

<b>CSM – 17/18</b>
<b>Chemistry</b>
<b>Paper – II</b>

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.

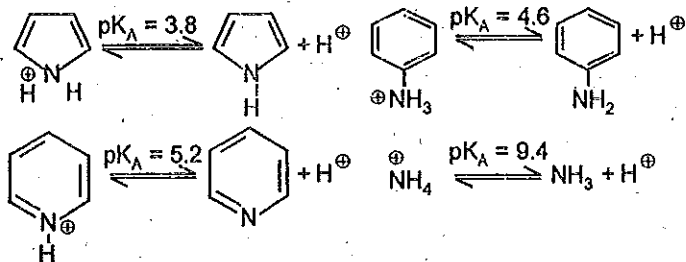
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**SECTION – A**

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 :

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(i)



(ii)



(iii)

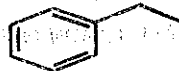
(iv) Rate the relative stability in descending order of the following carbocations (in comparison to one another) :



(i)

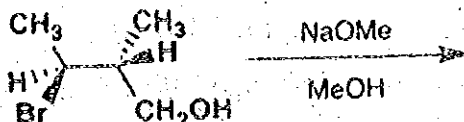


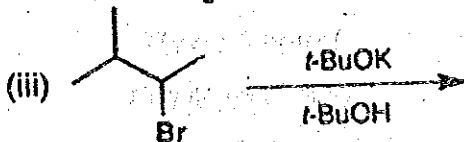
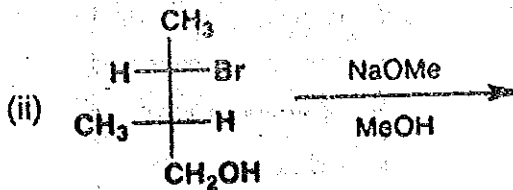
(ii)



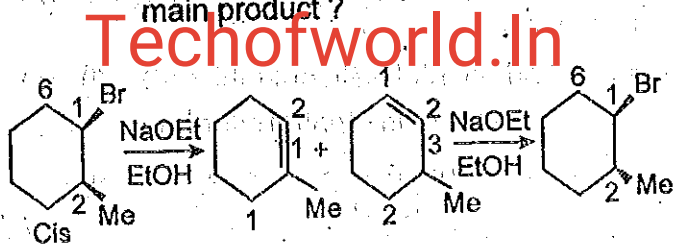
(iii)

(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  $1690\text{ cm}^{-1}$ .  $^1\text{H NMR}$

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.

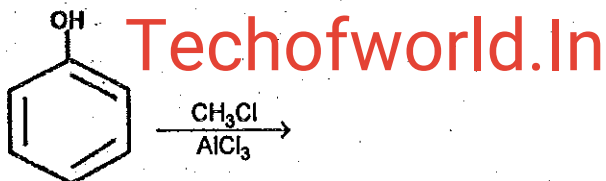
IR :  $1760 \text{ cm}^{-1}$

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

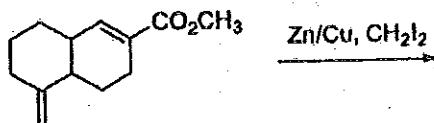
$^{13}\text{C NMR}$  chemical reference (ppm) : 170 (carbonyl carbon). What is compound Q ?

- (iv) A 0.1 M solution of compound A shows 50% transmittance when a cell of 1 cm width is used at  $\lambda_1$  nm. Another 0.1 M solution of compound B gives the optical density value of 0.1761 using 1 cm cell at  $\lambda_1$  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 ? [ $\log 1.301$ ;  $\log 1.4771$ ;  $\log 50 = 1.699$ ].

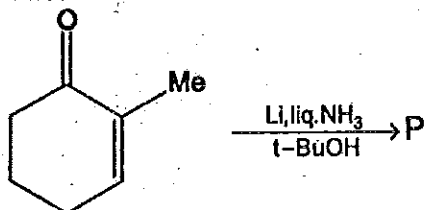
- (d) (i) Write the structure of the product in the given reaction. Give the mechanism of the reaction :



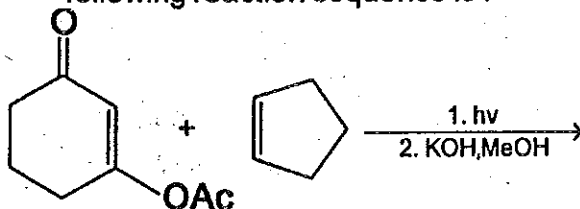
- (ii) The major product formed in the following reaction is :



