3 (Sem–5) CHM M 1

2014

CHEMISTRY

(Major)

Paper : 5.1

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer any *five* questions : 5×5=25

(a) Deduce Planck's formula in connection with blackbody radiation experiment. 5

(b) For a particle moving in a 3-D box of lengths a, b and c, where potential energy is zero, find the energy expression and wave function. 5

(c) For a particle in 1-D box, show that the average value of momentum along x-axis is zero. Find the wavelength of a radiation emitted when a particle of mass $9 \cdot 0 \times 10^{-31}$ kg in a one-dimensional box of length 3 Å undergoes transition from $\eta = 3$ level to the ground level. 2½+2½

(d) The threshold wavelength for photoelectric emission in tungsten is 2300 Å. Calculate wavelength of radiation that must be used to eject electron with maximum kinetic energy of $1 \cdot 5$ eV. State how Einstein explained the results of photoelectric effect observed by Lenward. 3+2

(e) Normalize the function $\cos \frac{n\pi x}{a}$ within the interval $0 \le x \le a$, where n is a constant. Find the lowest energy of a particle with mass $9 \cdot 0 \times 10^{-31}$ kg enclosed in a three-dimensional box of lengths $1 \cdot 0 \times 10^{-15}$ m, $2 \cdot 0 \times 10^{-15}$ m and $3 \cdot 0 \times 10^{-15}$ m assuming potential energy to be zero. 2+3

(f) Treating the π-electrons in butadiene as particles in one-dimensional box, calculate the lowest absorption frequency of the absorbed radiation, given that the length of the butadiene molecule to be $0 \cdot 56$ nm. 5

(g) Answer the following questions in brief :

(i) Which of the following sets of quantum numbers gives rise to real hydrogen like wave function?

(1) $n = 2, l = 1, m_l = -1$

(2) $n = 2, l = 1, m_l = +1$

(3) $n = 2, l = 1, m_l = 0$

State reason. 1

(ii) State how many folds a particular energy level of free axis rigid rotator will be degenerated. 1

(iii) Consider an atom with an excited state where it spends 10^{-8} s and then comes back to the ground state. Calculate the uncertainty in the energy of excitation. 2

(iv) Define linear operator. 1

2. Answer any *four* questions : 5×4=20

(a) Calculate the average value of potential energy of electron of H-atom in 1*s* state. 5

(b) State the Hund's set of rules for deciding the relative energies of state in a system containing equivalent electrons. Determine the term symbols for—

(i) $L = 2, \; S = \frac{1}{2}$;

(ii) $L = 1, \; S = \frac{3}{2}$. 5

(c) Find the operators for x-, y- and z-components of angular momentum. Which physical quantity is represented by Hamiltonian operator? Find operator for kinetic energy in x-dimension. 3+1+1

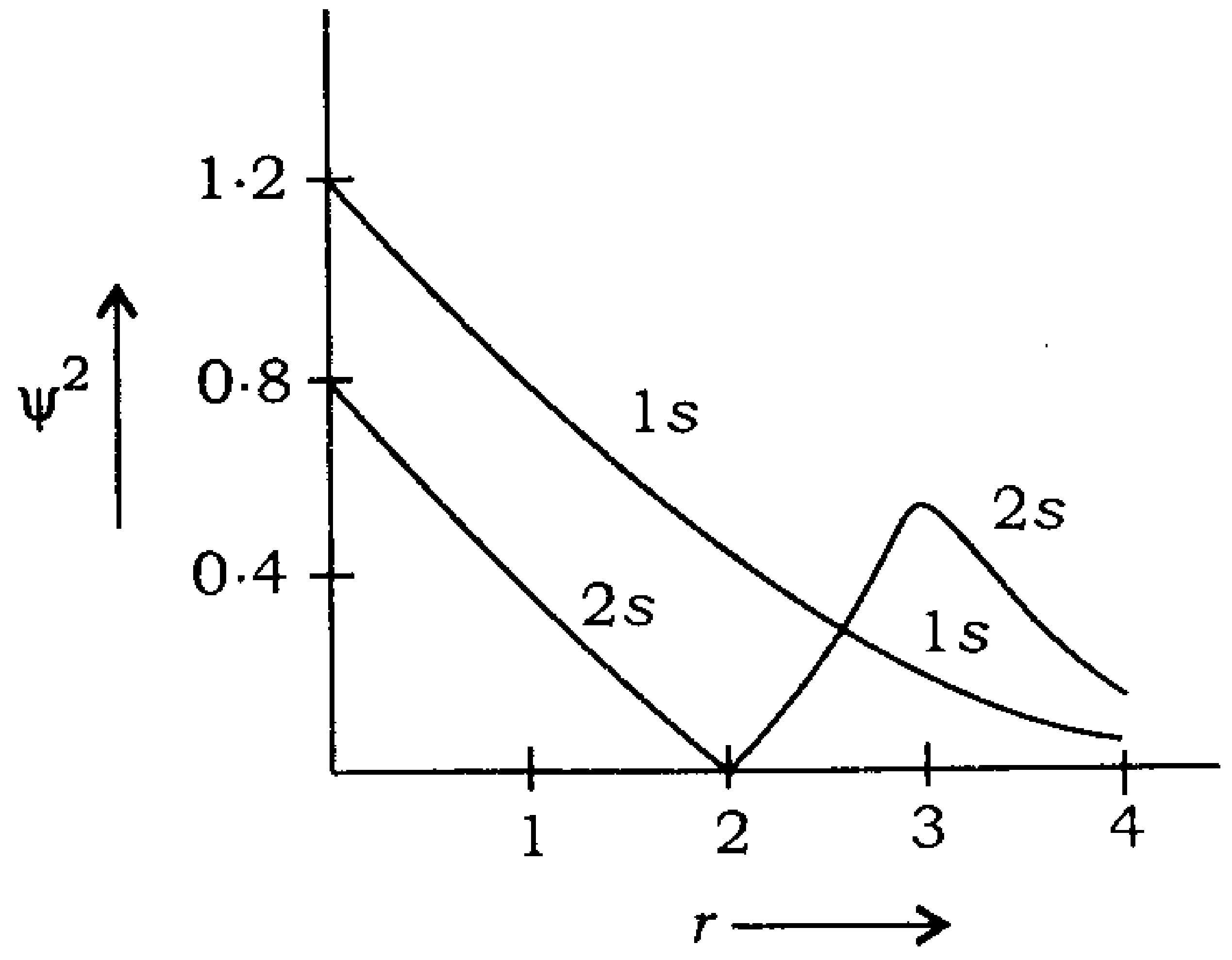
(d) The Hamiltonian for hydrogen atom and the 1s wave function in atomic units are

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} e^{-r}$$

respectively. Calculate the ground-state energy of hydrogen atom in SI units. Express your result also in electron volts. 4+1

(e) For a chemist, ψ^2 (probability density) is of more interest than ψ. Variation of ψ^2 with r for various states (of 1s and 2s) of H-atom is shown below :



However, Bohr's theory predicts that the electron in 1s state of H-atom is to be found at $r = a_0$ (Bohr radius). Solve this confusion and also draw actual radial probability at different values of r for H-atom. 5

(f) (i) A hydrogen-like wave function is given below with r in atomic units :

$$\psi = \frac{\sqrt{2}}{81\sqrt{\pi}} Z^{3/2} (6 - Zr)\, Zr \exp(-Zr/3) \cos\theta$$

Determine the quantum numbers n, l and m_l just from this expression. 1½

(ii) State Pauli's principle of anti-symmetric wave functions. 1

(iii) What do you mean by complete wave function? Write the complete wave function for ground state of He-atom. 1½+1

3. Answer any *three* questions : 5×3=15

(a) Use LCAO-MO theory to solve the Schrödinger equation for the electron of H_2^+ to find the normalized wave functions and corresponding energy expressions. 5

(b) (i) From the molecular orbital energy-level diagram of CO, explain whether the molecule is paramagnetic or not. 2

(ii) Show that $[\hat{x}, \hat{p}_x] = i\hbar$. 3

(c) Use Hückel method to explain the stability of benzene molecule. 5

(d) Calculate the rotational energy of CO molecule in the first excited state considering it to be rigid rotator, given that the bond length of CO is 113 pm. 5

(e) (i) A homonuclear diatomic molecule has the ground state molecular orbital configuration

$$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2\ 1\pi_g^2$$

(1) What is the net number of bonding electrons?

(2) What will be the spin multiplicity for the ground state?

