

**2007**

CHEMISTRY

PAPER-VI

*Full Marks : 75**Time : 3 hours*

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

*The figures in the right-hand margin indicate marks*

*Candidates are required to give their answers in their own words as far as practicable*

*illustrate the answers wherever necessary*

**Write the answers to questions of each Group in separate books**

*( Organic Spi. )*

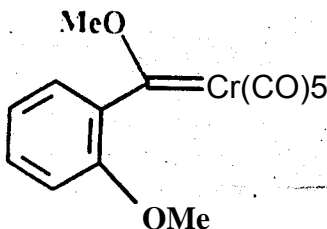
GROUP -A

- 1** Define-Gels-.Qassfy the-different-types of Gels. How are **the supramolecular gels prepared** ? How can **one get an insight of the gel morphologies** ? Write the applications of gels. What type **of interactions** lead to gel formation? 2+3+2+2+4+2
- 2. (a)** Define hydrophobic effect.
- (b) What are cyclodextrins?

*( Turn Over )*

- (c) How can cyclodextrins be used for the selective chlorination of anisole in water?
- (d) How are the rates of common Diels-Alder reactions affected when carried out in water?
- (e) How do you **explain the effects of added salts such as LiCl or LiClO<sub>4</sub> in benzoin condensation reaction in water?** 2+2+3+4+4

3. (a) **'Even though the carbon metal bond in (alkoxy carbene) Cr(CO)<sub>5</sub>, mimics the carbonyl function, the carbene complex is much more reactive than an ester.'** **Substantiate the above statement with a specific example.** 4
- (b) What are **the respective driving forces behind the reactivities of a Fischer carbene complex via polar and non-polar mechanistic pathways?** 3
- (c) **Discuss the mechanistic pathway followed by the reaction undergone by the following Fischer carbene complex with isopropyl acetylene leading to the regioselective formation of the appropriate naphthoquinone.**



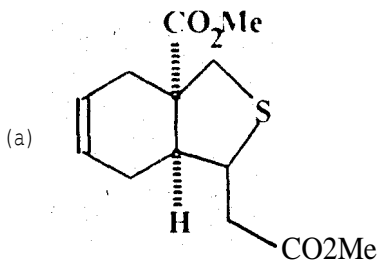
Why the regioselectivity is less when methyl ethyl acetylene is used? 8

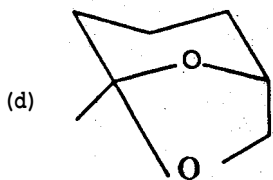
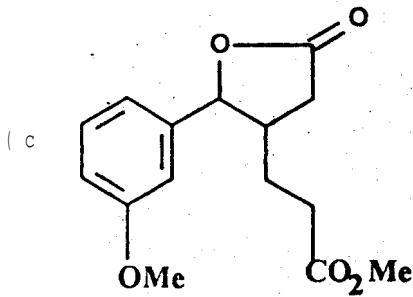
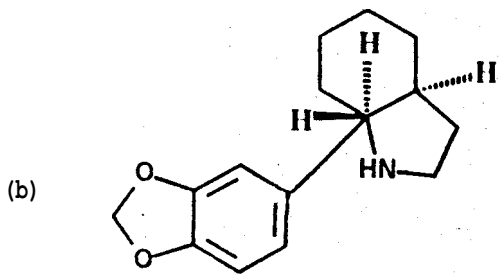
4. (a) **Why the formation** of  $\text{i}12\text{-Fe}(\text{CO})_4$  complex with methyl acrylate requires less energy than the formation of similar complex with ethylene? What is the product obtained when the complex with methyl acrylate is reacted with methyl malonate anion followed by methyl iodide? 5

(b) Account for the enhancements of the acidities of ring and benzylic protons in an aromatic compound upon complexation with  $\text{Cr}(\text{CO})_6$ . 4

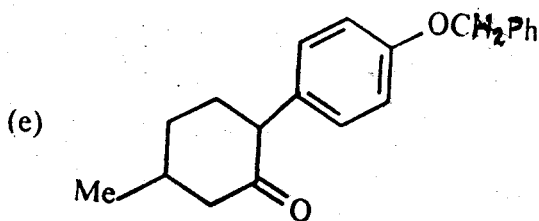
(c) Explain the origin of the diastereoisomerism in the chromiumtricarbonyl complex of 1-methoxycarbonyl indane. Account for the formation of a single product when both the diastereomers of the above compound are treated successively with a base and an alkylating agent. 6

