

CSM – 17/18
Chemistry
Paper – II

Time : 3 hours

Full Marks : 300

The figures in the right-hand margin indicate marks.

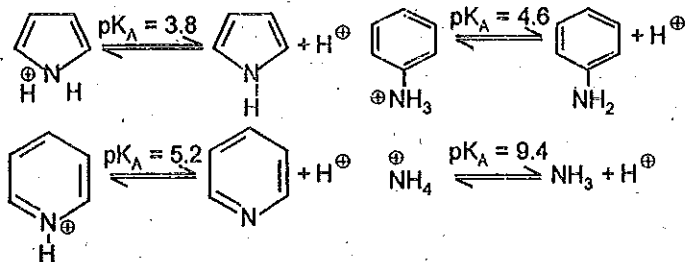
Candidates should attempt Q. No. 1 from Section – A and Q. No. 5 from Section – B which are compulsory and three of the remaining questions, selecting at least one from each Section.

SECTION – A

1. Answer any three of the following questions :

20×3 = 60

(a) (i) Consider the pKa data for the following aromatic N containing systems :



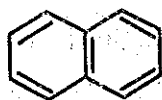
Henderson-Hasselbach equation :

$$pK_a = pH + \log \left(\frac{[A^-]}{[HA]} \right)$$

Which species is the strongest acid ?

(ii) Why normally benzene does not undergo addition reaction although benzene is highly unsaturated ?

(iii) Arrange in terms of the resonance energies (in comparison to one another) of each of the following compounds :



(i)



(ii)



(iii)

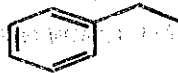
(iv) Rate the relative stability in descending order of the following carbocations (in comparison to one another) :



(i)

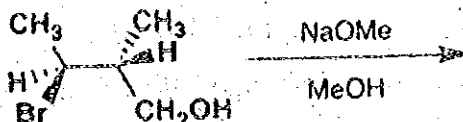


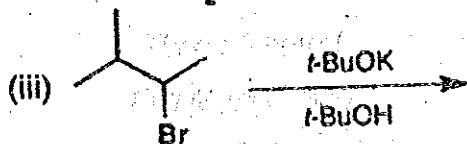
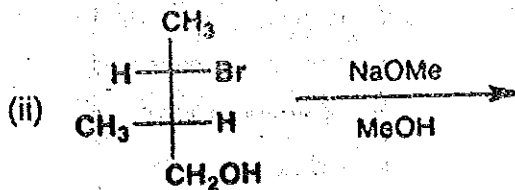
(ii)



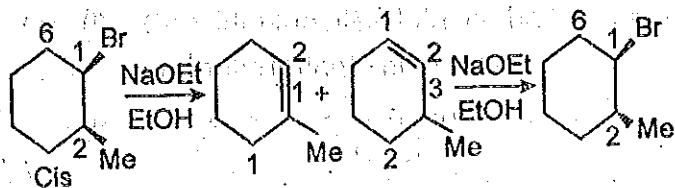
(iii)

(b) (i) Which is the main product of the following reaction ?





(iv) Elimination reactions of *cis*- and *trans*-1-bromo-2-methylcyclohexanes with NaOEt in EtOH can give the same or different main product, 1-methylcyclohexene (1) or 3-methylcyclohexene, (2) which is the main product?



(c) (i) Write the order of decreasing vibrational frequency for the following :

C-Cl, C-Br, C-C, C-O and C-H

(ii) A compound of molecular formula C_8H_7ClO shows a prominent band in its IR spectrum at 1690 cm^{-1} . $^1\text{H NMR}$

spectrum revealed only two major types of protons in the ratio of 5 : 2. Which one of the following structures best fits the above data ?

- (iii) An organic compound Q exhibited the following spectral data obtained by mass spectroscopy.

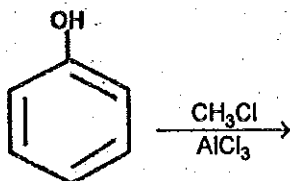
IR : 1760 cm^{-1}

^1H NMR : Chemical reference (ppm) : 7.2 (1H, d, 16.0 Hz), 5.1 (1H, m), 2.1 (3H, s), 1.8 (3H, d, $J = 7.0 \text{ Hz}$)

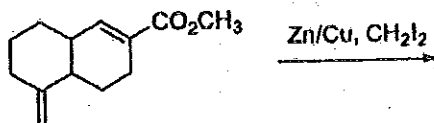
^{13}C NMR chemical reference (ppm) : 170 (carbonyl carbon). What is compound Q ?