(3) What would be the spin multiplicity of the resulting molecule ion if one goes out of the $1\pi_g$ level? 1½

(ii) Predict the stability of HeH molecule on the basis of molecular orbital theory. 1½

(iii) Explain why HCl is more polar than HF on the basis of energy of atomic orbitals. 2

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(d) Explain the variation of chemical potential with temperature for solid, liquid and vapour phases of a pure non-subliming substance. 3

(e) 1 mol of H_2 and 2 mol of O_2 are mixed together. Assuming that no chemical reaction occurs and the gases behave ideally, calculate entropy of mixing. 3

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3 (Sem–5) CHM M 2

2014

CHEMISTRY

(Major)

Paper : 5.2

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer in brief : 1×7=7

(a) State why a heterogeneous catalyst is often taken in the form of finely divided powder rather than as a smooth surface.

(b) Yellow phosphorus glows in air at room temperature. State the reason behind it.

(c) State what you mean by inter-system crossing as given in Jablonski diagram.

(d) Using the concept of chemical potential, state under what condition the three phases of water will be in equilibrium.

(e) State why absolute alcohol cannot be prepared by fractional distillation.

(f) Let a pure substance has four phases α, β, γ and δ. State whether these four phases can exist in equilibrium at a particular temperature and pressure or not.

(g) State the main condition involving energy requirement that should be fulfilled in order to photolyze a molecule using a sensitizer.

2. Answer the following : 2×4=8

(a) In the photochemical dissociation of HI, the first step is

$$\mathrm{HI} \xrightarrow{h\nu} \mathrm{H} + \mathrm{I}$$

Assuming H-atom formed to be in excited state while I-atom to be in ground state, calculate the excess energy that the excited H-atom carries as compared to the ground state H-atom. Justify your answer. Given photochemical dissociation energy and bond enthalpy of HI are 367 kJ $\mathrm{mol^{-1}}$ and 299 kJ $\mathrm{mol^{-1}}$ respectively.

(b) $CaCO_3$ (s) is heated in a closed vessel when the following reaction occurs :

$$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$

Find the number of components.

(c) The eutectic temperature of NaCl-ice system is 252 K. Explain why temperature falls when NaCl is added to ice. What is the minimum temperature that can be attained by adding NaCl to ice?

(d) 2 mol of substance *A* and 3 mol of substance *B* are mixed together when the total volume becomes $2 \cdot 1 \times 10^{-4}\ \mathrm{m^3}$. If the partial molar volume of *A* is $2 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$, calculate the partial molar volume of *B*.

3. Answer any *three* questions : 5×3=15

(a) Write the basic assumptions of the collision theory of rates of reactions. Hence find out an expression for the rate constant of bimolecular gas-phase reaction.

(b) The rate constant of the second-order reaction

$$H_2\ (g) + I_2\ (g) \rightarrow 2HI\ (g)$$

is $2 \cdot 34 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}\ s^{-1}}$ at 400 °C. The activation energy of the reaction is 150 kJ $\mathrm{mol^{-1}}$. Calculate enthalpy of activation and free energy of activation.

2+3=5

(c) For the bimolecular gas-phase reaction

$$X + Y \rightarrow A^{\ddagger} \xrightarrow{k} \text{Products}$$

find an expression relating the pre-exponential factor with entropy of activation.

(d) Discuss how the rate of uncatalysed ionic reaction is affected by the ionic strength of the solution.

(e) Write in brief about the molecular beam technique of studying molecular reaction dynamics. Name the different types of scattering of particles that may be observed in this technique. State how the scattered beams are studied. 3+1+1=5

4. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) Write the mechanism of the H_2—Cl_2 photochemical reaction. Prove that the rate of formation of HCl is directly proportional to the intensity of the absorbed radiation. 2+3=5

(b) In the photochemical decomposition of acetone using 313 nm radiation, $7 \cdot 57 \times 10^{-6}$ mol CO is formed in 20 minutes. If the energy of radiation absorbed corresponds to $2 \cdot 41 \times 10^{-3}$ J s^{-1}, calculate quantum efficiency for the formation of CO. 4

(c) State the reason why light emission during phosphorescence is slow. 1

Or

(d) State Stark-Einstein law of photochemical equivalence. Under what condition of radiation this law is applicable? 1+1=2

(e) When irradiated with a radiation of wavelength 253 · 7 nm, H_2 and O_2 react in presence of Hg vapour, but not in its absence. Explain this observation. 3

(f) In a certain photochemical reaction using 464 nm radiation, the incident light power was 15 · 5 W and the system absorbed 75% of the incident light. The quantum yield of the reaction was found to be 0 · 15. How many mol of the product was formed in the reaction in 100 s? 5

5. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) Deduce Langmuir's adsorption isotherm. Show that at low pressure adsorption corresponds to first-order reaction, while at high pressure it corresponds to zero-order reaction. 3+2=5 *(b)* For adsorption of a substance from aqueous solution at 20 °C the Freundlich constants are $n = 2$ and $K = 0 \cdot 5$, the concentration of the solution being expressed as g L^{-1}. What mass of the substance will be adsorbed on 2 g of the solid from 1 L of the solution initially containing 2 g of the substance? 3

(c) The activation energy for the uncatalysed decomposition of NH_3 is 350 kJ mol^{-1}. But activation energy for the decomposition of NH_3 in presence of tungsten catalyst is 162 kJ mol^{-1}. Explain why this difference in activation energy occurs. 2

Or

(d) Show that for a gas obeying Langmuir equation a plot of $\ln \frac{\theta}{p}$ against θ will be linear with slope -1. (Symbols signify their usual meanings) 3

(e) Discuss the different steps of the Langmuir-Hinshelwood mechanism of gaseous reaction taking place on solid surface. 3

(f) At STP the volume of butane gas required to cover 1 kg of a sample of Ni catalyst is $1 \cdot 385 \times 10^{-6}$ m^3. If the surface area per kg of Ni catalyst is 9 m^2, find the area occupied by a butane molecule. 4

6. Answer *either (a), (b) or (c), (d),* and *(e)* :

(a) Taking the example of phenol-water system, discuss about the variation of mutual solubility of the two liquids with temperature. What is the effect of adding $0 \cdot 1$ M KCl on the critical solution temperature of the phenol-water system? 3+1=4

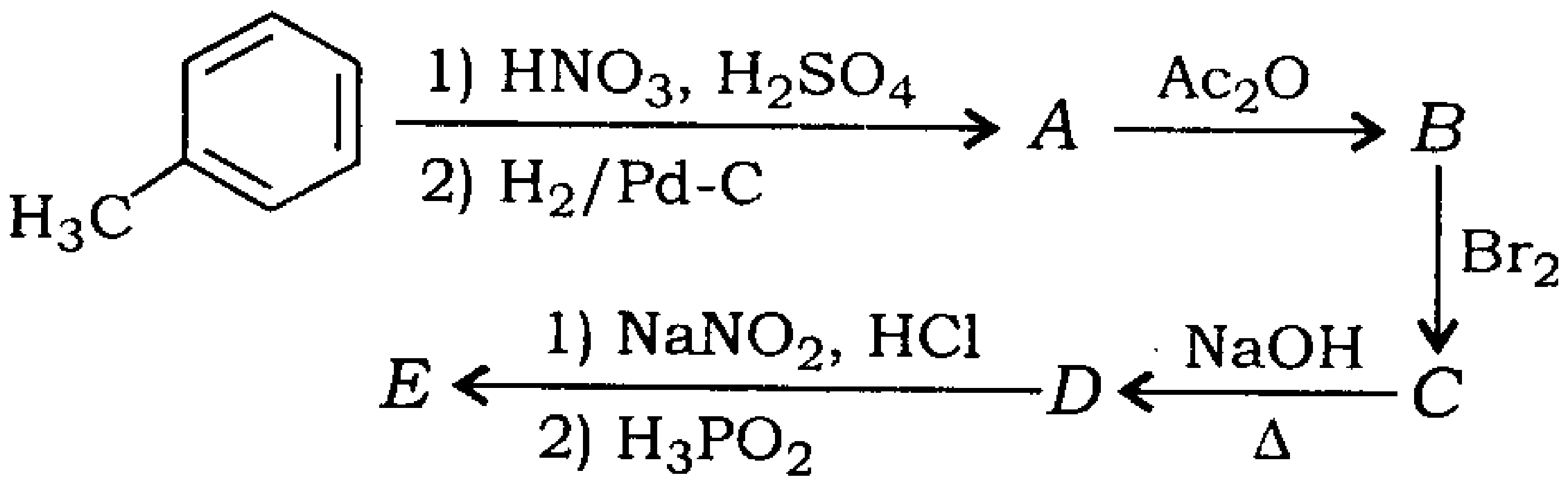
(b) Draw the phase diagram of water and explain what the different curves signify. Using Clapeyron equation, predict the slope of each curve. 3+3=6