Using the principles of retrosynthetic analysis, suggest syntheses of any *three* of the following compounds : 3 x 5



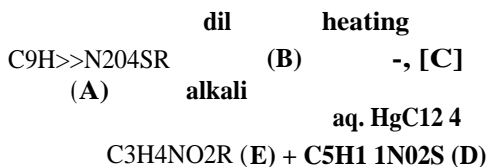


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GROUP -B

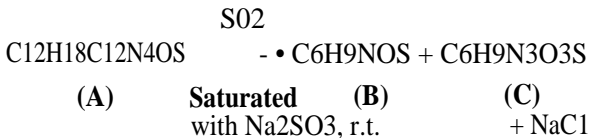
6. (a) Complete the following transformation,



Compound (D) was identified as  $\alpha$ ,  $\beta$ -dimethyl cysteine and compound (E) as substituted amino aldehyde, hence draw backward and deduce the structure of (A) by spectral evidences. 6+5

(b) Synthesise compound (D) starting from  $\alpha$ ,  $\beta$ -1-valine and chloro acetyl chloride stating mechanism wherever applicable.

7. (a) In the following transformation of vitamin (A)

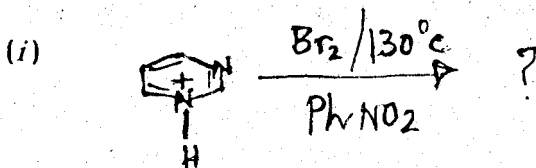


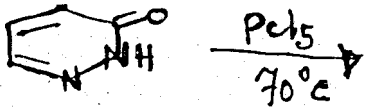
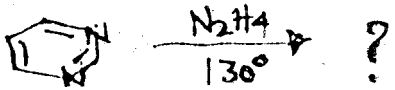
Compound (B) was identified as thiazole and (C) as pyrimidine derivative. Identify compound (B) and (C) and deduce the structure of (A). Confirm the structure by a synthesis. 5+5+2

(b). Write all steps for the synthesis of ascorbic acid starting from L-Lyxose. 3

(a) `Diazines` are much weaker base than pyridine'- explain. Why b.p. of pyridarine is much higher than the other two isomers ?. 2+1

(b) Predict the product(s) of the following reaction with mechanism: (attempt any *three*) 2x3



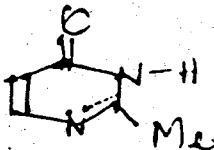


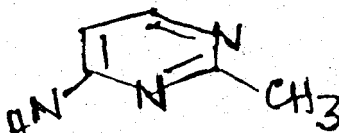
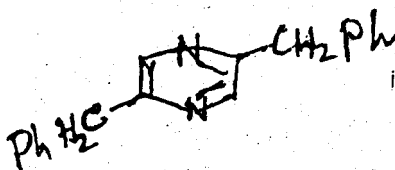
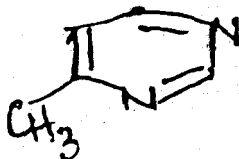
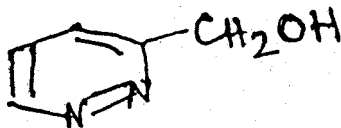
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room tern?

?, (c) Logically develop the synthesis of the following compounds: (attempt any three) 2x3

(i)

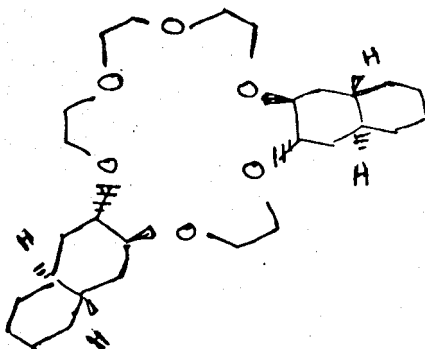




- (a) Define molecular recognition.
- (b) What are the principal forces involved in molecular recognition'?
- (c) Name the following compound and propose a synthetic route:



( 9 )



(d) Define cryptands.

(e) What are the applications of crown ethers and cryptands

	2+2+2+2+3+4
10. (a) Why proline is called helix breaker?	2
(b) Define the following (any three):	2x3

a-helix, (3-pleated sheet, (3-turn, 3.10-helix.