- (iv) A 0.1 M solution of compound A shows 50% transmittance when a cell of 1 cm width is used at λ_1 nm. Another 0.1 M solution of compound B gives the optical density value of 0.1761 using 1cm cell at λ_1 nm. What will be the transmittance of a solution that is simultaneously 0.1 M in A and 0.1 M in B using the same cell and at the same wave length ? [$\log 1.301$; $\log 1.4771$; $\log 50 = 1.699$].

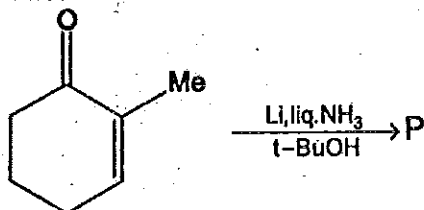
- (d) (i) Write the structure of the product in the given reaction. Give the mechanism of the reaction :



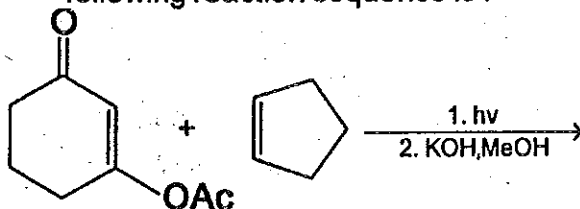
- (ii) The major product formed in the following reaction is :



- (iii) The major product P of the following reaction is :

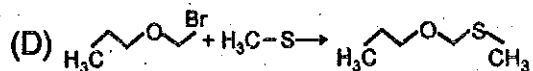
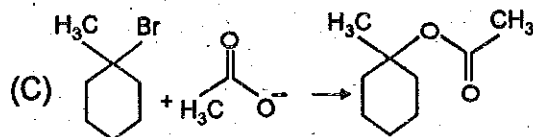
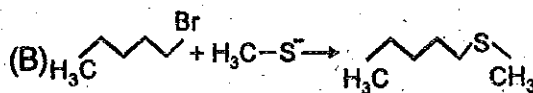
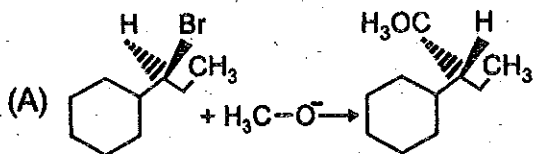


- (iv) The major product formed in the following reaction sequence is :

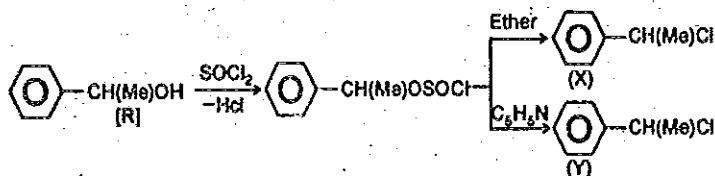


2. (a) Answer the following as directed :

(i) Identify two reactions from the following which will go faster if the concentration of the nucleophile is raised. Explain with mechanism : 10



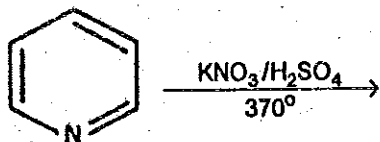
(ii) Which configuration will be adopted by X and Y respectively ? 10



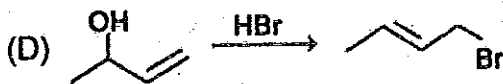
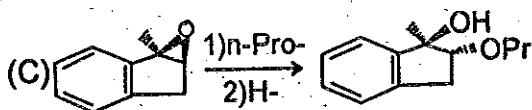
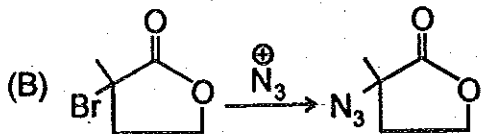
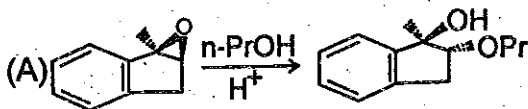
(b) Answer all questions as directed :

5×4 = 20

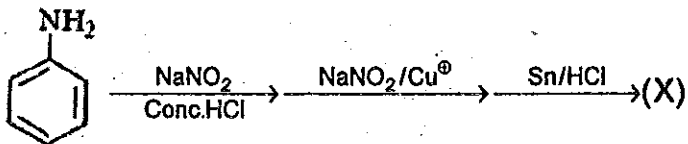
(i) Predict the product of the following reaction ?



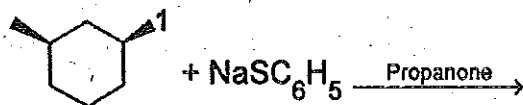
(ii) Out of the following four reactions, one is incorrect ? Find the reaction and explain.



(iii) What will be the (X) in the below mentioned reaction sequence ?

