CGPDTM
Patent Examiner

Previous Year Paper
(Mains) (Chemistry)
Oct, 2015

CHY101/AP01

Chemistry

QP. Sr. No. **0636**

TIME : **3** HOURS

MAXIMUM MARKS : **300**

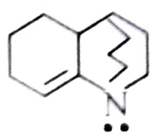
INSTRUCTIONS :

1. *All questions are **compulsory**.*
2. *Question Paper may be divided into **4 (four)** Sections from **Section-A** to **Section-D** and carry marks as under :*
   - **a.** ***Section - A** - Total **3** Questions having **two** parts, i.e. **(a) and (b),** each question carries **12** marks × 3 Questions = Total **36** Marks.*
   - **b.** ***Section - B** - Total **3** Questions having **two** parts, i.e. **(a) and (b),** each question carries **20** marks × 3 Questions = Total **60** Marks.*
   - **c.** ***Section - C** - Total **3** Questions having **two** parts, i.e. **(a) and (b),** each question carries **28** marks × 3 Questions = Total **84** Marks.*
   - **d.** ***Section - D** - Total **3** Questions having **two** parts, i.e. **(a) and (b),** each question carries **40** marks × 3 Questions = Total **120** Marks.*

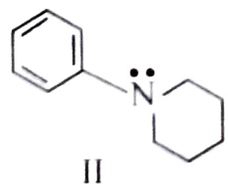
SECTION - A

(Each question is of **12** marks and each sub part **(a)** and **(b)** are of **6** marks each)

1 (a) Comment on the basic strength of the following molecules giving reasons :



I



II

(b) Giving reasons, predict the most stable conformation of cyclohexan–1, 4– diol.

2 (a) Trialkylphosphines are good trans-directors and as expected the reaction of Bu_3P with $[PtCl_4]^{-2}$ gives the trans isomer as a major product. However, when one uses Ph_3P in this reaction, only the insoluble 'cis' product is obtained. Offer an explanation for this apparent violation of the 'trans' effect prediction.

(b) Give chemical equations for the possible reactions of trimethyl-aluminium and tetramethyl silane with water and identify the difference in bonding in the two compounds that accounts for the difference in behaviour.

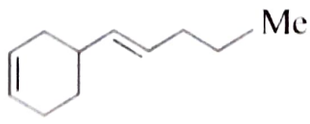
3 (a) The density of Li metal is 0.53g cm^{-3} and the separation of the (100) planes of the metal is 350 pm. Determine whether the lattice is f.c.c. or b.c.c. M(Li) = 6.941 g mol^{-1}.

(b) For the molecule BH, w_e = 2368 cm^{-1} and anharmonicity constant $w_e x_e$ = 49 cm^{-1}. Calculate the vibrational terms of the first four vibrational levels and determine the spacing between them.

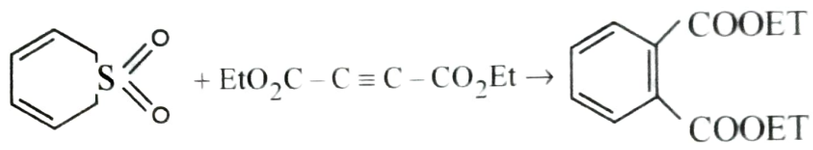
SECTION - B

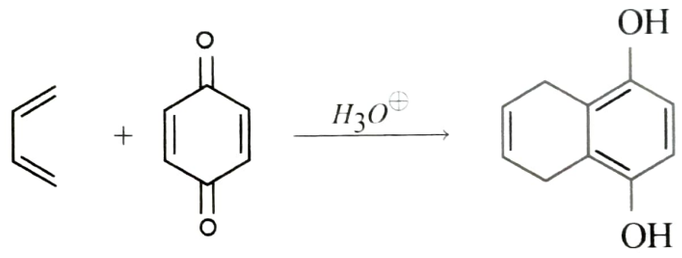
(Each question is of **20** marks and each sub part **(a)** and **(b)** are of **10** marks each)

4 (a) Suggest the reterosynthetic analysis of the following target material (TM).



(b) Suggest a mechanism for the following transformations :

(i) 

(ii) 

5 (a) The toxic species Tl^+ is used as an NMR probe for K^+ binding in proteins. Explain why Tl^+ is suited for this purpose and account for its high toxicity.

(b) The Fe=O oxidising centre in cytochrome P-450 is characterised as Fe(IV) complex with the porphyrin also oxidised by one electron. This feature is supported from ^{57}Fe Mossbauer spectrum of the species. The magnetic susceptibility of the complex indicates the presence of three unpaired electrons. To which orbitals are they assigned ? Explain.

6 (a) For the thermal decomposition of O_3 to O_2, the following mechanism has been suggested -

Step 1 $O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$

Step 2 $O_3 + O \xrightarrow{k_2} 2O_2$

Use steady state approximation (s.s.a.) and other suitable approximation to account for the observed rate - law, viz.

$r = -k[O_3]^2/[O_2]$ when $k = \frac{2k_1k_2}{k_{-1}}$

(b) Calculate the potential for each half cell and the total emf at 25°C for the cell represented schematically as -

$Pb \mid Pb^{+2}(0.001\ N) \| Cl^{-}(0.1\ N) \mid Pt, Cl_2(1\ atm)$ and

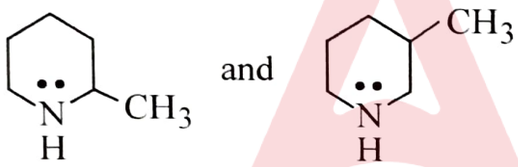
$E^{\circ}_{Cl_2|2Cl^-} = +1.358$ Volt

$E^{\circ}_{Pb^{+2}|Pb} = -0.126$ volt.