(c) Define Ramachandran Plot.

5

(d) Locate the position of the following structural elements in Ramachandran Plot : a-helix (right handed), (3-pleated sheet.

2

(Inorganic Spl)

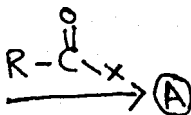
GROUP-A

1. (a) Give the product O A 5 B r D E \_P

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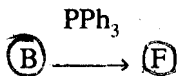
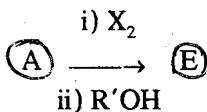
RX

E- [Fe (CO)<sub>4</sub>]<sup>2-</sup>



R'X<sub>m</sub>,

H<sup>+</sup>



(b) How will you synthesis the following (any three) :

(i) [V (CO)<sub>5</sub>]<sup>3-</sup> from IV(CO)<sub>6</sub><sup>1-</sup>



(ii) McCMn (CO)<sub>5</sub> from [Mn (CO)<sub>5</sub>]<sup>0</sup>

(iii) [Cr (CO)<sub>6</sub>]<sup>2-</sup> from Cr (CO)<sub>6</sub><sup>0</sup>

(iv)  $e^{-}$   $i_2$  from ...\_e.\_\_p)<sub>5</sub>

(c) Write down the different bridging carbonyl ligand.

3

2. (a) What do you mean by a cluster compound? 1
- (b) Discuss the structure of the following cluster compounds (any two) : 4
- (1)  $\text{Co}_3(\text{CO})_{10}$
- (ii)  $\text{Fe}_3(\text{CO})_{12}$
- (iii)  $\text{Co}_2(\text{CO})_8$
- (c) Predict the structure of the following (any two) :
- (i)  $\text{Co}_6(\text{CO})_{15}]^{2-}$
- (ii)  $\text{Os}_7(\text{CO})_{21}$
- (iii)  $\text{Os}_5(\text{CO})_{16}$
- (d) Discuss 'edge sharing bioctahedra' geometry with example.
- (e) ' $\text{Re}_2\text{Cl}_2$  is eclipsed whereas  $\text{Os}_2\text{Cl}_2$  staggered' — Explain. 2
3. (a) Discuss the catalytic cycle for alkene hydrogenation by Wilkinson's catalyst. 6
- (b) Write explanatory note on insertion reaction.

- (c) **Discuss the catalytic cycle for Wacker process catalysed by  $[PdCl_4]^{2-}$**  5
4. (a) **What is hydroformylation reaction? Discuss the catalytic cycle for the reaction.** 6
- (b) **Write explanatory note on-Ziegler-Natta polymerization.**
- (c) **What do you mean by 'reductive elimination'?**
- (d) **Point out the merits and demerits of homogeneous and heterogeneous catalysis.** 2
5. (a) **Write names and approximate compositions of two important ores of lanthanides. Draw a sketch of base treatment procedure to obtain lanthanide metals.** 1+3
- (b) **Mention some modern uses of lanthanides.**
- (c) **What do you mean by lanthanide contraction? What are the consequences ?** 4
- (d) **Valence change is also an useful tool to separate some of the lanthanides-Elucidate with example.** 4

GROUP-B

6. (a) **Discuss hemocyanin with respect to-** 3+2+2
- (i) **active site structure**

(ii) O<sub>2</sub> binding

(iii) magnetic behaviour.

(b) What do you understand by 'ceruloplasmin' and 'azurin' ? 2+2

(c) Discuss the active site structure of hemerythrin. Give one model complex of hemerythrin. 4

7. (a) Explain superoxide dismutase with respect to- 2+3+2

(i) structure	
(ii) biofunction	
(iii) model study.	
(b) Give the active <b>site</b> structure of chlorophyl.	2
(c) Write short <b>notes on</b> (any <i>two</i> ) :	6

(i) ascorbic acid oxidase

(ii) cytochrome-C-oxidase

(iii) catalase.

8. (a) Compare and contrast the spectral- parties of lanthanides to that of transition elements. 3

(b) ESR spectrum of UF<sub>3</sub> in CaF<sub>2</sub> lattice is quite different from Nd F<sub>3</sub> . 2

(c) Oxidation states of lanthanides are mainly restricted to +3, but actinides can show higher oxidation states-Explain.