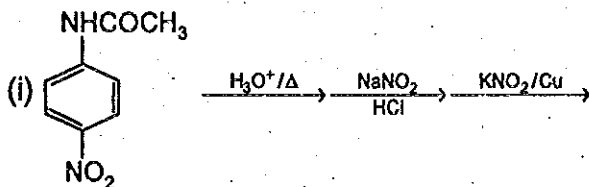


(iv) Which is the main product of the following reaction ?

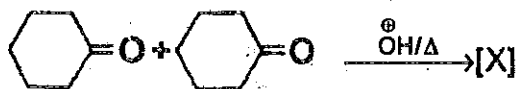


(c) Predict the product in each of the reaction :

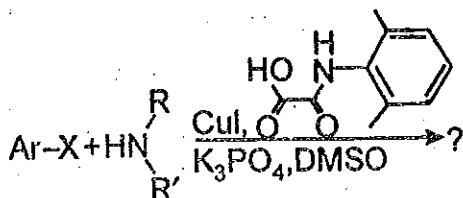
5×4 = 20



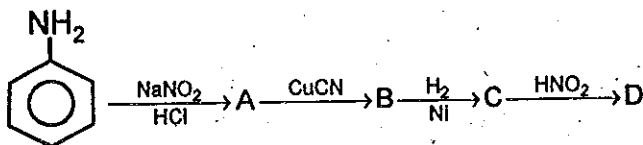
(ii) Where will nucleophile (–OH) will attack to form the product X ?



(iii) Predict the product for the following reaction :



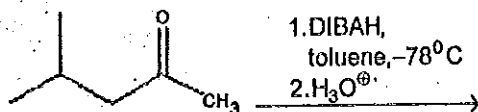
(iv) Write the structure of A, B, C, D in the following reaction :



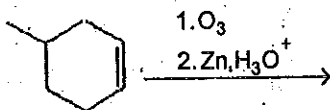
3. (a) Answer the following questions as directed :

5×4 = 20

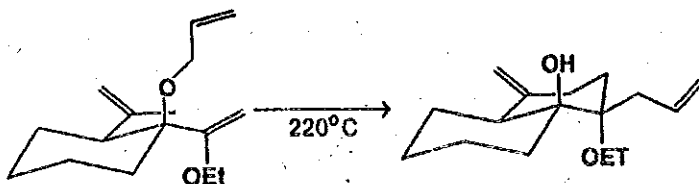
(i) What is the major organic product obtained from the following reaction ?



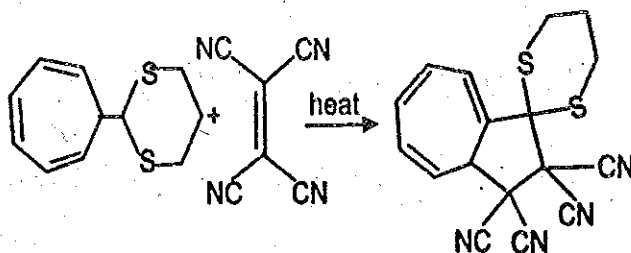
(ii) Predict the product obtained from the following reaction :



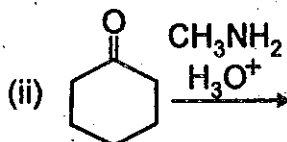
(iii) The following transformation involves sequential :



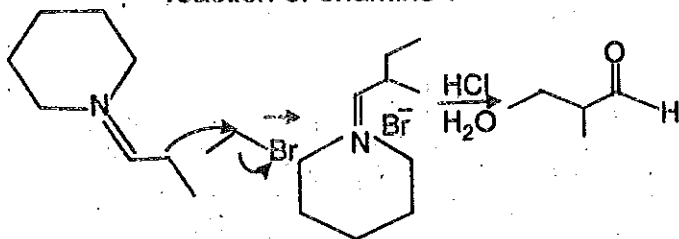
(iv) The following reaction is an example of which type of pericyclic reaction.



(b) Predict the product obtained from the following reaction : 5×4 = 20

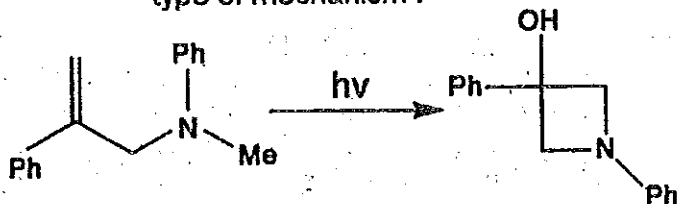


(iv) What is the name of the following reaction of enamine ?