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

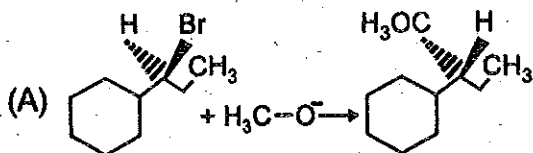


- (iv) The major product formed in the following reaction sequence is :

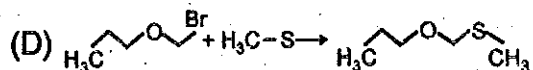
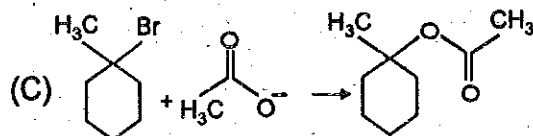
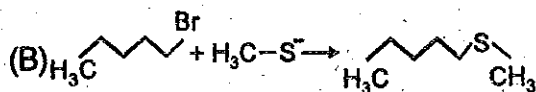


2. (a) Answer the following as directed :

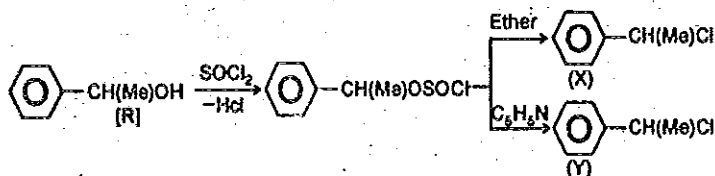
(i) Identify two reactions from the following which will go faster if the concentration of the nucleophile is raised. Explain with mechanism : 10



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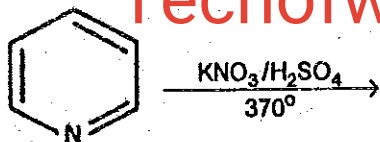
(ii) Which configuration will be adopted by X and Y respectively ? 10



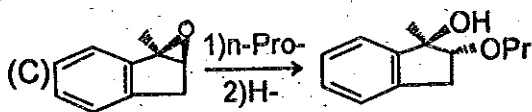
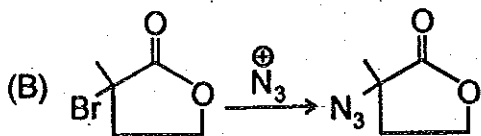
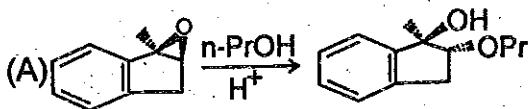
(b) Answer all questions as directed :

5×4 = 20

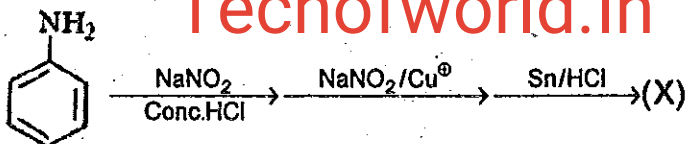
- (i) Predict the product of the following reaction ?



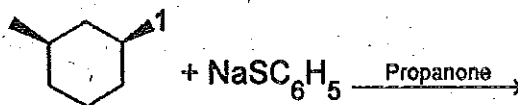
- (ii) Out of the following four reactions, one is incorrect ? Find the reaction and explain.



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

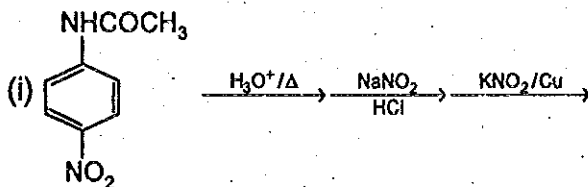


(iv) Which is the main product of the following reaction ?

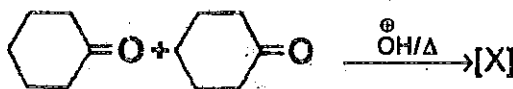


(c) Predict the product in each of the reaction :

5×4 = 20



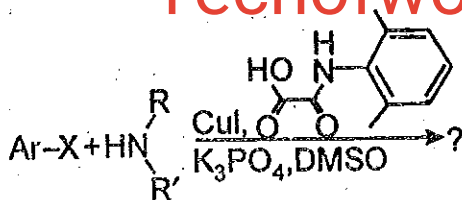
(ii) Where will nucleophile (–OH) will attack to form the product X ?



