2009

CHEMISTRY

PAPER—CH-2102

Full Marks : 40

Time : 2 hours

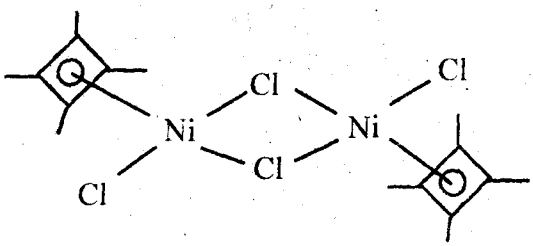
The figures in the right-hand margin indicate marks

(*Inorganic Spl.*)

Answer any *four* questions

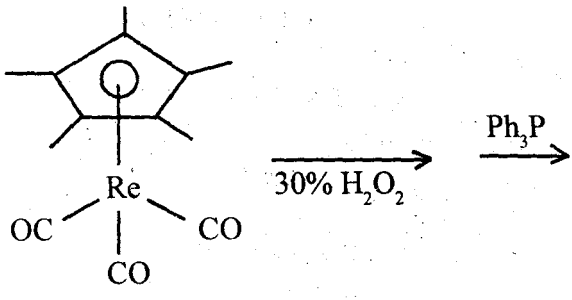
1. (*a*) Show the 'transoid' binding modes of 1, 3-butadiene. Cite example for each case. 3

(*b*) How will you synthesize 2

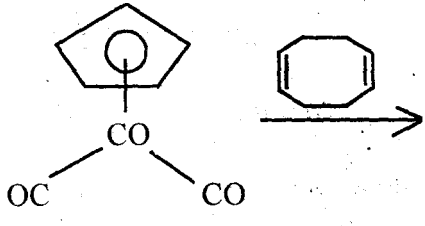


(*c*) Predict the product of the following reaction. 3

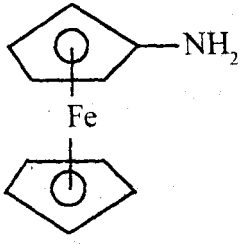
(*i*)



(*ii*)

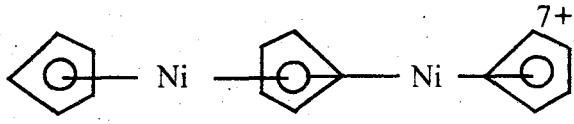


(*d*) Write down the synthesis of. 2



Starting from ferrocene

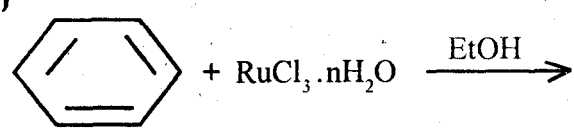
2. (*a*) How you will synthesize 2



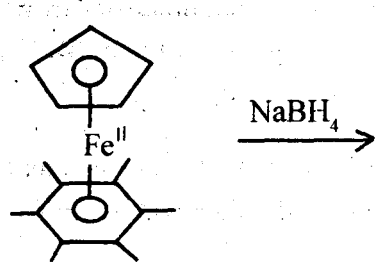
(*b*) Predict the final product when $[(C_6Me_6)_2 Re]PF_6$ is reacted with Li(I) at 200°C. Write down the probable structure of the final product. 2

(*c*) Write the product of the following reaction. 4

(*i*)



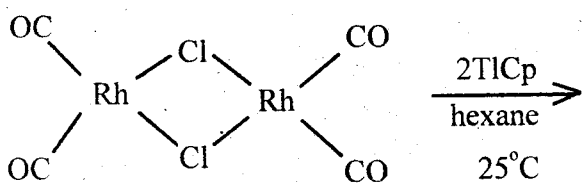
(*ii*)



(*iii*)

$$ZrCl_4(THF)_2 \xrightarrow[\text{[2, 2, 2] Crypt}]{KC_{10}H_8} \text{1, 2-dimethoxyethane, } -60^\circ C$$

(*iv*)



(*d*) How will you synthesize Cp_2MoCl_2 i.e. a metallocene halide starting from $MoCl_4$? Write down the structure of Cp_2MoCl_2. 2

3. (*a*) What do you mean by oxidative addition reaction ? Explain with example. 2

(*b*) Explain the catalytic cycle involving oxo-process. 6

(*c*) Why Cu^{2+} is used in Wacker oxidation ? 2

4. (*a*) Show that reciprocal lattice to the fcc is a bcc lattice. 4

(*b*) Distinguish between primitive and nonprimitive cell. For an fcc lattice what will be the fractional atomic coordinates ? Derive the same for a bcc lattice. $1+\frac{1}{2}+\frac{1}{2}$