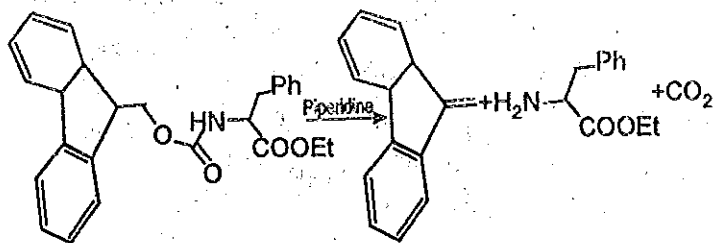
(c) Answer the questions as directed : 5×4 = 20

(i) The following photochemical transformation proceeds through which type of mechanism :



(ii) Draw the resonance structure of azulene and predict the dipole moment.

(iii) What is the mechanism involved in the following conversion ?

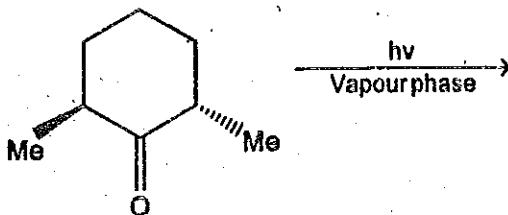


BD - 17/11

(11)

(Turn over)

(iv) The cyclic product (S) of the following photochemical reaction is :



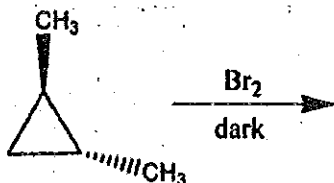
4. Answer any ten questions as directed :

6×10 = 60

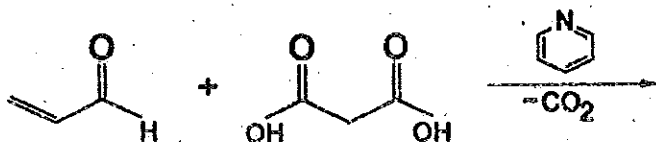
(a) Write the products of the following reaction :



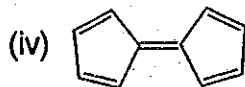
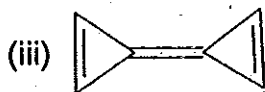
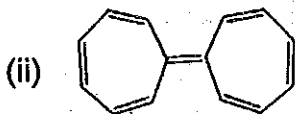
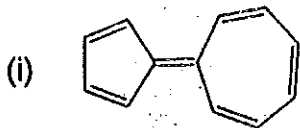
(b) Write the product of the following reaction :



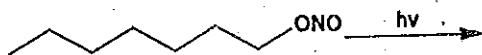
(c) Write the products of the following reactions :



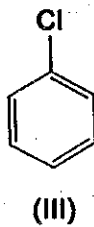
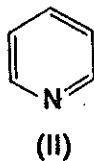
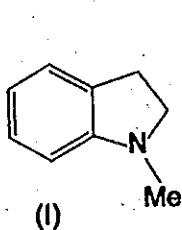
(d) Which of the following compound is aromatic ?



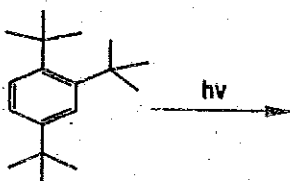
(e) The major product formed in the following photochemical reaction is :



(f) The correct order for the rates of electrophilic substitution of the following compound is :



- (g) The major product formed during the hydroboration-oxidation of 1-methyl cyclopentene is _____.
- (h) The major product formed in the reaction of 1, 5-cyclooctadiene with 0.5 equivalent of diborane is _____.
- (i) The product formed in the following reaction is :



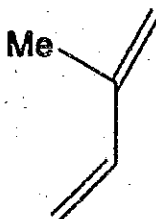
- (j) Order of reactivity of the following dienes X, Y and Z in Diels-Alder reaction is :



X



Y



Z

- (k) The conversion of excited singlet (S_1) of a molecule to triplet state (T_1) is known as :
- (i) Fluorescence

- (ii) Phosphorescence
 - (iii) Intersystem crossing
 - (iv) Internal conversion
- (l) Which of the following reaction is an example of an atom economy reaction ?
- (i) Wittig reaction
 - (ii) Grignard reaction
 - (iii) Dieckmann condensation
 - (iv) Diels-Alder reaction

SECTION – B

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

20×3 = 60

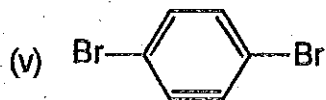
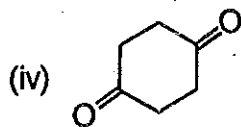
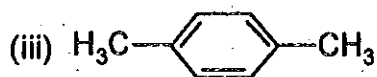
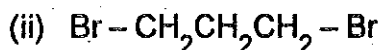
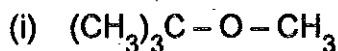
(a) Write the synthesis of the following polymer with chemical equation :

Polyvinyl chloride, Teflon, Synthetic rubber, Borazines, Polythene.