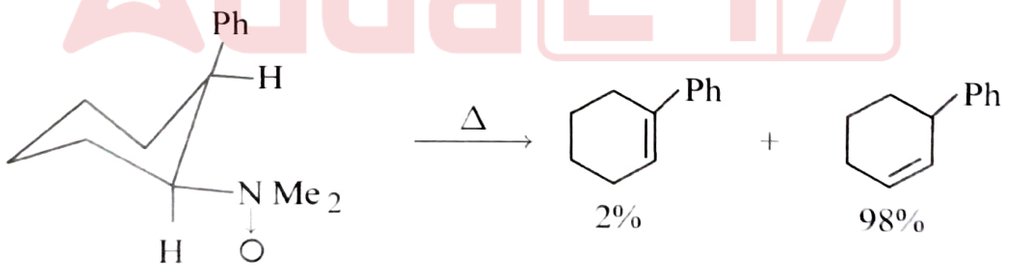
SECTION - C

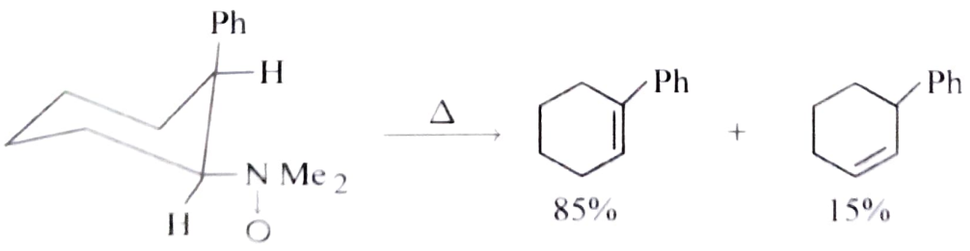
(Each question is of **28** marks and each sub part **(a)** and **(b)** are of **14** marks each)

7 (a) Predict the product(s) obtained after Hofmann exhaustive methylation of the following cyclic amines.



(b) Explain the following observations :





8 (a) What product, including its stereochemistry would you expect from the reaction between PPh_3 and $\left[Mn(Me)(CO)_5\right]$?

(b) Predict the products formed when Pent-1-ene reacts with CO and H_2 in the presence of $\left[Co_2(CO)_8\right]$. Comment on the effect of adding PMe_3 or PPh_3 to the reaction mixture. How would increasing the CO partial pressure, affect the ratio of any linear or branched products.

9 (a) Derive Kirchoff's equation relating to the variation of enthalpy of a reaction with temperature. Write down the integrated form of the equation.

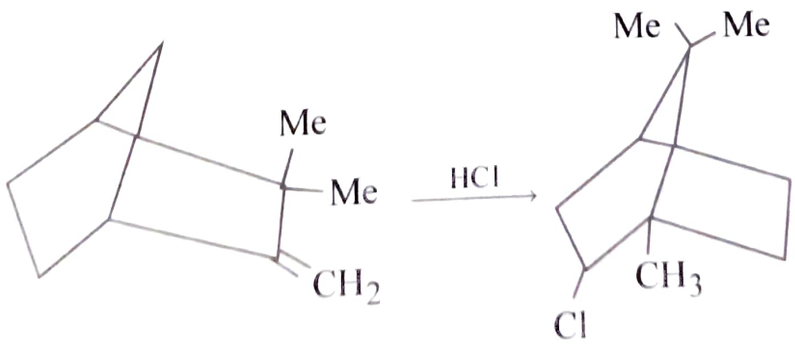
(b) Derive an expression for the equilibrium constant of an ideal gaseous mixture in terms of the partition functions of the reactants and the products.

SECTION - D

(Each question is of **40** marks and each sub part **(a)** and **(b)** are of **20** marks each)

10 (a) An organic compound having molecular formula $C_6H_{13}O_2N$ shows absorption band at $1735cm^{-1}$ in its infrared spectrum and signals at $\delta 1.30(3H, t)$, $2.40(6H, S)$, $3.20(2H, S)$ and $4.20(2H, q)$ in the NMR spectrum. Find the suitable structure with explanation.

(b) Give the mechanism of the following transformation -



11 (a) The two SALCs of H 1s orbitals in the C_2v molecule H_2O are $\phi_1 = \psi_{A1s} + \psi_{B1s}$ and $\phi_2 = \psi_{A1s} - \psi_{B1s}$. Which oxygen orbitals can be used to form molecular orbitals with them ?

(b) The oxides of formula MO, which all have octahedral coordination of the metal ions, have the following lattice enthalpies :

CaO	TiO	VO	MnO	
3460	3878	3913	3180	kJ/mol.

Account for the trends in terms of LFSE.

Provided : Character Table of C_{2v}

C_{2V}	E	C_2	$6_{v(xz)}$	$6_{v'(yz)}$	h = 4	
A_1	1	1	1	1	Z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	zx
B_2	1	−1	−1	1	y, R_x	yz

12 (a) Show that the 1s and 2s wave functions of hydrogen atom, are given by -

$$\psi_{1s} = \psi_{1,0,0} = \frac{1}{\sqrt{\pi}\, a_0^{3/2}} \exp\left(-r/a_0\right) \text{ and}$$

$$\psi_{2s} = \psi_{2,0,0} = \frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left(2 - \frac{\gamma}{a_0}\right) \exp\left(-r/2a_0\right) \text{ are orthogonal}$$

to each other.

(b) Set up the Hückel's secular equation for cyclobutadiene. Calculate the energies of the π orbitals and determine the wave function for molecular orbitals.