Or

(c) Ag and Pb form an eutectic mixture with $2 \cdot 6\%$ of Ag by mass. The eutectic temperature is 576 K. The melting points of Pb and Ag are 600 K and 1243 K respectively. Draw schematic phase diagram of Pb-Ag system and mark the stable phases in various regions. Explain the changes that would occur if melt containing 60% Ag is cooled. 1+1+2=4

(iii) Give two reactions which show the reducing property of alkyl isocyanides. 2

(iv) Identify *A*, *B*, *C*, *D* and *E* from the following : 2½



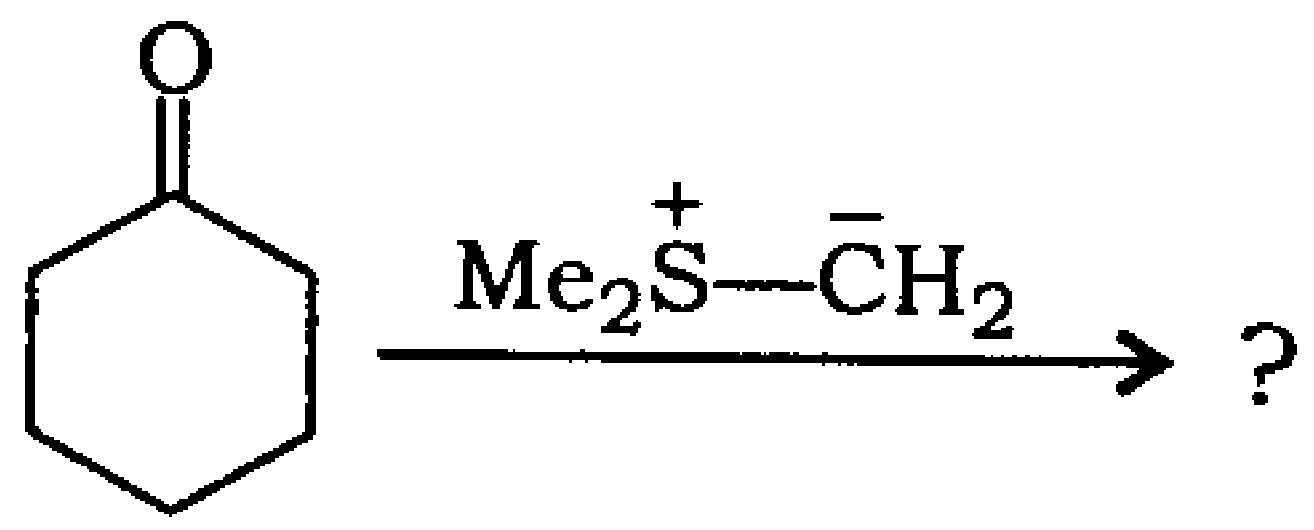
(v) Write the mechanism for diazotization of a primary amine. 2½

Or

(f) (i) Describe a method for synthesis of pyrrole. 3

(ii) Give the products in each of the following reactions : 2

(1)



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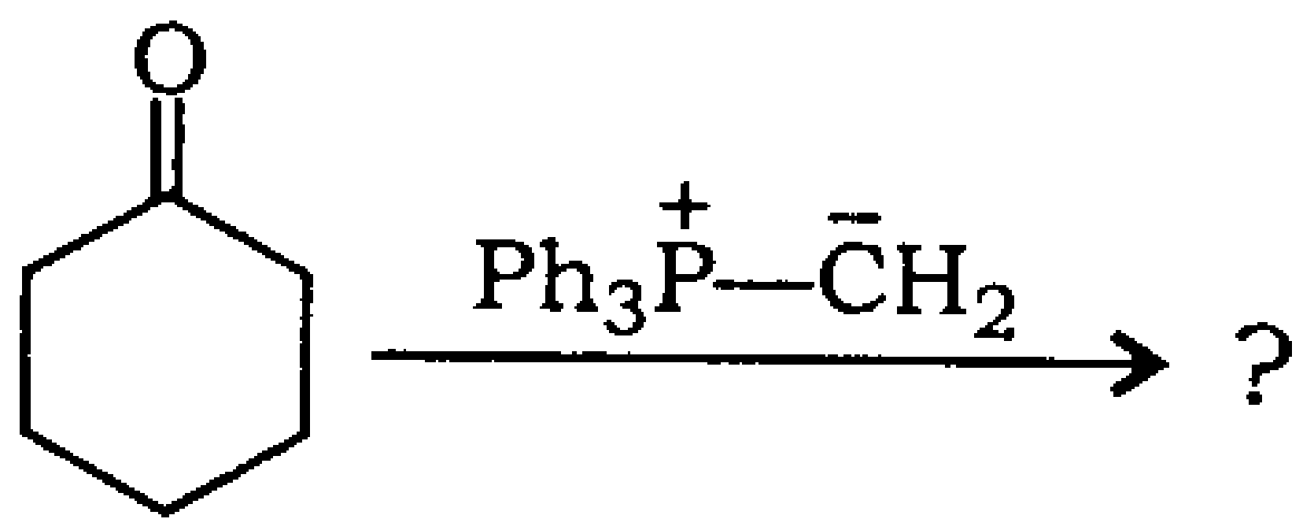

(iii) What are stabilized and non-stabilized ylides? Propose a mechanism for Wittig reaction. 2+3

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2014

CHEMISTRY

(Major)

Paper : 5.3

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

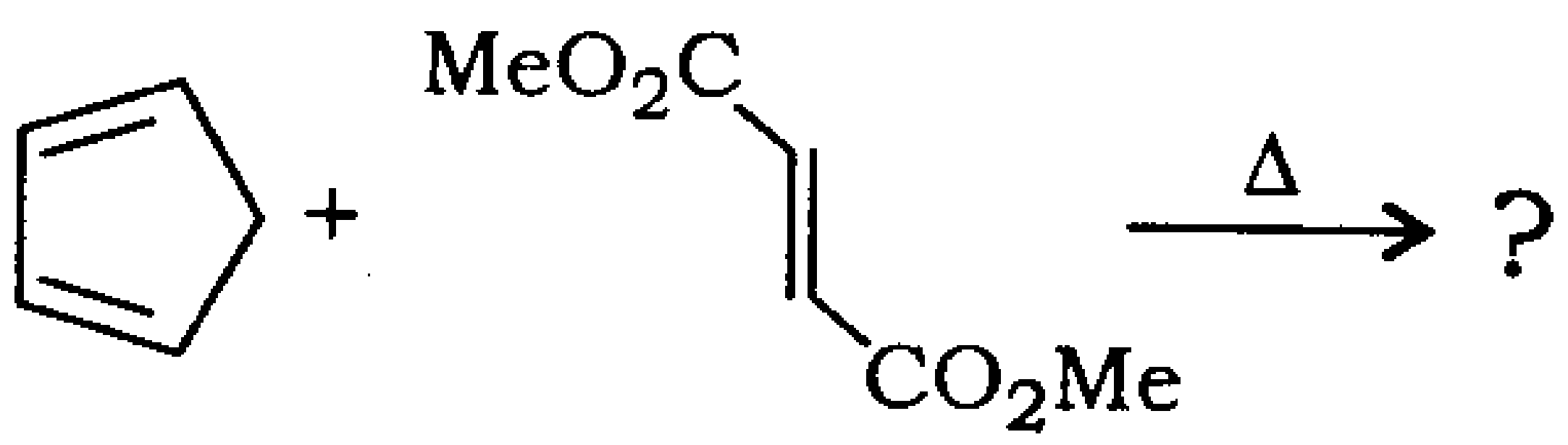
1. Answer the following questions : 1×7=7

(a) Arrange the following in order of increasing migratory aptitude in a pinacol rearrangement :

p-Chlorophenyl, *p*-tolyl, *p*-methoxyphenyl, phenyl

(b) How can you convert nitrobenzene to azobenzene?

(c) Write the product, taking care of stereochemistry :

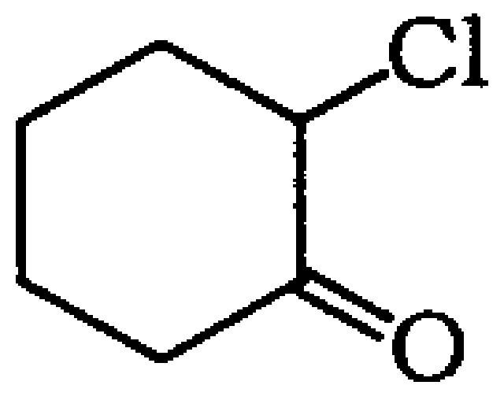


(d) Give one natural source each for pyrrole and pyridine.