(b) Write any two most important synthetic uses of the following compounds (all compounds) :

HIO_4 , NBS, NaBH_4 , mCPBA.

(c) Explain the chemical shift in NMR spectroscopy. Which of the following compounds would be expected to show spin-spin splitting in their ^1H NMR spectra ?



(d) Consider the molecules CCl_4 , CHCl_3 and CH_2Cl_2 :

(i) Write the rotor in these compounds.

(ii) Will they show pure rotational spectra ?

Assume that ammonia shows a pure rotational spectrum. If the rotational constants are 9.44 and 6.20 cm^{-1} , use the energy

expression : $E = (A - B) K^2 + B J(J + 1)$, to calculate the energies (in cm^{-1}) of the first three lines (i. e. those with lowest K, J quantum number for the absorbing level) in the absorption spectrum (ignoring higher order terms in the energy expression).

6. Answer any five questions of the following :

$$12 \times 5 = 60$$

(a) Write the process step by step for the determination of the molecular weight of a polymer by osmotic pressure method.

Find out number average molecular weight (M_n) and weighted average molecular weight (MW) for a sample obtained by mixing 10g of polystyrene (MW = 100,000 and M_n = 70,000) with 20g of another polystyrene (MW = 60,000 and M_n = 20,000) ?

(b) Write short notes on any two of the following :

(i) Silicones

(ii) Polyvinyl chloride

(iii) Flory-Huggins Model

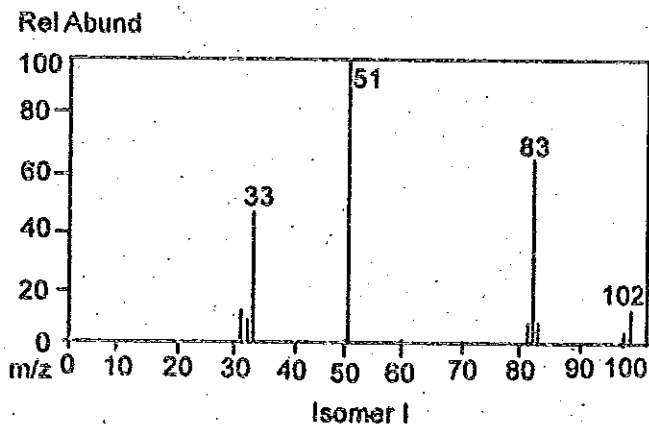
- (c) An organic compound Q exhibited the following spectral data obtained by different spectroscopy :

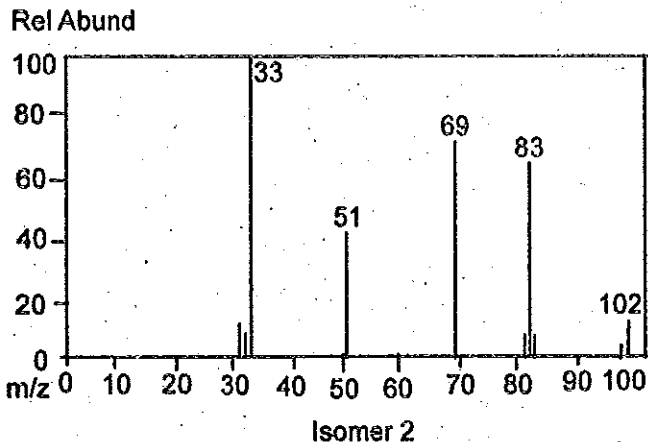
IR : 1760 cm^{-1}

^1H NMR : Chemical reference (ppm) : 7.2 (1H, d, 16.0 Hz), 5.1 (1H, m), 2.1 (3H, s), 1.8 (3H, d, $J = 7.0\text{ Hz}$)

^{13}C NMR chemical reference (ppm) : 170 (carbonyl carbon). What is compound Q ?

- (d) The mass spectra of two constitutional isomers are presented below. Both are gases at room temperature. The molecular ion is the small peak at $m/z = 102\text{ amu}$.





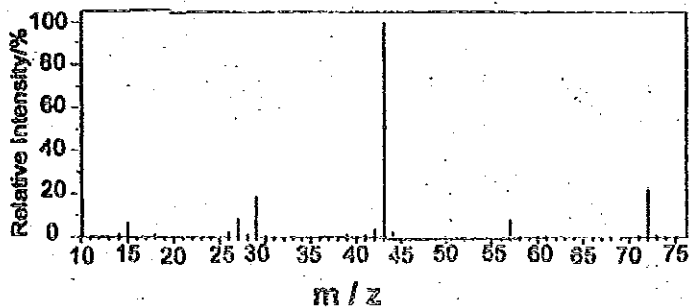
Write the name of the isomer that would give mass spectrum 1 and mass spectrum 2.