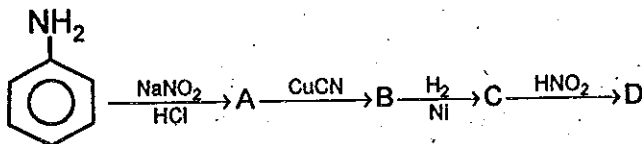


(iii) Predict the product for the following

reaction : **Techofworld.In**



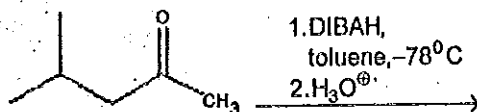
(iv) Write the structure of A, B, C, D in the following reaction :



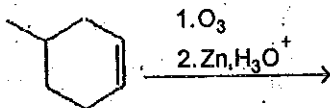
3. (a) Answer the following questions as directed :

5×4 = 20

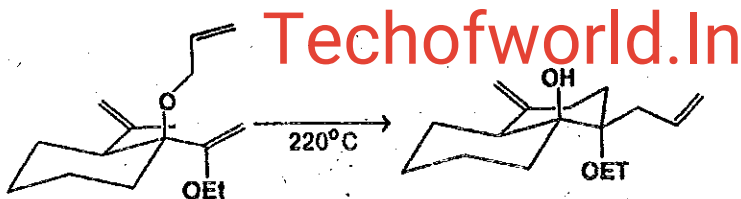
(i) What is the major organic product obtained from the following reaction ?



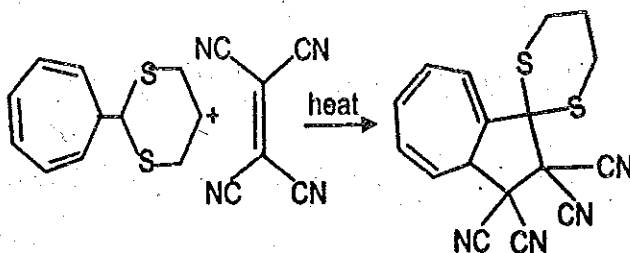
(ii) Predict the product obtained from the following reaction :



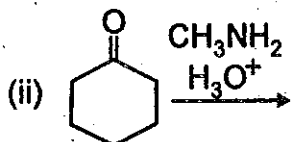
(iii) The following transformation involves sequential :



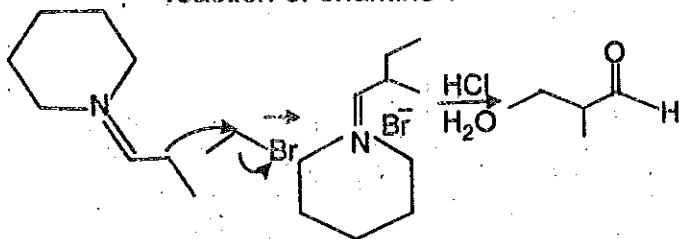
(iv) The following reaction is an example of which type of pericyclic reaction.



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



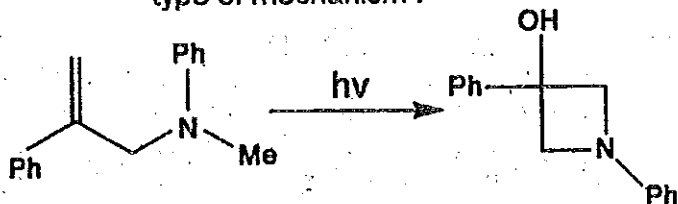
(iv) What is the name of the following reaction of enamine ?



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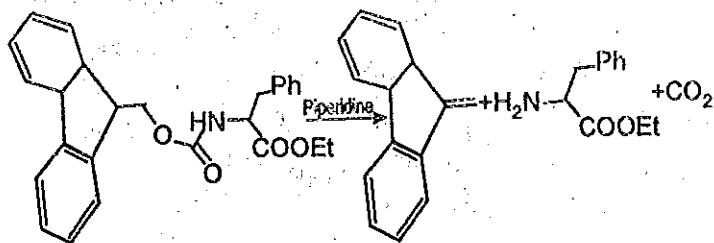
(c) Answer the questions as directed :  $5 \times 4 = 20$

(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 ?

