This question paper contains 8 printed pages]

CODE : FS-17

CHEMISTRY

Time : 3 Hours   *Maximum Marks : 200*

Note :— (1) The candidates are required to attempt *five*
                 questions in all attempting the compulsory
                 questions 1 and 5 and *three* other questions out
                 of remaining six questions, taking at least *one*
                 question from each Part-I and II. In this way,
                 at least *two* questions will be attempted from each
                 part i.e. one compulsory and one more question.

        (2) Parts of the same questions must be attempted
                 together and not to be attempted in between the
                 answers to other questions.

Part I

1.   (*a*)   How does the valance band theory explain the
                 shape and magnetic property of $[Mn(CN)_6]^{4-}$?

                                                                    10

      (*b*)   What is lanthanide contraction and what are
   its consequences ?   10

(c) Giving the postulates of the quantum mechanics calculate the ground state energy of an electron in a box of the size 10^{-14} m. 10

(d) Give the outline solution of Schrödinger equation for H_2^+ ion and draw the BMO and ABMO. 10

2. (a) What are fuel cells ? Explain the working of Hydrogen-Oxygen fuel cell in detail. 10

(b) Explain and discuss the structure of $Fe_3(CO)_{12}$.

10

(c) Discuss the kinetics of free radical polymerisation.

10

(d) Give a neat diagram for the relative energies of pi-molecular orbitals in octahedral complexes. 10

3. (a) Briefly describe the most effective method for separation of lanthanides ? 10

(b)   Derive the Michaelis-Menten equation by steady-state approach for a Uni-Uni system and explain why the reaction rate changes from first order to zero-order as substrate concentration increases.   10

(c)   What do you mean by desorption activation energy ? Calculate how long a hydrogen atom will remain on the surface of the solid at 298K if its desorption activation energy is (a) 15 kJ/mol (b) 150 kJ/mol assuming that $\tau_o = 10^{-13}$ s.   10

(d)   How does VBT account for the following facts ?   10

(i) $[Ni(CN)_4]^{2-}$ is diamagnetic and square planar

(ii) $[Cu(Cl)_4]^{2-}$ is paramagnetic and tetrahedral.   10

4. (a) Explain the factors influencing the magnitude of crystal field splitting ? 10

(b) Why is paramagnetic behaviour of actinides difficult to interpret ? 10

(c) What is the third law of thermodynamics ? How are the absolute entropies of the substances determined using this law ? 10

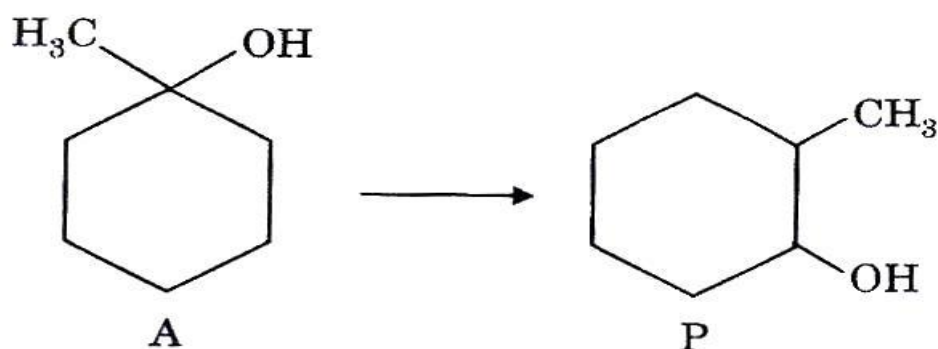(d) What is the overvoltage ? Explain the important application of this phenomenon. 10