- (e) What are the main criteria on which mass spectrometer used for ? A PMR spectrometer operates at 300 MHz. Find the value of magnetic field.

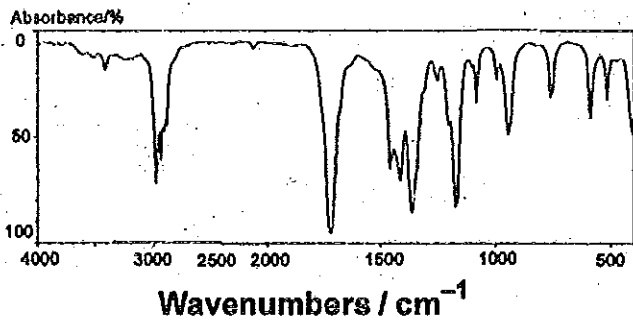
Given : $g_N = 5.585$ and $B_N = 5.05 \times 10^{-27} \text{ JT}^{-1}$.

- (f) From the following data of a compound, draw the structure of the compound :

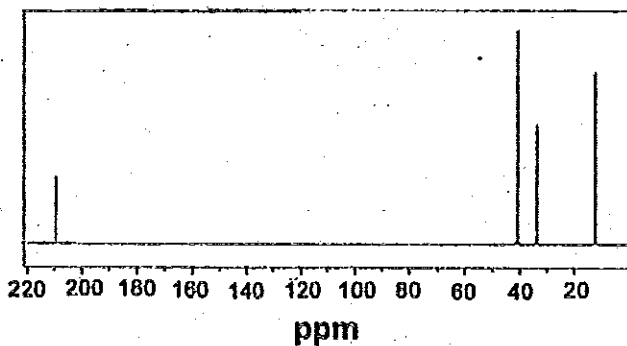
Mass Spectra :



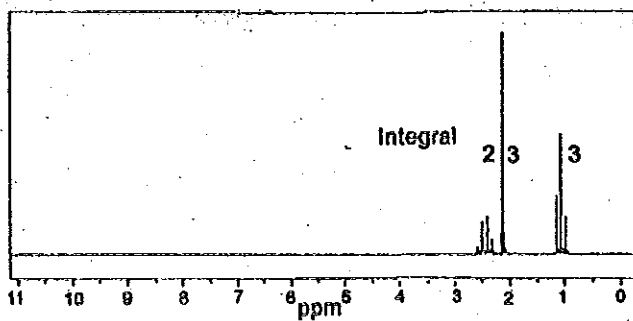
IR Spectra :



CNMR :



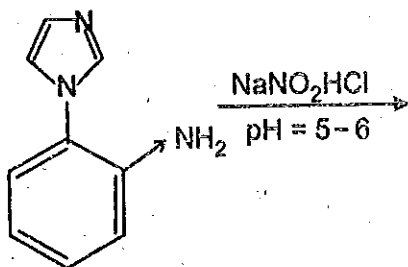
HNMR :



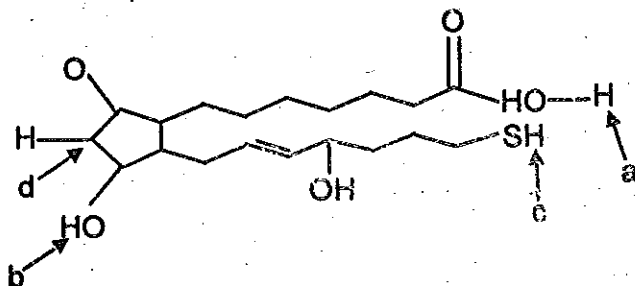
7. Answer any ten from the following questions :

6×10 = 60

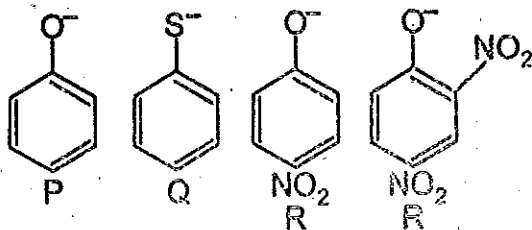
(a) The major product formed in the following reaction is :



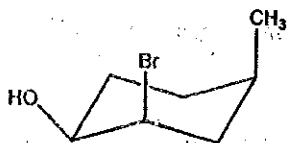
(b) Identify most acidic hydrogen in given compound and explain, why it is more acidic :