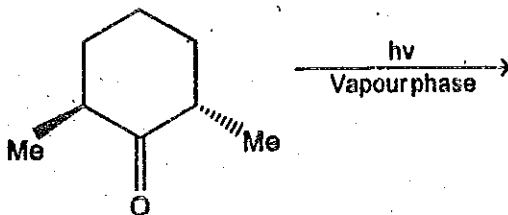


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(11)

(Turn over)

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



4. Answer any ten questions as directed :

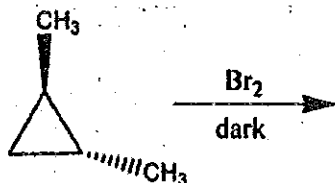
6×10 = 60

(a) Write the products of the following reaction :

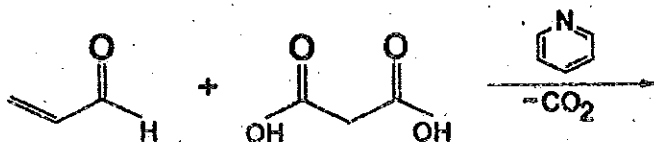


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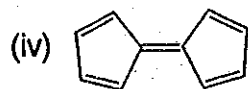
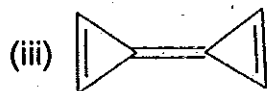
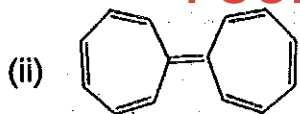
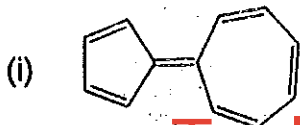
(b) Write the product of the following reaction :



(c) Write the products of the following reactions :

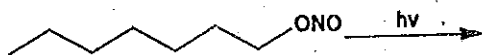


(d) Which of the following compound is aromatic ?

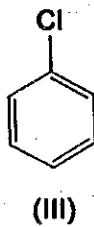
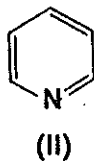
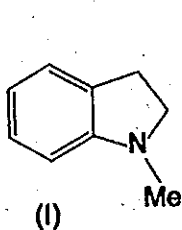


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(e) The major product formed in the following photochemical reaction is :

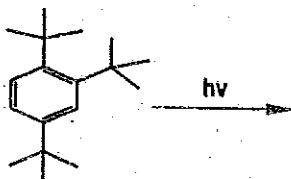


(f) The correct order for the rates of electrophilic substitution of the following compound is :



- (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 :

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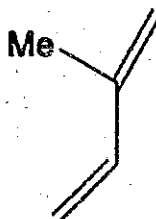
- (j) Order of reactivity of the following dienes X, Y and Z in Diels-Alder reaction is :



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

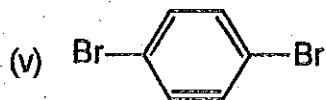
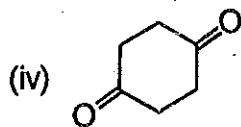
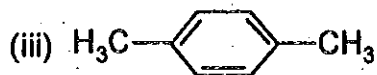
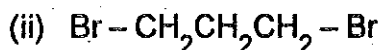
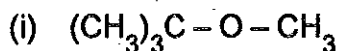
(a) Write the synthesis of the following polymer with chemical equation :

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

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

$\text{HIO}_4$ , NBS,  $\text{NaBH}_4$ , mCPBA.

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



(d) Consider the molecules  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  :

(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  $6.20 \text{ cm}^{-1}$ , use the energy



expression :  $E = (A - B) K^2 + B J(J + 1)$ , to calculate the energies (in  $\text{cm}^{-1}$ ) 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 :

**Techofworld.In**  $12 \times 5 = 60$

(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

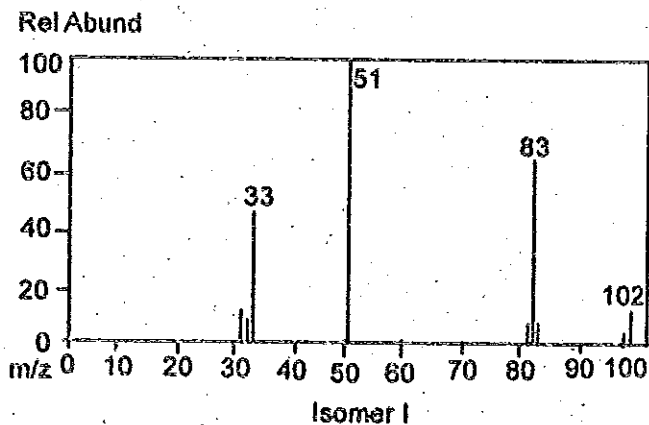
- (c) An organic compound Q exhibited the following spectral data obtained by different spectroscopy :

