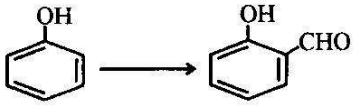
(c) Suggest a suitable mechanism for the following : **15**



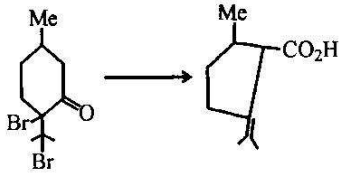
(d) Discuss the mechanism of formation of terylene, teflon and PVC. **15**

3. (a) Suggest the reagents/conditions involved in the following conversions with proper mechanisms : **10 × 4 = 40**

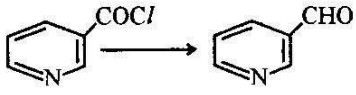
(i)



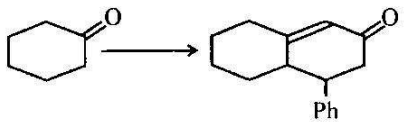
(ii)



(iii)

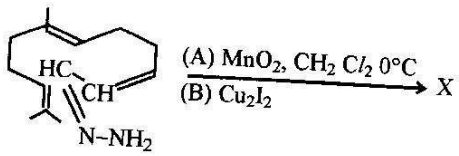


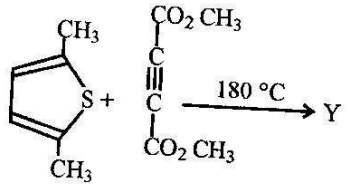
(iv)



(b) Identify the products in each of the following reactions. Give mechanism.

10 × 2 = 20

(i) 

(ii) 

4. (a) Mention any **two** uses with reaction mechanism of the following reagents in Chemistry.

3 × 5 = 15

(i) O_SO_4

(ii) $NaBH_4$

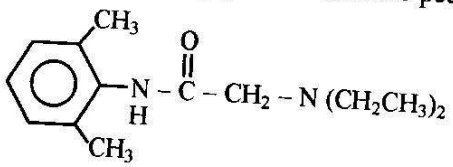
(iii) mCPBA

(b) (i) Comment on the structure of "DNA".

15

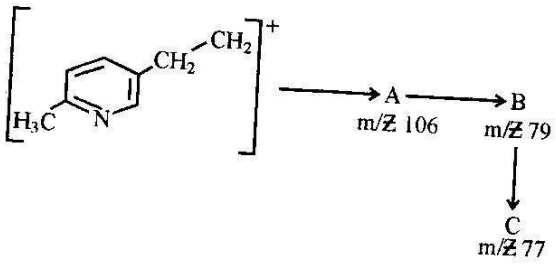
(ii) Predict the number of principal peaks in the ^1H NMR spectrum of the following compound. Which acts as a local anesthetic (Xylocaine). Give the splitting patterns of these peaks.

15



(iii) Suggest the fragmentation pattern for the following compound in the mass spectrum :

15



SECTION – B

5. Answer any **three** of the following :

(a) Explain the Physical concepts of free energy (G) and entropy (s) functions. Discuss how free energy and entropy functions change on mixing two dilute polymer solutions. State the conditions of ideal behaviour of polymer solutions. **20**

(b) Discuss how molecular weight of polymers can be determined using the following methods :

(i) Light scattering

OR

(ii) Viscometry **20**

(c) (i) Derive the expression for the separation between two adjacent rotational spectral lines of a rigid diatomic molecule. Show that the moment of inertia of the molecule can be determined from the study of rotational spectra of diatomic molecule. **10**

(ii) What do you mean by normal vibration ? How many normal modes of vibration are present in carbon dioxide (CO_2) molecule ? Explain with the help of sketches all the normal modes of vibration of CO_2 molecule. Which of these modes are infrared active and why ? **10**

(d) Derive the expression for resonance frequency in Electron Spin Resonance (ESR) spectroscopy. Explain why water and alcohol are not suitable solvent in this spectroscopy. **20**

6. (a) (i) Explain what do you mean by 'number average molecular weight' and 'weight average molecular weight' of a polymer. Write down the mathematical expressions of the two quantities. **10**

(ii) Equal masses of polymers molecules with $M_1 = 10,000$ and $M_2 = 1,00,000$ are mixed. Calculate $\bar{M}_N$ and $\bar{M}_M$. **10**

(b) Discuss the principle of sedimentation method to determine the numbers-average molar mass of a polymer. Calculate also the sedimentation coefficient. **20**

(c) Considering a diatomic molecule to be a harmonic oscillation find the expression for vibrational energy of a diatomic molecule and show that vibrational spectra consist of a single line of frequency equal to the natural frequency of oscillation. Calculate zero point energy and discuss the limitation of harmonic oscillator model of diatomic molecule. What are hot band ? **20**

7. (a) Considering a diatomic molecule as a non-rigid rotator calculate the energy levels of the molecule. Stating the selection rule find also the frequency of transition. Compare the spectra with that of the rigid rotation. What useful informations can be derived from centrifugal distorsion constant ? **20**

(b) (i) Explain the change of pattern of rotational spectral lines when one of the atoms of a diatomic molecule is substituted by a heavier atom. **10**

(ii) Calculate the relative population for rotational quantum number J = 1 for a molecule with rotational constant $\bar{B} = 2.0\ cm^{-1}$ at temperature 300 K. (Given $h = 6.6 \times 10^{-34}$ Js, Boltzmann constant $K = 1.38 \times 10^{-23}$ JK^{-1}) **10**

(c) Explain why a diatomic molecule is to be treated as an anharmonic oscillator. Write the expression for Morse potential function and derive the expressions for the frequencies of fundamental and first overtone bands of anharmonic oscillator. Discuss the effect of anharmonicity on vibrational spectra. State the conditions under which the vibrational spectra of a diatomic molecule is observed. **20**

8. (a) Derive the expression for resonance frequency in electron spin resonance spectroscopy stating the condition of resonance. Describe how the spectroscopic splitting factor (g) varies with different situations. What do you mean by isotropic and anisotropic 'g' values ? Explain why ESR spectrum is recorded in derivative mode. Show the relationship between absorption spectrum and derivative spectrum with reference to peak position and line width. **20**

(b) (i) Explain the origin of hyperfine splitting of ESR spectrum line. What are the different types of hyperfine interactions that give rise to hyperfine splitting of ESR spectrum lines ? State some applications of ESR spectroscopy. **10**

(ii) The hyperfine splitting pattern of Mn^{55} give rise to six ESR lines. Calculate the nuclear spin of Mn^{55}. **5**

(iii) Calculate the frequency for an unpaired electron in a magnetic field of strength 0.35 T

(Given g = 2.0023 and Bohr magneton $\beta = 9.273 \times 10^{-24}\ JT^{-1}$) **5**

(c) A microwave spectrometer capable of operating between 60 cm^{-1} and 90 cm^{-1} was used to observe rotation spectrum of HI and DI molecules. The absorption were measured as

HI (cm^{-1})	DI (cm^{-1})
64.275	65.070
77.130	71.577
89.985	78.094
	84.591

Calculate rotational constant, moment of inertia and internuclear distance of each molecule and determine the 'J' values between which transitions occur for first line above for each. Does your result supports the usual assumption that bond length is unchanged by isotopic substitution ? **20**