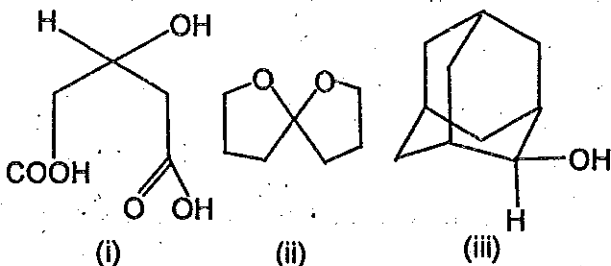
(c) The order of nucleophilicity of the following anions in a S_N2 reaction is :



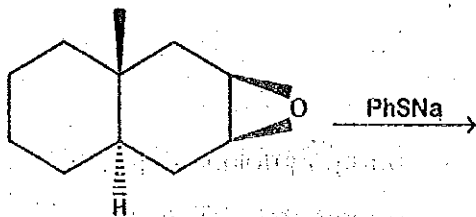
(d) Ring flipping of the compound in the following conformation leads to :



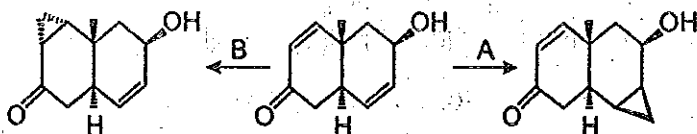
(e) Which of the following molecules is chiral ?



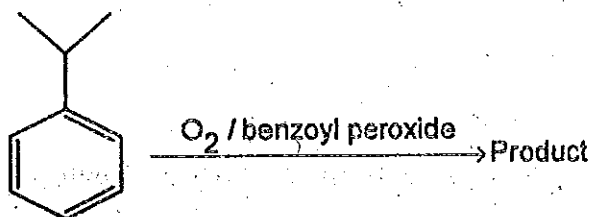
(f) The major product formed in the following reaction is :



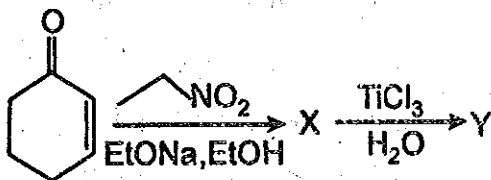
(g) What are the reagents A and B in the following reactions ?



- (h) What is the major product formed in the reaction between benzoic acid and isobutylene in the presence of a catalytic amount of sulfuric acid ?
- (i) Predict the most probable product in the given reaction :



- (j) The major products X and Y formed in the following reaction sequence are :



- (k) Explain the Norrish-Type-II reactions with suitable example.
- (l) Explain Cope rearrangement with suitable example with mechanism.

8. Answer any six questions of the following :

10×6 = 60

(a) Calculate the magnetic moment (μ_1) of a ^{13}C nucleus.

(b) Using the rigid rotor approximation, estimate the bond length in a $^{12}\text{C}^{16}\text{O}$ molecule if the energy difference between $J = 1$ and $J = 3$ are equal to $14,234\text{ cm}^{-1}$.

(c) Answer as required :

(i) Which of the following organic compound with molecular formula C_3HCl_2 exhibits only one signal in the ^1H NMR spectrum ?

(A) 2, 2-dichloropropane

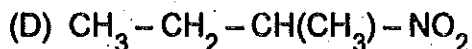
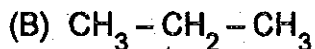
(B) 1, 2-dichloropropane

(C) 1, 3-dichloropropane

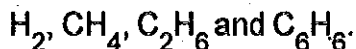
(D) 1, 1-dichloropropane

(ii) An organic compound with molecular formula $\text{C}_4\text{H}_9\text{NO}_2$ shows following ^1H NMR spectrum : δ 5.30 (broad, 1H), 4.10 (q, 2H), 2.80 (d, 3H) 1.20 (t, 3H) ppm. Draw the structure of the compound.

(iii) In which of the following four compounds, three types of hydrogens are present :



(iv) What type of PMR spectra will be exhibited by the following compounds :



(v) Which form of Electromagnetic radiation are used in NMR spectroscopy ? Give the descending order of Electromagnetic radiation in terms of energy.

(d) Answer the question as directed :

(i) Find out the wavelength of a photon having a wavenumber 100 cm^{-1} .

(ii) Calculate the moment of inertia, I , of the molecule $^1\text{H}^{35}\text{Cl}$. The masses of the two atoms are $m_{\text{H}} = 1.673 \times 10^{-27} \text{ kg}$ and $m_{\text{Cl}} = 5.807 \times 10^{-26} \text{ kg}$. The equilibrium bond length of the molecule is 1.275 \AA .