Part II

5. (a) Write the product(s) including their stereochemistry in the following reactions and support them from their mechanism : 10
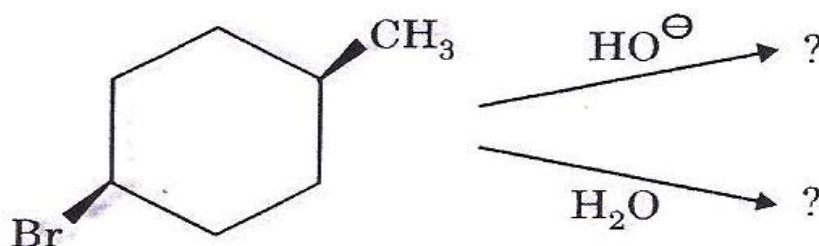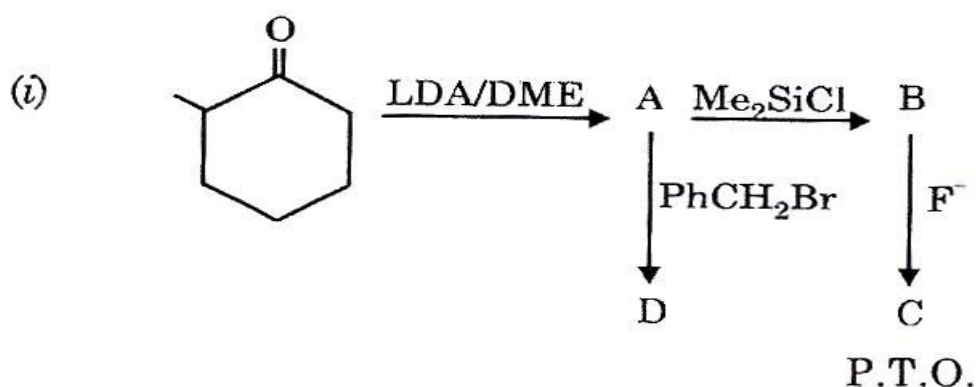
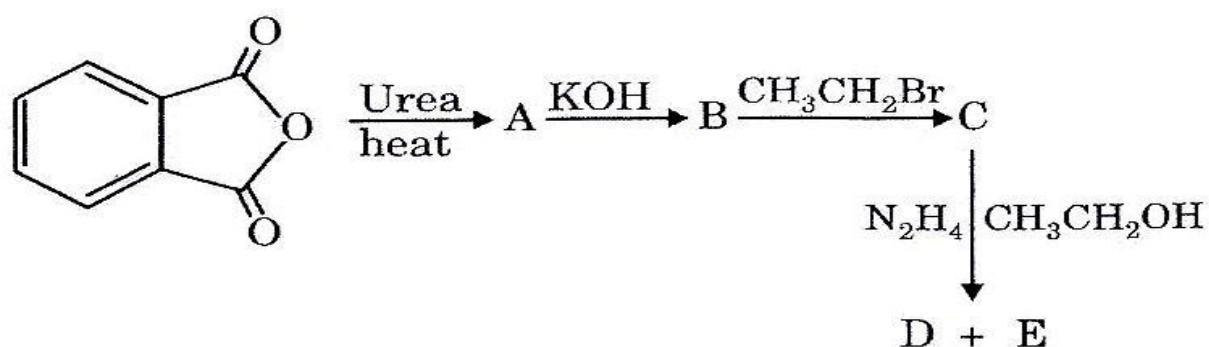(b) Giving the stepwise mechanism write the product(s) in the following reaction : 10

$$\text{vinylcyclopentane} \xrightarrow{\text{HBr}} ?$$

(c) Devise the synthesis of P from A : 10

A   P

(d) Explain in detail the reaction of 2-bromotoluene with $NaNH_2$/liq. NH_3. 10

6. (a) Prepare salicylaldehyde starting from benzamide. 10

(b) Identify the missing entities in the following sequences of reactions : 10

(i)

$$\text{cyclohexanone} \xrightarrow{\text{LDA/DME}} A \xrightarrow{Me_2SiCl} B$$

A $\xrightarrow{PhCH_2Br}$ D

B $\xrightarrow{F^-}$ C

(ii)

$$\text{Phthalic anhydride} \xrightarrow[\text{heat}]{\text{Urea}} A \xrightarrow{\text{KOH}} B \xrightarrow{CH_3CH_2Br} C$$

$$C \xrightarrow[\;N_2H_4\;|\;CH_3CH_2OH\;]{} D + E$$

10

(c) Define the term "Mutarotation". Explain this behaviour of glycosides in basic and acidic media. 10