(e) $C_3H_7NO_2$ is a nitroalkane. It reacts with nitrous acid to form a colourless compound which turns red when sodium hydroxide solution is added. What is the possible structure of the parent compound?

(f) Which is more acidic CH_3SH or CH_3OH? Why?

(g) Which one of the following two compounds will exhibit scrambling in a Favorskii rearrangement?



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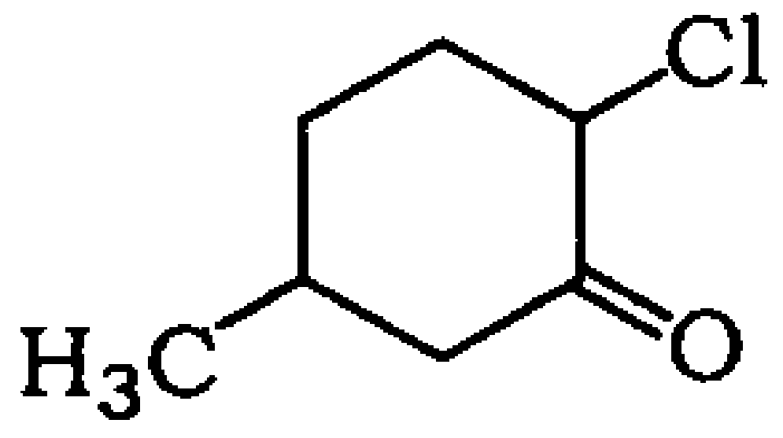
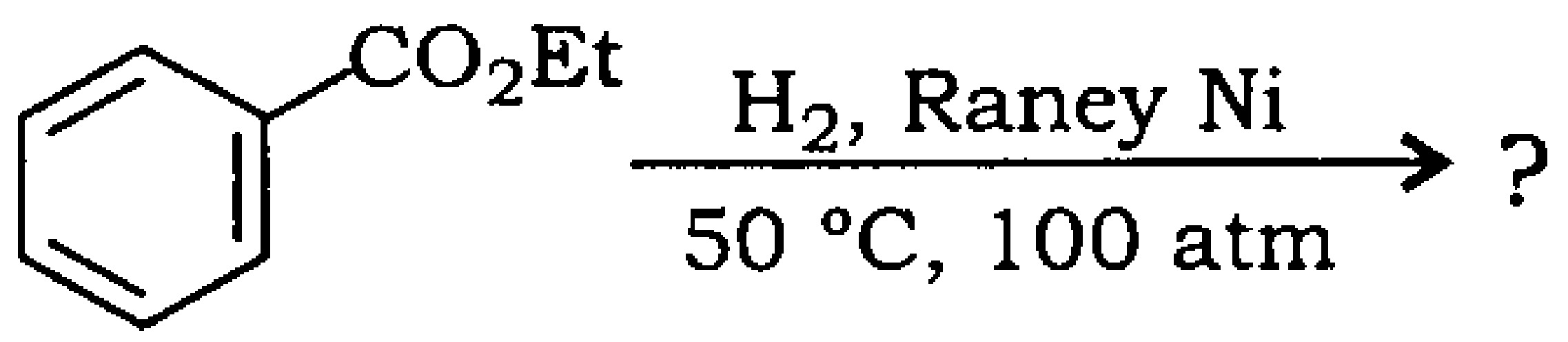


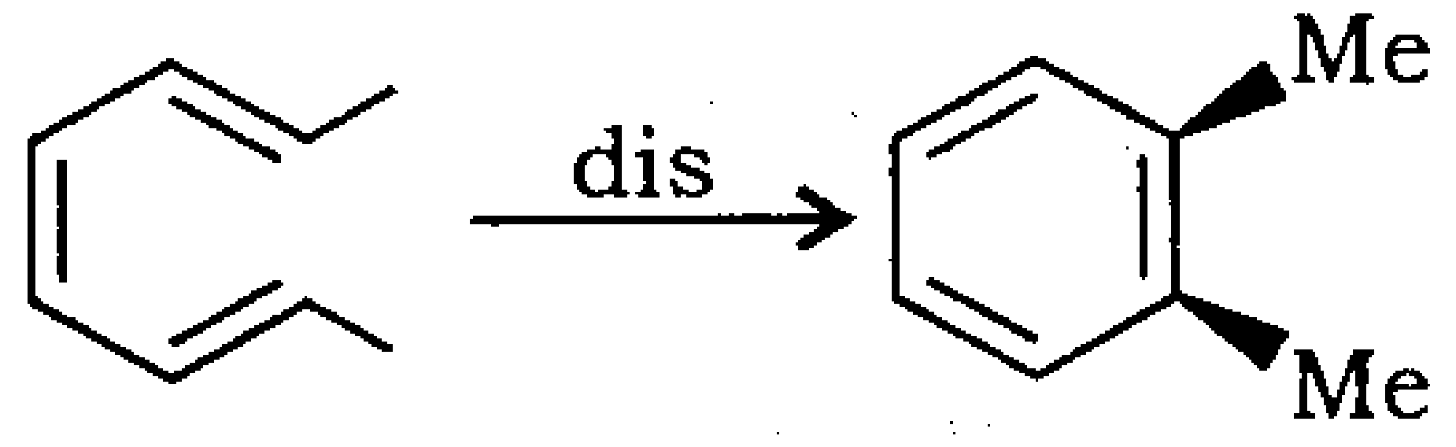
2. Answer the following questions (any *four*) : 2×4=8

(a) What is Raney nickel? Write the appropriate product for the following reaction :

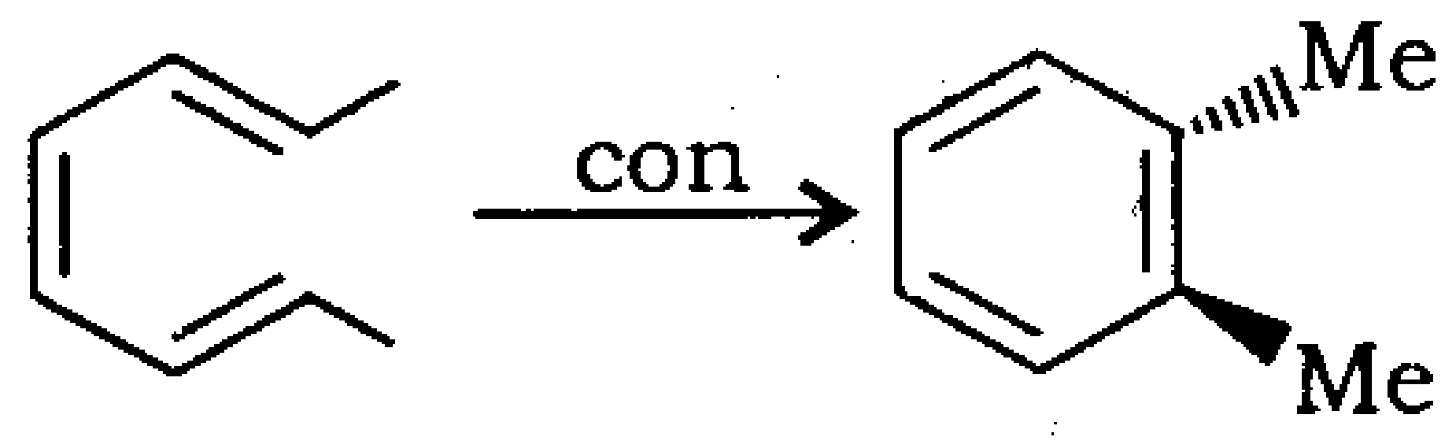


(b) State whether the given reactions are thermally allowed or photochemically allowed :

(i)



(ii)



(c) Which position(s) of quinoline undergo nucleophilic aromatic substitution?