- (iii) Calculate the position in cm^{-1} of the $J=67$ line in the pure rotational spectrum of the hydrogen deuteride molecule, HD. The masses of the two atoms are $m_{\text{H}} = 1.0078 \text{ u}$ and $m_{\text{D}} = 2.0141 \text{ u}$ and the equilibrium bond length of the molecule is 0.749 \AA .
- (iv) The molecule $^{12}\text{C}^{32}\text{S}$ has been detected in interstellar clouds using microwave spectroscopy. Predict which rotational level in $^{12}\text{C}^{32}\text{S}$ will have the greatest population at a temperature of 70K. The masses of the two atoms are $m_{\text{C}} = 12.00 \text{ u}$ and $m_{\text{S}} = 31.972 \text{ u}$ and the equilibrium bond length of the molecule is 1.534 \AA .
Note : The Boltzmann constant, k , has a value in wavenumbers of 0.69503 cm^{-1} .
- (v) The first Stokes line and the first anti-Stokes line in the rotational Raman spectrum of N_2O are displaced from the Rayleigh line by 2.514 cm^{-1} and $+2.514 \text{ cm}^{-1}$ respectively. Determine the rotational constant of N_2O .

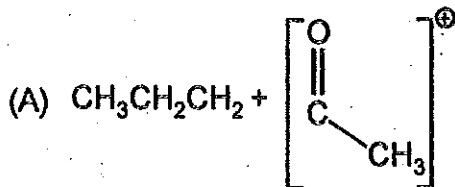
- (e) (i) In a 9.25GHz ESR spectrometer two lines appear at 357.3 T and 306.6 MT. Calculate the hyperfine constant.
- (ii) Calculate the frequency required at a magnetic field strength of 0.3 T.
- (iii) Explain the Hyperfine splitting.
- (iv) The benzene anion has $g = 2.0025$. At what magnetic induction B , would its ESR spectral line be centred at frequency 9.350 GHz ?
- (v) The ESR spectrum of a radical with a single magnetic nucleus is split into four lines of equal intensity. What is the spin of the nucleus ?
- (f) (i) Bromine possesses two isotopes (^{79}Br and ^{81}Br) in an approximate 1 : 1 ratio. In the mass spectrum of Br_2 , how many peaks will the parent ion contain ?
- (ii) While running a new reaction, a chemist notices the evolution of a gas. A sample of this gas gave a mass spectrum in

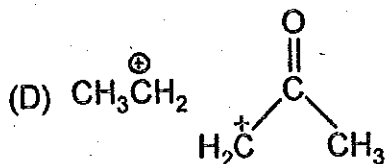
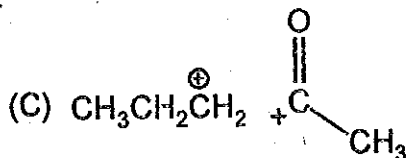
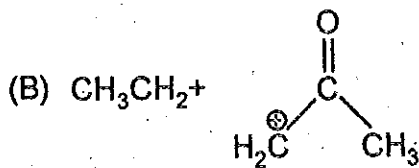
which the molecular ion ($m/z = 44$) was the largest ion peak. The only other significant peaks were observed at $m/z = 28$ and $m/z = 16$.

(iii) Calculate the resolving power (R_p) of a mass spectrometer for two adjacent signals in a mass spectrum due to O_3^+ at $m/z = 47.9847$ and $H_2NO_2^+$ at $m/z = 48.0085$.

(iv) Calculate the degrees of unsaturation, i.e. number of RDBs (rings + double bonds) associated with a $C_7H_5NOF_2^+$ ion.

(v) Which of the following pairs of species are the major products formed by alpha-cleavage of 2-pentanone ?





- (g) (i) The molecule $^{12}\text{C}^{32}\text{S}$ has been detected in interstellar clouds using microwave spectroscopy. Predict which rotational level in $^{12}\text{C}^{32}\text{S}$ will have the greatest population at a temperature of 70 K. The masses of the two atoms are $m_{\text{C}} = 12.00$ u and $m_{\text{S}} = 31.972$ u and the equilibrium bond length of the molecule is 1.534 \AA .
 Note : The Boltzmann constant, k , has a value in wavenumbers of 0.69503 cm^{-1} .

(ii) How many normal modes of vibration are there for C₆₀ ?

(iii) The force constants of four diatomic molecules are given below :

Molecule	K/N m ⁻¹
F ₂	450
HCl	510
CO	1860
N ₂	2240

Which of the four molecules has the highest vibrational wavenumber ?

(iv) Identify which of the following pairs of molecules exhibit both a pure rotational spectrum and a rotational Raman spectrum :

- (A) O₂ and H₂O
- (B) CO₂ and N₂O
- (C) CO and CH₄
- (D) NO and DCCH

- (v) Calculate the position in cm^{-1} of the $J=67$ line in the pure rotational spectrum of the hydrogen deuteride molecule, HD. The masses of the two atoms are $m_{\text{H}} = 1.0078 \text{ u}$ and $m_{\text{D}} = 2.0141 \text{ u}$ and the equilibrium bond length of the molecule is 0.749 \AA .