(d) Comment upon the structure of carbenes. 10

7. (a) Giving the proper explanations, draw the most stable conformational structures of : 10
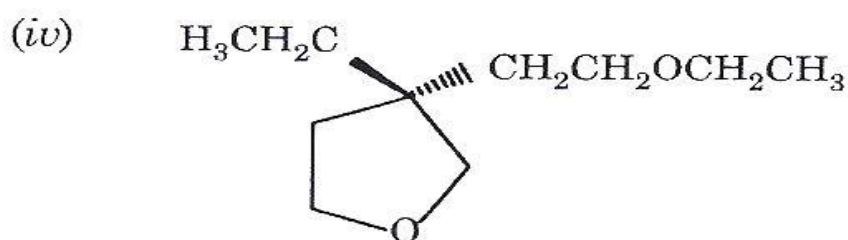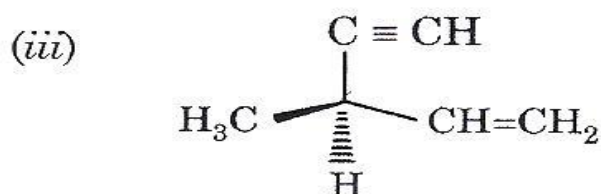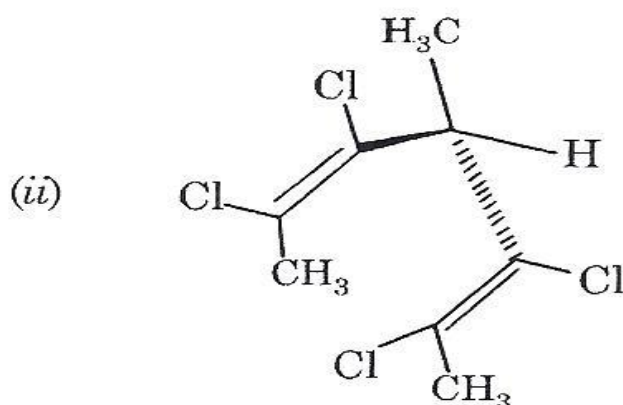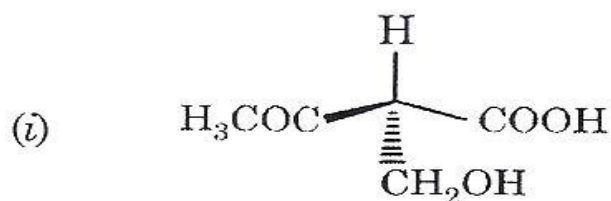
    (i) cis-2-Methylcyclohexanol

    (ii) cis-1,3-Cyclohexanediol

    (iii) cis-1,4-Cyclohexanediol

    (iv) 2-Bromocyclohexanone and

    (v) 2-Bromo-4, 4-dimethylcyclohexanone

(b) Assign the configurational notations(R/S) to the chiral centres to the following molecules : 10

(i)

$$H_3COC \overset{H}{\underset{CH_2OH}{|}} COOH$$

(ii)

(iii)

$$H_3C \overset{C \equiv CH}{\underset{H}{|}} CH=CH_2$$

(iv)

(c) Comment upon the nitration of pyridine and quinoline. 10

(d) Comment upon the nucleophilicity of F', Cl', Br', and I' in ethanol and DMSO solvents separately. 10

8. (a) Write an elaborate note on Paterno-Buchi reaction.

10

(b) Draw the neat and clean Jablonskii diagram. 10

(c) Write the molecular structures of :   10

(i) Riboflavin

(ii) Cellulose

(iii) Quinine

(iv) Adrenalin and

(v) Amylopectin.

(d) Explain the acid-catalysed dehydration of the

following alcohols :   10