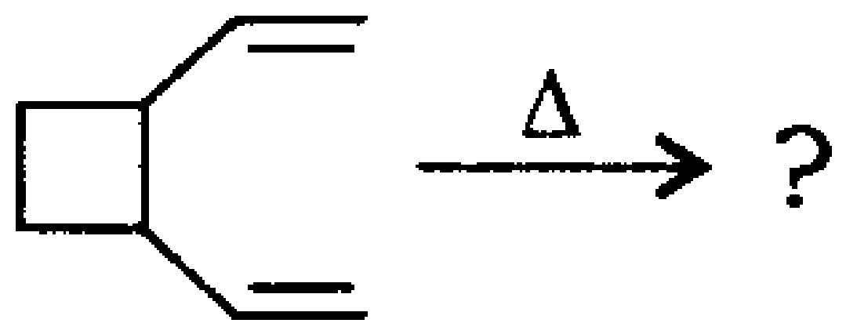
(d) 'Pyridinium ion' is about as strong an acid as carboxylic acid. Explain.

(e) What is mustard gas? What is the cause of its toxicity?

3. Answer any *three* of the following questions [any *one* from *(a)* and *(b)*, any *two* from *(c)*, *(d)* and *(e)*] : 5×3=15

(a) How can you convert acetic acid to propanoic acid, using a rearrangement reaction? Name the rearrangement. Write the mechanism of the rearrangement reaction. 2+1+2

(b) What will happen if 3-hydroxy-1,5-diene is heated? Propose a mechanism. Write the product(s) expected to be formed in the following reaction : 2+2+1



(c) (i) Acetoacetic ester has two structures which are readily interconvertible. Write down the structures. 1

(ii) How is ethyl cyanoacetate prepared? 2

(iii) Write the reactions involved in the preparation of adipic acid from diethyl malonate. 2

(d) Account for the observation that *ortho-*, *para-*directing substituents on the 1-position of naphthalene directs substituents to 2- and 4-positions, whereas the same substituent on the 2-position directs substitution almost exclusively to the 1-position. 5

(e) (i) Write the sequence of reactions involved in the Skraup synthesis of quinoline. 3

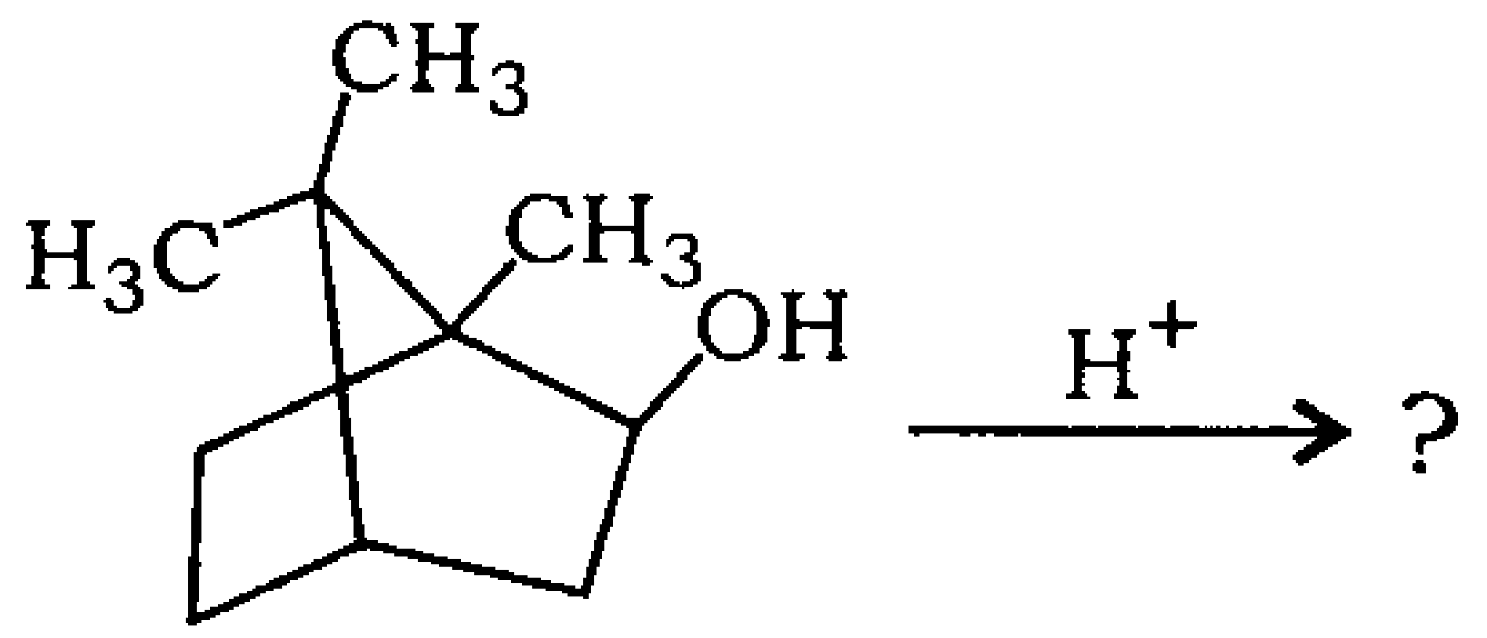
(ii) Which position of pyrrole undergoes aromatic electrophilic substitution easily and why? 2

4. Answer the following questions : 10×3=30

Either

(a) (i) Predict the product in each case and write the mechanistic steps involved : 2+3

(1)



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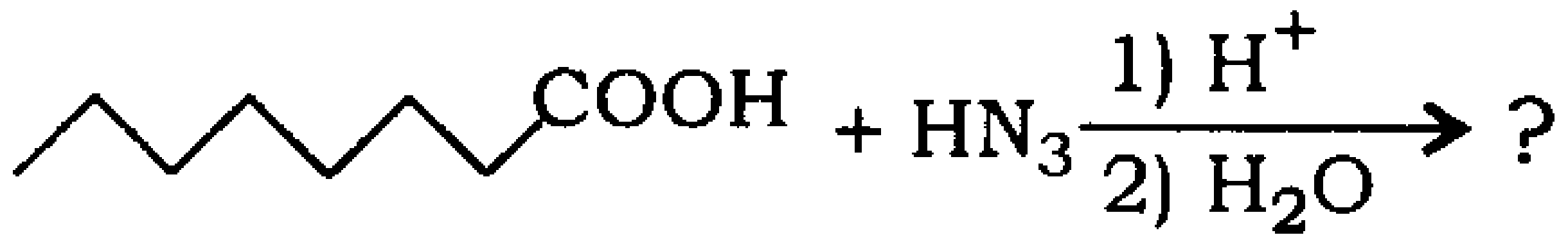
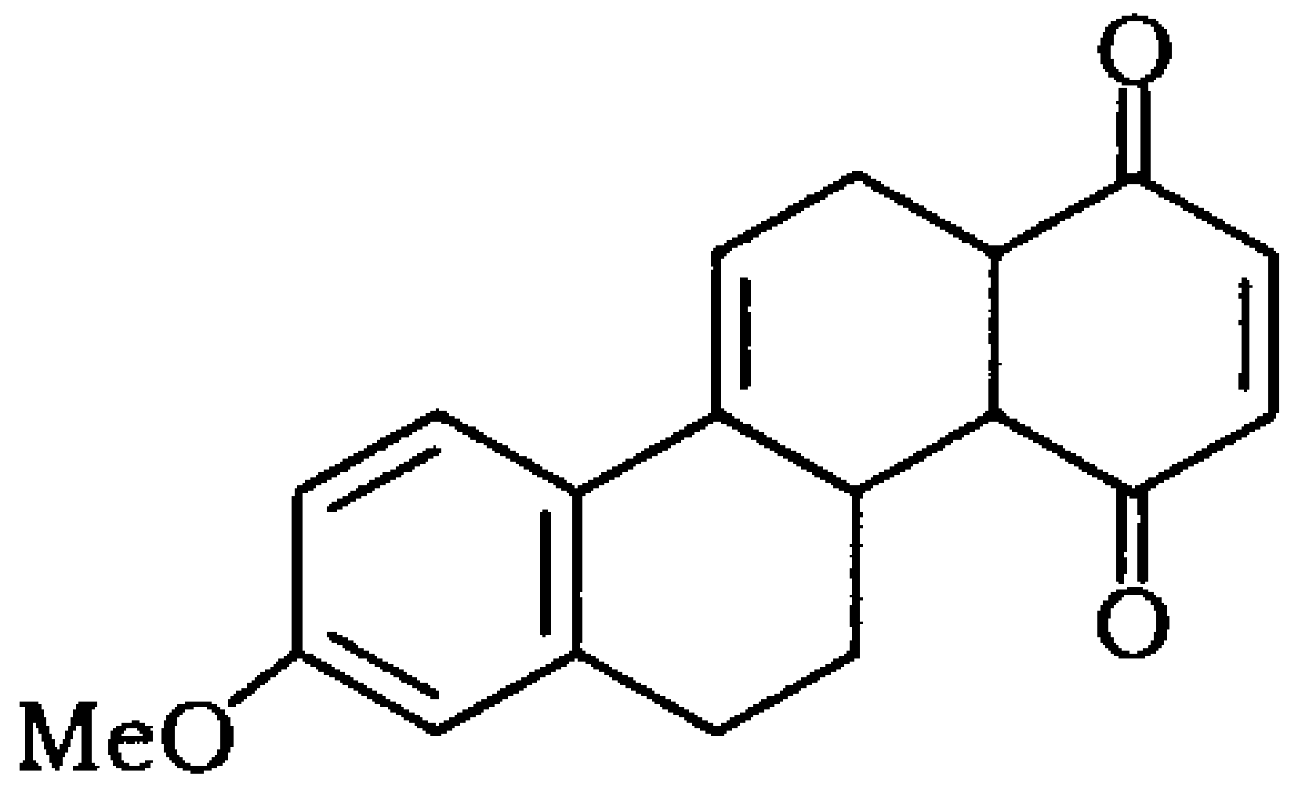