(*c*) Derive Bragg's law of X-ray diffraction from crystal lattice. 2

(*d*) Why X-rays are required for diffraction to happen from crystalline materials-but not the other rays ? 2

5. (*a*) "Ethylene is commonly chosen to illustrate the hydrogenation by Wilkinson's catalys, but the process is very slow with this alkene— why ? 2

(*b*) Briefly discuss the catalytic cycle involving the production of CH_3COOH from CH_3OH. 5

(*c*) What is insertion reaction ? 2

(*d*) What do you mean by 'Catalytic efficiency' ? 1

6. (*a*) Show that for an fcc lattice the value of structure factor $S = 4f$ when all indices are even or odd integers but $S = 0$ if only one of the integers are even. (f = atomic scattering factor). 4

(*b*) What is reciprocal lattice and why the concept of reciprocal lattice is so important in X-ray crystallography ? 2

(*c*) Express the condition of X-ray diffraction from a crystal lattice in terms of reciprocal lattice vector. 3

(*d*) What is phase problem in Crystallography ? 1

7. (*a*) Discuss briefly the kinetics of Platinum binding to DNA. 3

(*b*) How chloride ion concentration affects cis-DDP binding to its biological target molecule ? 3

(*c*) Which donor atoms on DNA are co-ordinated to Platinum ? 1

(*d*) Cite one example where Cobalt has been stabilized in + IV oxidation state. What are the reagents used to attain Co (IV) in this complex ? 3

(*Organic Spl.*)

Answer any *five* questions taking at least *two* from each Group

GROUP—A

1. (*a*) Define molecular recognition. 1

(*b*) What are the principal forces involved in molecular recognition ? 2

(*c*) How can one use 'U'-tube transport experiment for the separation of ions/molecules ? 2

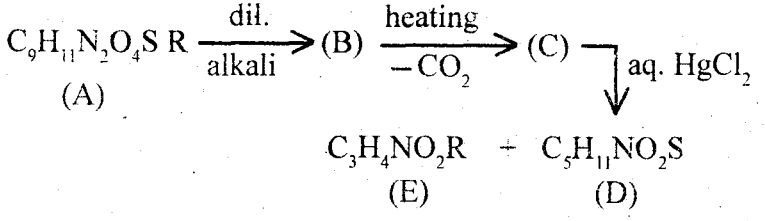
(*d*) Design, synthesize and explain the mode of action of a protease enzyme mimic. 3

2. (*a*) What is hydrophobic effect ? 2

(*b*) How the rates of common Diels-Alder reactions are effected when carried out in water ? 3

(*c*) Design, synthesize and explain the mode of action of a Ribonuclease of mimic based on cyclodextrins. 3

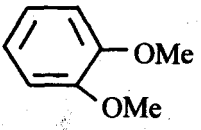
3. Penicillin (A) undergoes the following transformations :



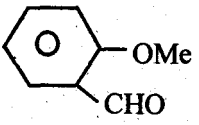
Identify (E) and (D) and other intermediate products (B) and (C). Hence, draw backwards and deduce the structure of Penicillin (A). 4 + 1 + 3

4. (*a*) Chromium tricarbonyl complex of which of the following disubstituted arene is chiral and why ?

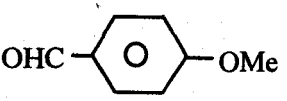
(*i*)



(*ii*)

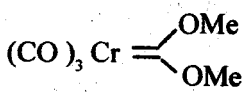


(*iii*)



Give the absolute configuration of the chiral compound justifying the priority attributed to the different carbon atoms. 4

(*b*) How can you use the following carbene complex in the synthesis of α–methylene–γ–butyrolactone ? 4

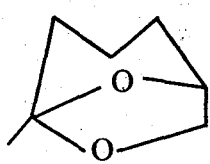


5. (*a*) Explain the terms. 5

(*i*) Functional Group Interconversion.

(*ii*) Control.

Illustrate their uses in the retrosynthetic analysis of the following compound.