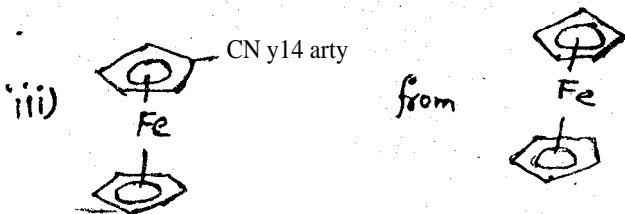
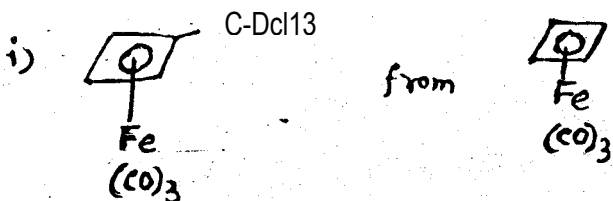
(d) Write note on Uranocene.

(e) Comment on the 'hot atom fusion' and 'cold atom fusion' for the synthesis of heavier actinides. 5

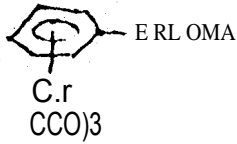
9. (a) How will you synthesize the following compounds

(any three):

2 x 3



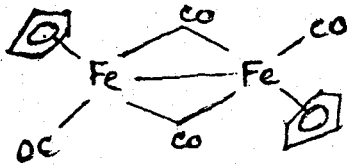
,v)



from



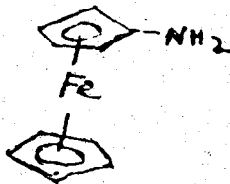
v)



from



(b) Synthesize



starting from ferrocene (mention every step).

3

(c.) Comment with examples on 'bent metallocene' and 'half-sandwich' compounds. 2+2

4d) Write **down the 'Fischer-Hafner', route for synthesizing** ( $\eta^6\text{-arene}$ )<sub>2</sub>Cr, starting from CrG<sub>3</sub>.

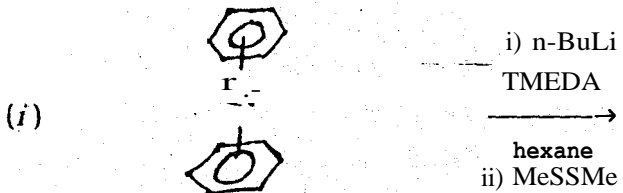
10. (a) How will you synthesize



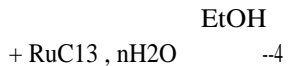
starting from nickelocene ?

3

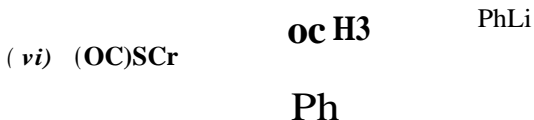
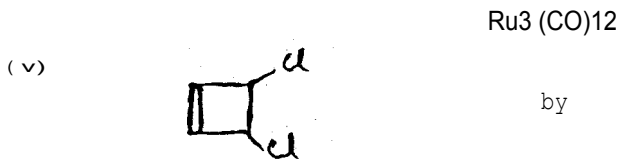
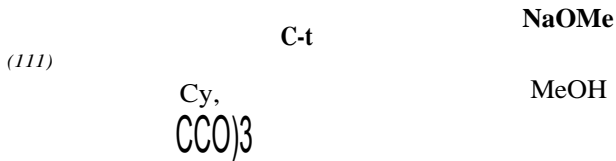
(b) Complete the following reactions (any four) : 2 x 4



[TMEDA = tetramethyl ethylene diamine]







(c) Write down the method of preparation of transition metal allyl complexes and transition metal carbene complexes. (one method for each)

(Physical Special)

GROUP -A

1. Define grand canonical ensemble and grand partition function. Obtain an expression for the grand partition function for a system of Bose particles and hence derive the Bose-Einstein distribution law. 15
2. Obtain an expression for the thermodynamic probability of distribution of particles describable by antisymmetric wavefunctions and arrive at the appropriate **quantum** statistical distribution law. Under what conditions does such a distribution reduce to Boltzmann distribution. 13+2
3. (a) Obtain an expression for the vibrational contribution to the molar entropy of a molecule.  
(b) Calculate, **using Boltzmann distribution, the ratio of population** at 27 °C of energy **levels separated by** 10 KT. 9+6
4. (a) **Derive an appropriate expression for the determination** of the molecular weight of a polymer by sedimentation equilibrium method.  
Why is this method more advantageous over sedimentation velocity method? 7+1  
(b) **What is sedimentation** coefficient?