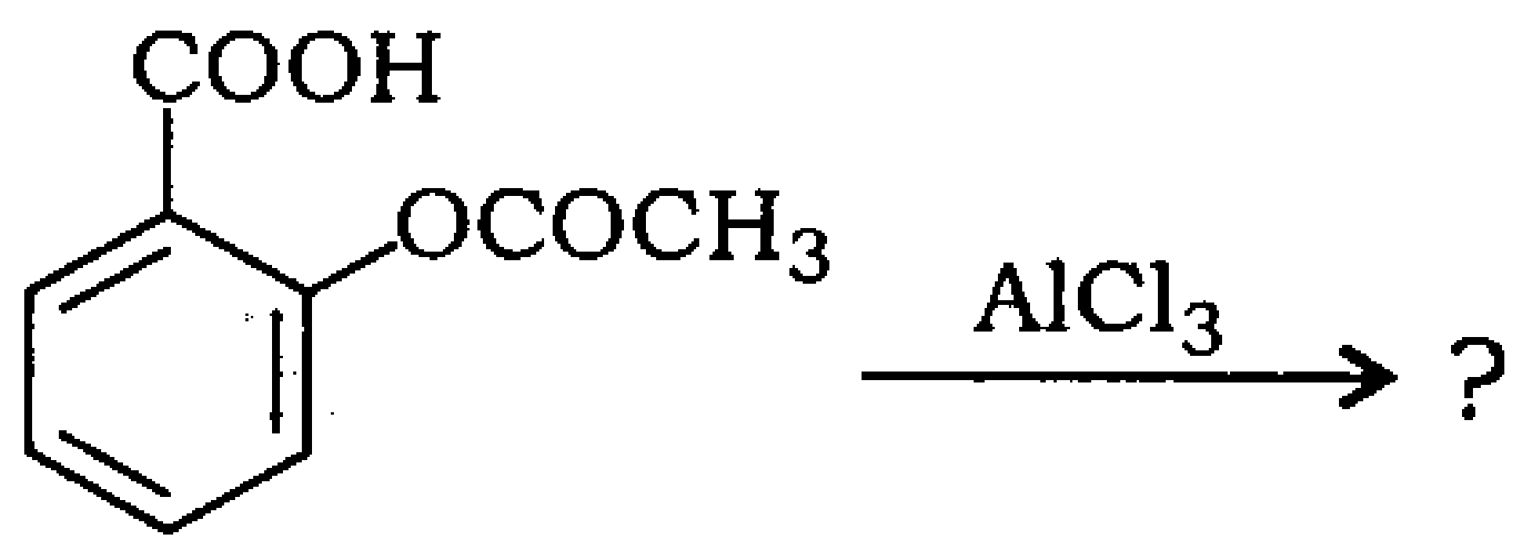
(ii) Diels-Alder reaction is stereoselective. Explain. Work out the diene and dienophile components in the given compound : 4+1



Or

(b) (i) Use HOMO-LUMO approach to show that [4 + 2] cycloaddition is thermally allowed. 5

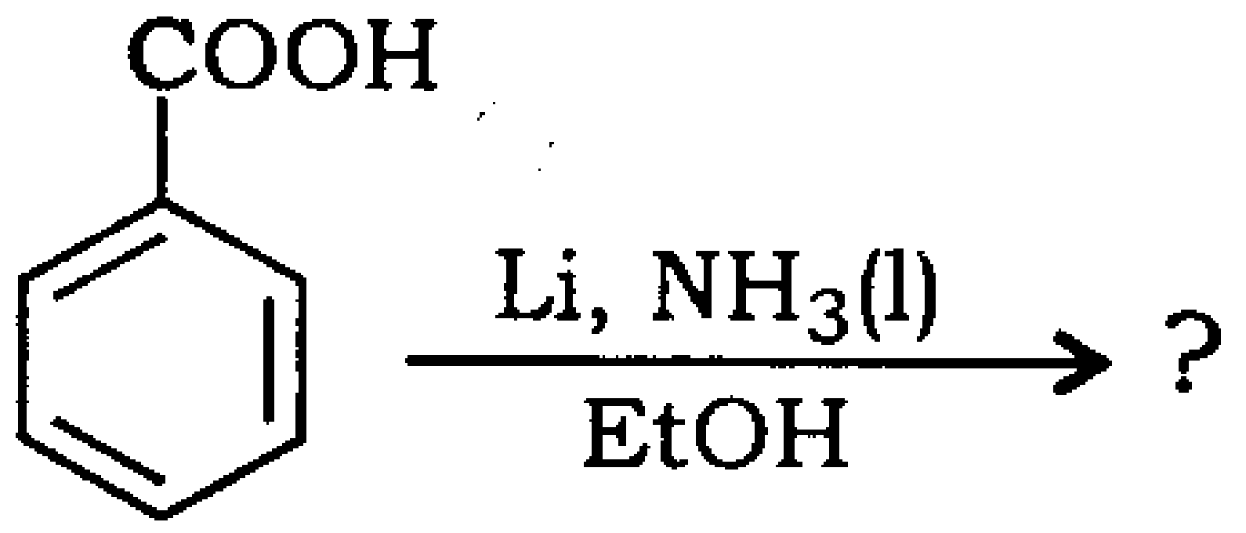
(ii) Give the product of the following reaction, name the rearrangement and propose a mechanism : 1+1+3