IR :  $1760\text{ cm}^{-1}$

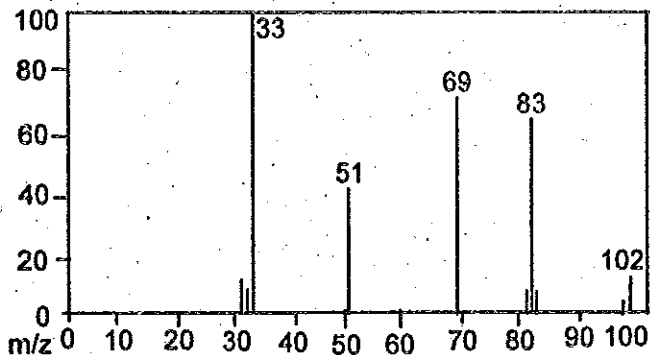
$^1\text{H}$  NMR : Chemical reference (ppm) : 7.2 (1H, d, 16.0 Hz), 5.1 (1H, m), 2.1 (3H, s), 1.8 (3H, d,  $J = 7.0\text{ Hz}$ )

$^{13}\text{C}$  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  $m/z = 102\text{ amu}$ .



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Isomer 2

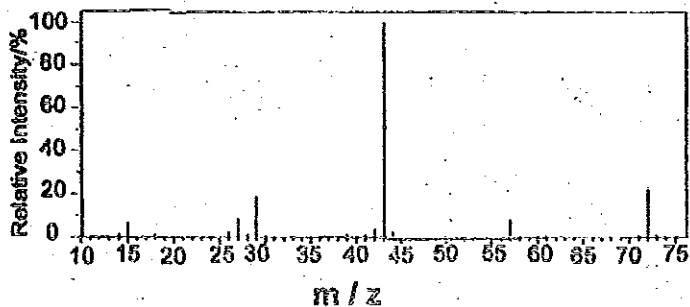
Write the name of the isomer that would give mass spectrum 1 and mass spectrum 2.

- (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.

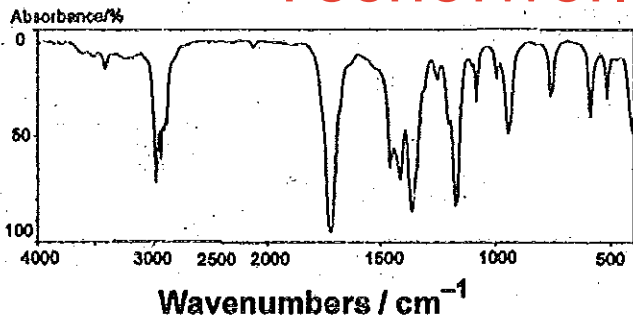
Given :  $g_N = 5.585$  and  $B_N = 5.05 \times 10^{-27} \text{ JT}^{-1}$ .

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

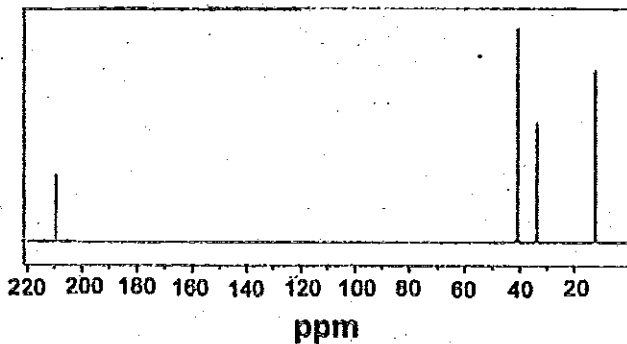
Mass Spectra :