(*b*) Define "Synthon and Synthetic Equivalent" with examples. Disconnection of the compound $PhCH_2\ CH\ (CO_2Et)_2$ gives four pairs of synthons. Which of these four pairs is the pair of choice? 3

GROUP—B

6. (*a*) What is aromatic-aromatic enteraction? 2

(*b*) Illustrate an example of Host-Guest complexation utilizing aromatic-aromatic interaction. 2

(*c*) Write the significance of multiple recognition sites in the selection of substrates during Host-Guest complexation. 2

(*d*) Design a suitable chiral host for complexing L-Trp. 2

7. (*a*) Define cryptands. 2

(*b*) How can one use cryptands as a light conversion device ? 3

(*c*) Design, synthesize and illustrate the mode of binding of a receptor for mono-potassium salt of dicarboxylic acids. 3

8. Write all the steps required for synthesis of phenoxy methyl penicillin starting from phthalimide as applied Sheehan et. al. Explain the synthetic methodologies applied in each of the steps. 6 + 2

(*Physical Spl.*)

Answer any *four* questions taking *two* from each Group

GROUP—A

1. What is meant by 'Bose-Einstein condensation'? Derive the expression for the temperature at which this condensation occurs. 2 + 8

2. Define the term 'grand partition function' and hence obtain the Fermi-Dirac distribution law. 3 + 7

3. (*a*) Obtain the expression for the rotational partition function of a diatomic molecule and hence derive the expression for rotational entropy. 5 + 3

   (*b*) Calculate the vibrational contributions to entropy for O_2 at 300 K. (Given the vibrational frequency $= 15800\ cm^{-1}$, $h = 6 \cdot 62 \times 10^{-34}$ JS and $K = 1 \cdot 38 \times 10^{-23}\ JK^{-1}$). 2

4. Establish the relationship between the multipliers α and β in term of chemical potential. 10

5. Using appropriate partition function. Find out the rate constant according to transition state theory. 10

GROUP—B

6. (*a*) The kinetic reaction between $K_2S_2O_8$ and KI was carried out in water (dielectric constant $\epsilon = 78 \cdot 5$) at 25°C. The rate constant of the reaction was found k_1 at 25°C. Now some methanol was added to the water at the same temperature so that the solvent medium becomes 60% water and 40% methanol. The new rate constant was obtained k_2 at 25°C. It was seen that $k_2 > k_1$ at 25°C. Justify. 6

(*b*) What type of reaction is carried out in shock tube and how? Describe by taking a suitable example. 4

7. (*a*) Define potential energy surface (PES) and COL or saddle point. $2\frac{1}{2}+2\frac{1}{2}$

(*b*) The gas-phase rearrangement reaction

Vinyl allyl ether → allyl acetone

has a rate constant of $6\cdot015\times10^{-5}s^{-1}$ at 420K and a rate constant of $2\cdot971\times10^{-3}s^{-1}$ at 470K. Calculate the values of the Arrhenius parameters A and Ea. Calculate the values of $\Delta^{\neq}H°$ and $\Delta^{\neq}S°$ at 420K. (Assume ideal gas behavior). 5

Or

(*a*) State and explain 'density matrix'. Show that ensemble average of mechanical property, $\overline{M}=Tr\,(\hat{M}\,\hat{\varrho})$, where $\hat{\varrho}$ is the density matrix operator. 3+4

(*b*) If there is one conduction electron per sodium atom, calculate the Fermi energy and Fermi temperature of sodium ($\varrho=0\cdot95$ gm/cc.) at 298K. 3

8. (*a*) A full diffusion controlled reaction is carried out in a solution between two uncharged molecule A and B. Which have same radii. i.e. $r_A = r_B$ where r_A and r_B are the radii of $A \& B$ respectively. Now the same reaction is carried out in same solvent and same temperature where $r_A = 1 \cdot 5\ r_B$. The rate of the reaction remains almost equal in both the cases. How does it possible? 6

(*b*) Calculate the rate constant in $dm^3m^{-1}s^{-1}$ of a diffusion controlled reaction between two nonionic species A and B in water at 298 K.

Given, radius of A i.e. $r_A = 4 \cdot 0 \text{Å}$

radius of B i.e. $r_B = 5 \cdot 0 \text{Å}$

and viscosity of water, $\eta = 0 \cdot 9$ centipoise. 4

9. (*a*) Distinguish between polarizable and non-polarizable electrodes. 3

(*b*) Derive the thermodynamic expressions of them considering the electrochemical cell as an open system. 4

(*c*) Give an account of the Stern theory of double layer. 3

10. (*a*) "The electro capillary curve is a perfect parabola for a parallel plate condenser model of an electrified interface." Explain. 3

(*b*) How do you determine the transfer co-efficients of an electrochemical reaction experimentally ? 3

(*c*) How does the transfer co-efficient help in determining the mechanism of the hydrogen evolution reaction ? (Give *two* examples). 4

Or

(*a*) Stating the essential features of Born model derive an expression for the free energy change of ion–solvent interaction, ΔG_{I-S} according to the model. 7

(*b*) Describe the basic principle of determination of heat of Ion-Solvent Interaction. 3