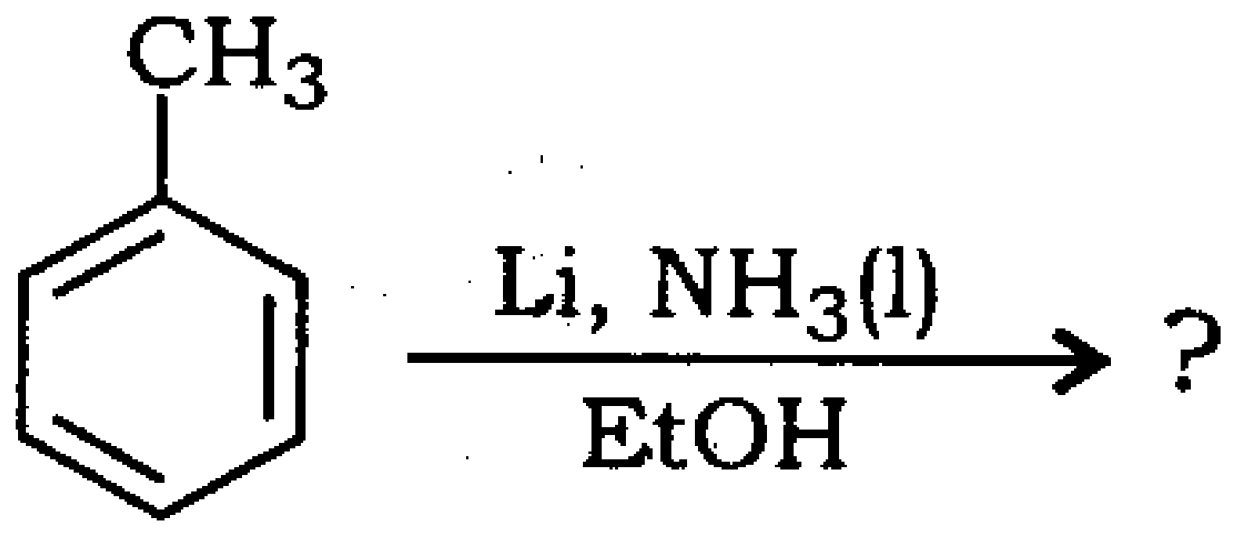


Aspirin

Either

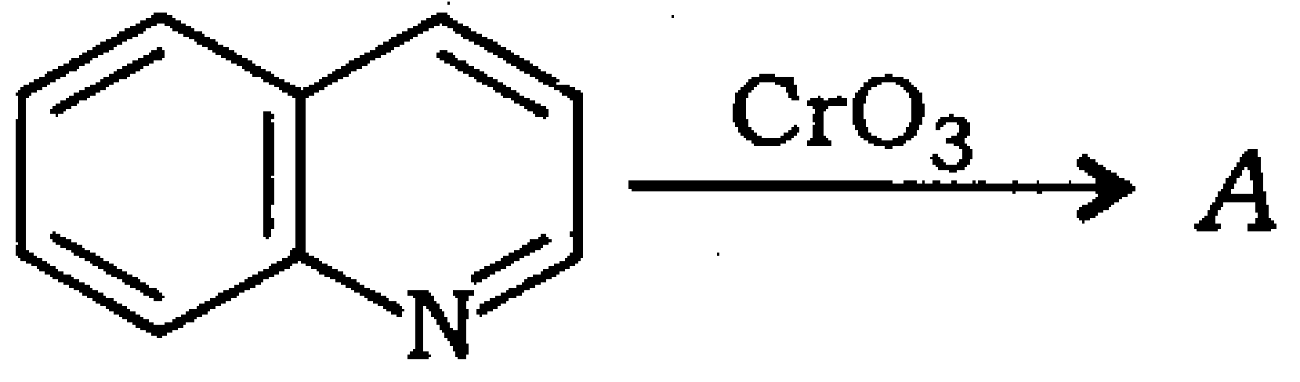
(c) *(i)* Complete the following reactions :

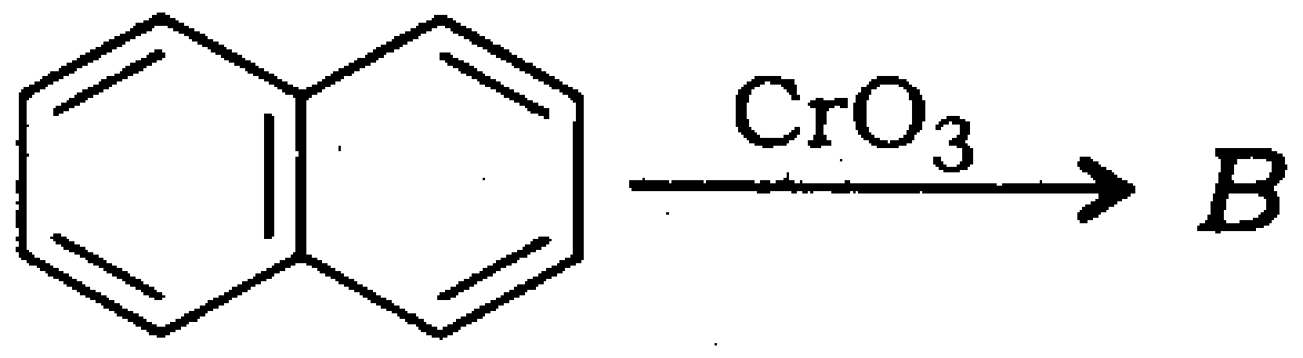
(1) 

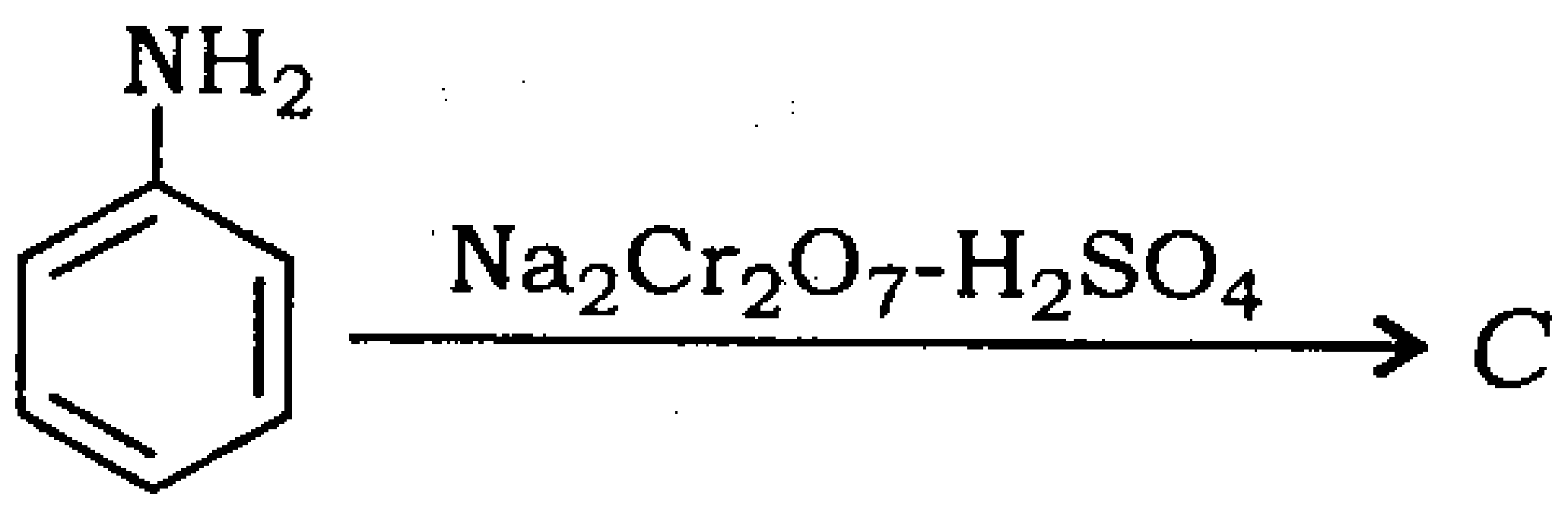
(2) 

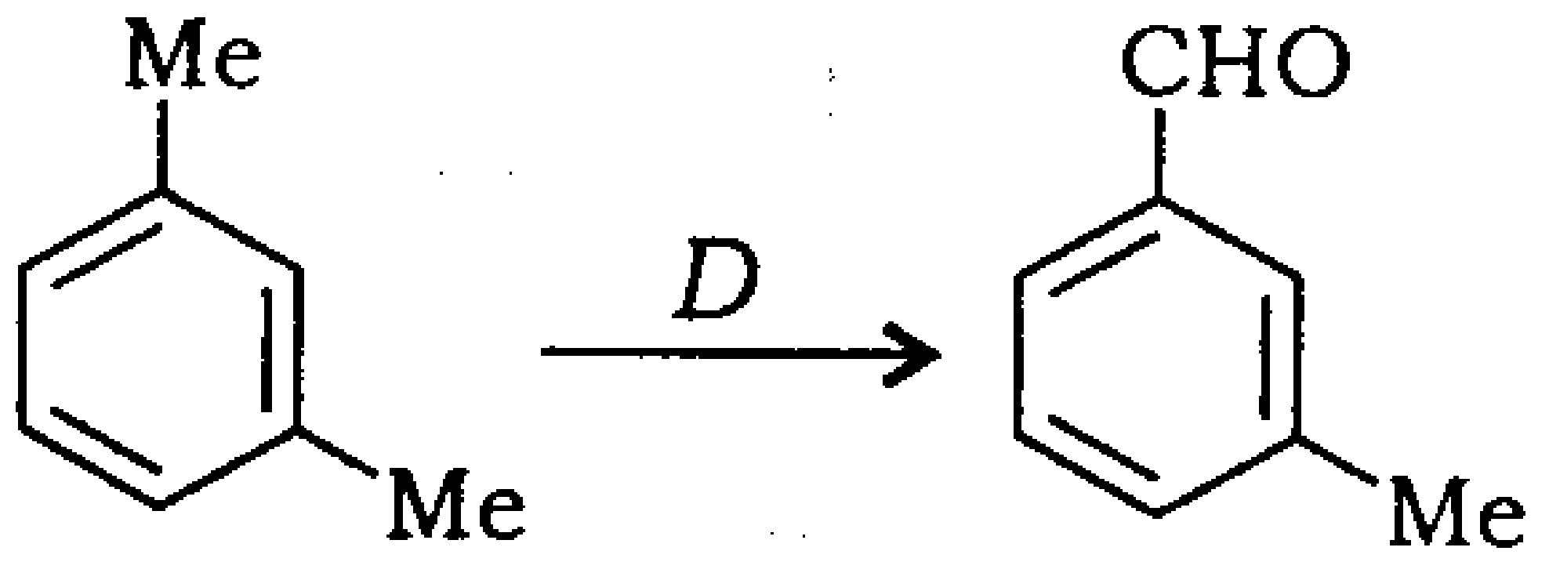
Account for the product obtained in each case. 2½+2½