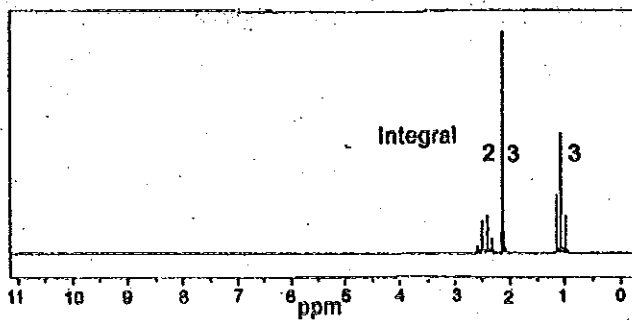
IR Spectra: [Techofworld.In](http://Techofworld.in)



CNMR:



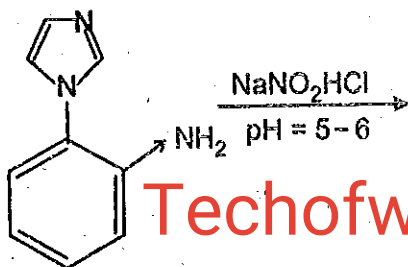
HNMR:



7. Answer any ten from the following questions :

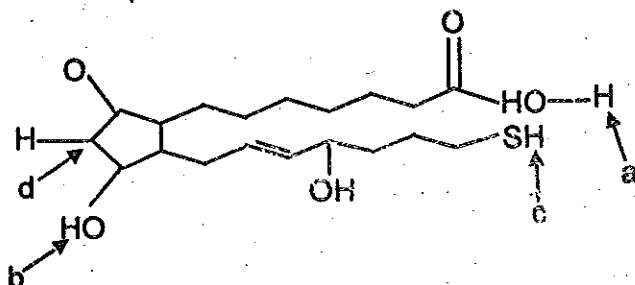
6×10 = 60

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

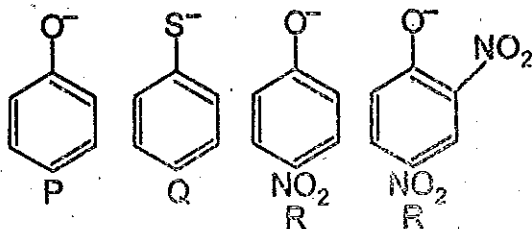


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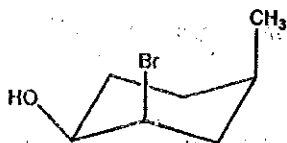
(b) Identify most acidic hydrogen in given compound and explain, why it is more acidic :



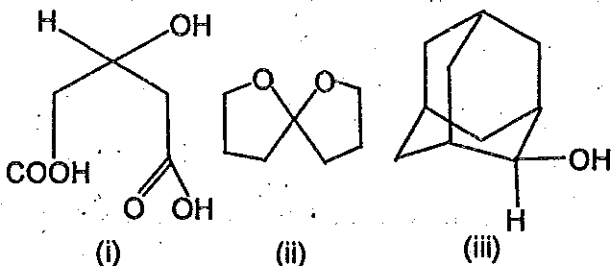
(c) The order of nucleophilicity of the following anions in a  $\text{S}_{\text{N}}2$  reaction is :



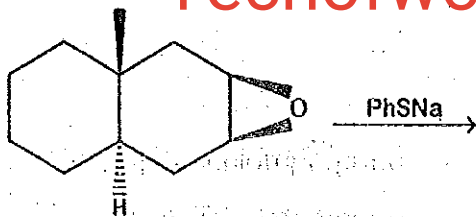
- (d) Ring flipping of the compound in the following conformation leads to :



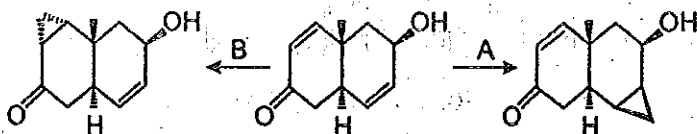
- (e) Which of the following molecules is chiral ?



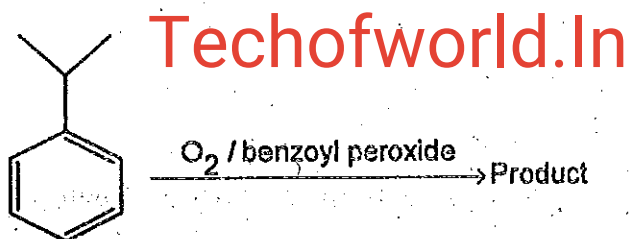
- (f) The major product formed in the following reaction is : [Techofworld.In](http://Techofworld.In)



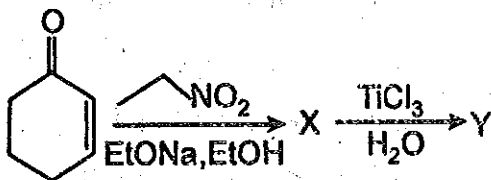
- (g) What are the reagents A and B in the following reactions ?



