IIT-JEE-2001

CHEMISTRY

MAINS

[Time allowed: 2 hours] [Maximum Marks :100]

1. Compound (X) on reduction with $LiAlH_4$ gives a hydride (Y) containing 21.72 hydrogen along with other products. The compounds (Y) reacts with air explosively resulting in boron trioxide. Identify (X) and (Y). Give balanced reactions involved in the formation of (Y) and its reacton with air. Draw the structure of (Y).

2. A metal complex having compositon $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms (A) and (B). The form (A) reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) givens a pale yellow precipitate soluble in concentrated ammonia. Write the formula of (A) and (B) and state the hybridization of chromium in each. Calculate their magnetic moments (spin-only value).

3. Starting from $SiCl_4$, prepare the following in steps not exceeding the number given in parentheses (give reactions only):

(i) Silicon (1)

(ii) Linear silicone containing methyl groups only (4)

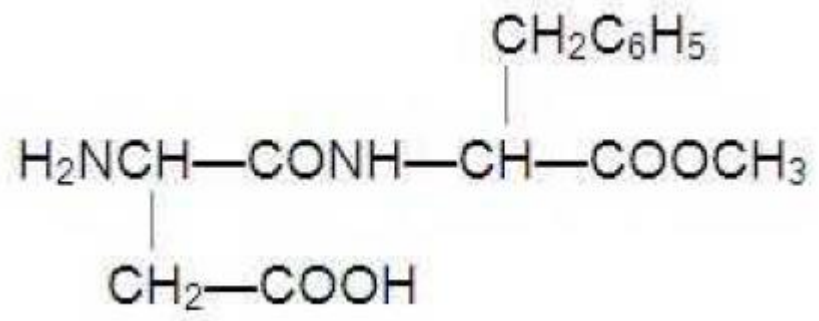
(iii) Na_2SiO_3 (3)

4. Hydrogen peroxide solution $(20\ ml)$ reacts quantitatively with a solution of $KMnO_4(20\ ml)$ acidified with dilute H_2SO_4. The same volume of the $KMnO_4$ solution is just decolourised by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10 ml of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2.

5. How would you synthesise 4-methoxyphenol from bromobenzene in NOT more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme.

6. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (A). The organometallic reacts with ehtanal to give an alcohol (B) after mid acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B).

7. Aspartame, an artificial sweetener, is a peptide and has the following structure:



(i) Identify the four functional groups.

(ii) Write the zwitterionic structure.

(iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.

(iv) Which of the two amino acids is more hydrophobic?

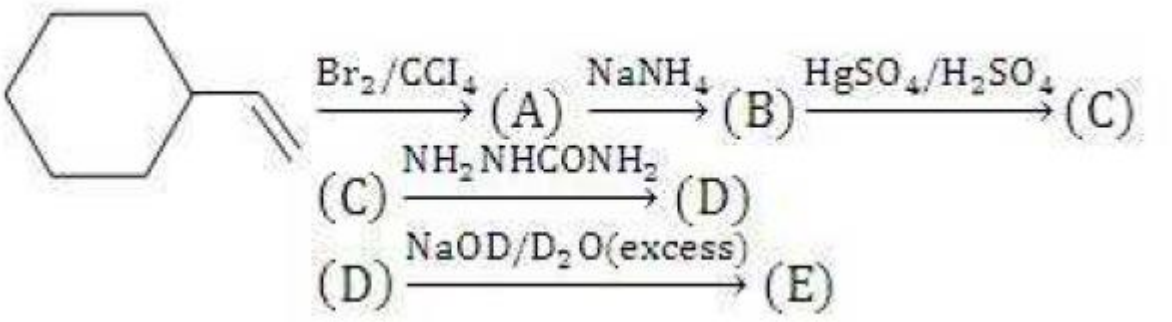
8. An alkene $(A)C16H16$ on ozonolysis gives only one product (B) $C8H8O$. Compound (B) on reaction with $NaOH/I2$ yields sodium benzoate. Compound (B) reacts with $KOH/NH2NH2$ yielding a hydrocarbon (C) $C8H10$. Write the structures of compounds (B) and (C). Based on this information two isomeric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation $(H2/Pd-C)$ gives a racemic mixture.

9. The compression factor (compressibility factor) for one mole of a Van der Waals gas at $0°C$ and 100 atmospheric pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the Van der Waals constant a.

10. The rate of first-order reaction is 0.04 mol litre-1 s-1 at 10 minutes and 0.03 mol litre-1 s-1 at 20 minutes after initiation. Find the half-life of the reaction.

11. A white substance (A) reacts with dilute $H2SO4$ to produce a colourless gas (B) and a colourless solution (C). The reaction between (B) and acidified $K2Cr2O7$ solution produces a green solution and a slightly coloured precipitate (D). The substance (D) burns in air to produce a gas (E) which reacts with (B) to yield (D) and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous $NH3$ or $NaOH$ to (C) produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify (A), (B), (C), (D) and (E). Write the equations of the reactions involved.

12. (a) Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures :



(b) Identify (X),(Y) and (Z) in the following synthetic scheme and write their structures. Explain the formation of labeled formaldehyde $(H2C*O)$ as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the $C*$ carbon in the entire scheme. $BaC*O3 + H2SO4$ --> (X) gas $[C*$ denotes C14$]$

$$CH_2 = CH - Br \xrightarrow[(iii)H_3O^+]{(i)Mg/ether\ (ii)X} (Y) \xrightarrow{LiAlH_4} (Z)$$

13. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175oC, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 1, 2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate the DGo for the following equilibria :

PoA $DG1o = ?$
PoC $DG2o = ?$

From the calculated value of $DG1o$ and $DG2o$ indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C).

14. The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 35°C.

$Pt\ |H2(g)|HCI(aq)|AgCI(s)|Ag(s)$

(i) Write the cell reaction.

(ii) Calculate the DHo and DSo for the cell reaction assuming that these quantities remain unchanged in the range 15°C to 35°C.

(iii) Calculate the solubility of AgCI in watr at 25°C.

Given : The standard reduction potential of the $Ag+\ (aq)/Ag(s)$ couple is 0.80 V at 25°C.

15. The vapour pressure of two miscible liquids (A) and (B) are 3000 and 5000 mm of Hg respectively. In a flask 10 moles of (A) is mixed with 12 moles of (B). However, as soon as (B) is added, (A) starts polymerizing into a completely insoluble solid. The polymerization follows first-order kinetics. After 100 minutes, 0.525 mole of a solute is dissolved which arrests the polymerization completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerization reaction. Assume negligible volume change on mixing and polymerization and ideal behavior for the final solution.