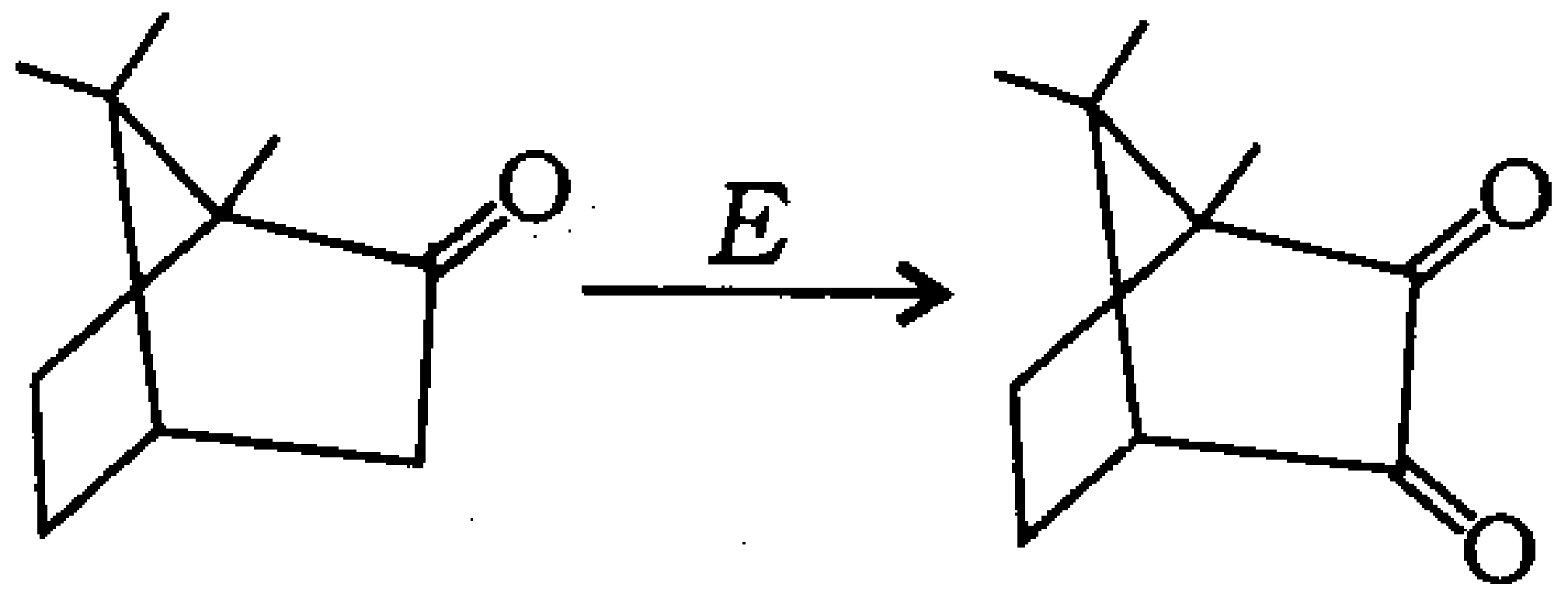
(ii) Identify *A*, *B*, *C*, *D* and *E* in the following reactions : 1×5=5

(1) 

(2) 

(3) 

(4) 

(5) 

Or

(d) *(i)* Propose a general mechanism for catalytic hydrogenation which can account for different types of product obtained in such a hydrogenation reaction. 5

(ii) How is Jones reagent different from Collins reagent? Propose a mechanism for the conversion of a primary alcohol to aldehyde with a Cr(VI) reagent. 2+3

Either

(e) *(i)* Suggest a method for preparation of alkyl isocyanides. 2

(ii) Alkyl isocyanides are insoluble in water. Why? 1

3 (Sem–5) CHM M 4

2014

CHEMISTRY

(Major)

Paper : 5.4

(Inorganic Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

Objective-type questions (choose the correct answers) : 1×5=5

1. Three-fold axes of symmetry are present in

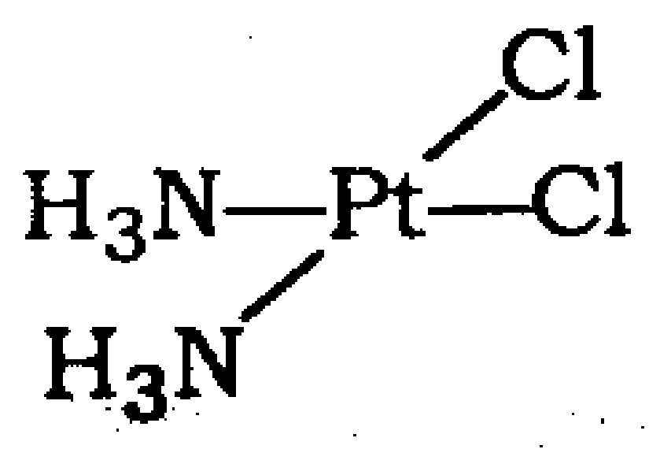
(a) octahedron

(b) tetrahedron

(c) trigonal bipyramid

(d) All of the above

2. The point group symmetry of the following complex



is

(a) T_d

(b) D_{4h}

(c) C_{2v}

(d) D_{2h}

3. The crystal field stabilization energy for a d^4-ion in a weak octahedral field is

(a) $0{\cdot}4\,\Delta_o$

(b) $0{\cdot}6\,\Delta_o$

(c) $0{\cdot}8\,\Delta_o$

(d) $1{\cdot}2\,\Delta_o$

4. The catalytically important metal in Ziegler-Natta polymerization is

(a) Rh

(b) Al

(c) Ti

(d) Pd

5. The metalloprotein which is involved in the storage of iron in living systems is

(a) ferredoxin

(b) haemoglobin

(c) myoglobin

(d) ferritin

Very short answer-type questions : 2×5=10

6. Why do five coordinate complexes commonly have a structure that is intermediate between trigonal bipyramidal and square pyramidal geometries?

7. Which of the following complexes has a larger crystal field splitting parameter?

$$[\mathrm{Co(NH_3)_6}]^{3+} \quad \text{or} \quad [\mathrm{Rh(NH_3)_6}]^{3+}$$

8. What is the M—M bond in the following compounds?

(a) $Mn_2(CO)_{10}$

(b) $K_2Re_2Cl_8$

9. Identify *A* and *B* in the following reaction :

$$[\mathrm{Mn(CO)_5}]^- + \mathrm{C_3H_5Cl} \rightarrow$$
$$A + \mathrm{Cl}^- \xrightarrow{\Delta \text{ or } h\nu} B + \mathrm{CO}$$

10. What is oxyhaemoglobin? What is the oxidation state of iron in this metalloprotein?

Short answer-type questions (any *three*) : 5×3=15

11. *(a)* Explain why CO is a strong field ligand while I^- is a weak field ligand.

(b) Write what are normal and inverse spinels giving examples. With the help of CFSE calculation, find out which type of spinel Mn_3O_4 is.

(c) What is the basis of the 18-electron rule? What kind of ligands form complexes that tend to follow the 18-electron rule? Why does not $V(CO)_6$ follow this rule, while $Co(CO)_4$ dimerize to obey the rule?

(d) Discuss the applications of organometallic compounds of zinc.

(e) Write a short note on dioxygen toxicity.

Essay-type questions (any *three*) : 10×3=30

12. *(a)* What are symmetry elements and symmetry operations? Illustrate all possible symmetry elements of an octahedral complex (ML_6) with the help of a diagram. 10

(b) Compare and contrast homogeneous and heterogeneous catalysis. Discuss the role of transition metal complexes as homogeneous catalysts for hydrogenation of alkenes by taking suitable examples. 3+7

(c) What are essential and trace elements in biological systems? Discuss the importance of calcium in biology. 5+5

(d) Draw the catalytic cycle of the hydroformylation of alkenes in presence of cobalt carbonyl catalyst and discuss the reactions involved in various steps. 10

(e) Give a brief description of molecular orbital theory as applied to coordination compounds. Construct a molecular orbital energy-level diagram for an octahedral complex involving metal-ligand σ-bonds only. 10

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