- (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 :

**Techofworld.In**  $10 \times 6 = 60$

(a) Calculate the magnetic moment ( $\mu_1$ ) of a  $^{13}\text{C}$  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  $\text{C}_3\text{HCl}_2$  exhibits only one signal in the  $^1\text{H}$  NMR spectrum ?

(A) 2, 2-dichloropropane

(B) 1, 2-dichloropropane

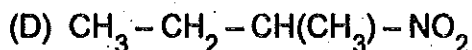
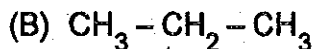
(C) 1, 3-dichloropropane

(D) 1, 1-dichloropropane

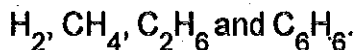
(ii) An organic compound with molecular formula  $\text{C}_4\text{H}_9\text{NO}_2$  shows following  $^1\text{H}$  NMR spectrum :  $\delta$  5.30 (broad, 1H), 4.10 (q, 2H), 2.80 (d, 3H) 1.20 (t, 3H) ppm. Draw the structure of the compound.



(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  $100 \text{ cm}^{-1}$ .

(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  $1.275 \text{ \AA}$ .

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(iii) Calculate the position in  $\text{cm}^{-1}$  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  $0.749 \text{ \AA}$ .

(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  $1.534 \text{ \AA}$ .  
Note : The Boltzmann constant,  $k$ , has a value in wavenumbers of  $0.69503 \text{ cm}^{-1}$ .

(v) The first Stokes line and the first anti-Stokes line in the rotational Raman spectrum of  $\text{N}_2\text{O}$  are displaced from the Rayleigh line by  $2.514 \text{ cm}^{-1}$  and  $+2.514 \text{ cm}^{-1}$  respectively. Determine the rotational constant of  $\text{N}_2\text{O}$ .

- (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 ( $^{79}\text{Br}$  and  $^{81}\text{Br}$ ) in an approximate 1 : 1 ratio. In the mass spectrum of  $\text{Br}_2$ , 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

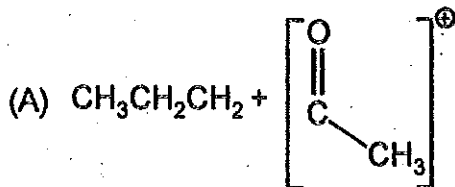
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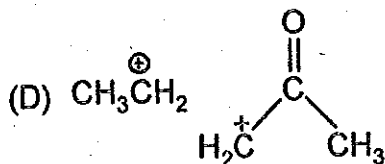
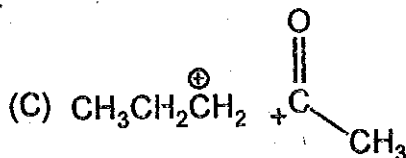
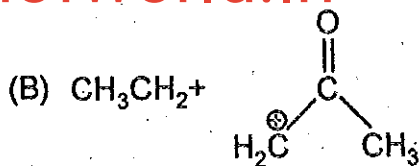
which the molecular ion ( $m/z = 44$ ) was the largest ion peak. The only other significant peaks were observed at  $m/z = 28$  and  $m/z = 16$ .

(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. **Techofworld.In**

(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  $m_c = 12.00$  u and  $m_s = 31.972$  u and the equilibrium bond length of the molecule is  $1.534 \text{ \AA}$ .  
 Note : The Boltzmann constant,  $k$ , has a value in wavenumbers of  $0.69503 \text{ cm}^{-1}$ .

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(ii) How many normal modes of vibration are there for C<sub>60</sub> ?

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

Molecule	K/N m <sup>-1</sup>
F <sub>2</sub>	450
HCl	510
CO	1860
N <sub>2</sub>	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) O<sub>2</sub> and H<sub>2</sub>O
- (B) CO<sub>2</sub> and N<sub>2</sub>O
- (C) CO and CH<sub>4</sub>
- (D) NO and DCCH

(v) Calculate the position in  $\text{cm}^{-1}$  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  $0.749 \text{ \AA}$ .

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