- (c) The sedimentation coefficient of the protein serum globulin is  $6.5 \times 10^{-13} \text{S}$ . Now this protein is placed in an ultracentrifuge which is operating at 50,000 rpm. How far will the solution boundary move in 30 minutes at a distance of 6.5 cm from the axis of rotation. 5
- S. (a) Describe how molecular weight of high polymers is determined using Zimm plot (Derivation of the equation is not required). 7
- (b) What do you understand by root-mean-square distance? Does it relate with the phenomena diffusion? 2+1
- (c) At  $25^\circ \text{C}$ , the diffusion coefficient, the molar mass and specific volume of haemoglobin are  $6.9 \times 10^{-11} \text{m}^2 \text{s}^{-1}$ ,  $64,500 \text{g mol}^{-1}$  and  $0.75 \text{cm}^3 \text{g}^{-1}$ , respectively. Calculate its frictional ratio and comment on your result. The coefficient of viscosity of water at the given temperature is 1.005 cP. 5

## GROUP -B

6. (a) Using the appropriate expressions for the partition functions, derive an expression for the rate constant of a reaction, based on the transition state theory. 11
- (b) Two reactions of the same order have identical pre exponential factors and activation energies differ by 20 kJ. Find the ratio of their rate constants at 300 K. 4

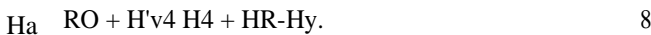
7. (a) What is molecular beam? What are its essential features? How does a reaction occur in molecular beam? Illustrate with an example. 1+2+2
- (b) Does the rate of a second order reaction between ionic species depend on ionic strength of the medium? If yes, justify your statement. 5
- (c) The radii of two nonionic solutes A & B are  $2 \times 10^{-10} \text{ m}$  and  $3 \times 10^{-10} \text{ m}$  respectively. For a reaction between A and B in water at  $25^\circ \text{C}$ . Calculate the rate constant, if the reaction be diffusion controlled. (Given : viscosity of the solvent is  $0.9 \text{ M}$ . 5
8. Show that at moderate **concentration** of an electrolytic **solution**, the simple Debye-Hückel (D-H) law given by  $\log f_{\pm} = -A(z_+z_-)l^{1/2}$  is modified as

$$\log f_{\pm} = -\frac{A(z_+z_-)l^{1/2}}{1 + Ka}$$

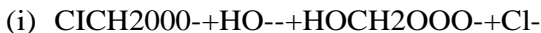
where  $a$  = ion size parameter,  $K = B/l^{1/2}$  ( $B$  is a constant and  $K$  = the thickness of ion atmosphere). Discuss the role of ion size parameter to explain the deviation from simple D-H law at moderate **concentration**. Also show that the modified equation **can explain** in a better way the experimental behavior of ionic solution at high concentration and that the equation reduces to the simple D-H law at low, concentration of ions.

Also justify the statement that the simple D-H law is a limiting law. 5

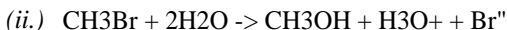
9. (a) What do you mean by potential energy surface and saddle point ? Explain with reference to the reaction,



- (b) Predict (with brief explanation) the sign of the entropy of activation for the following reactions : 4



s



- (c) Discuss the salient features of the structure of water that make it unique as solvent for electrolytes. 3

10. (a) What causes chemical shift in Mossbauer spectroscopy and what are the factors affecting the magnitude of the chemical shift? 6

- (b) Calculate the recoil velocity of a free Mossbauer nucleus of mass  $1.67 \times 10^{-25}$  kg, when emitting a  $\gamma$ -ray of wavelength of 0.1 nm. S

- (c) A particular Mossbauer nucleus has spins of  $5/2$  and  $3/2$  in its excited and ground states respectively. Into how many lines will the  $\gamma$ -ray spectrum splits if

- (i) the nucleus is under the influence of an internal electric field gradient but no magnetic field is applied
- (ii) both. **an internal** electric field **gradient and an** external magnetic field are present.

4