This question paper contains 7 printed pages.

4601–A *Your Roll No.* .....

B.Sc. Prog. / II **AS**

Paper CH–202 : CHEMISTRY

(Admissions of 2007 and before)

Time : 3 hours *Maximum Marks* : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Use separate answer-sheets for Sections A and B.

Use of calculators is allowed.

Log tables will be provided, if asked for.

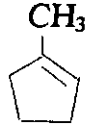
SECTION A *Marks* : 50

(Organic Chemistry)

Answer four questions in all.
Question No. 1 is compulsory.

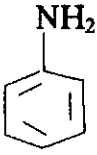
1. (*a*) Identify the products(s) of following reactions:

(*i*) $C_6H_5CHO + CH_3NO_2 \xrightarrow{KOH}$

(*ii*)  $+HBr \longrightarrow$

P. T. O.

(*iii*) $2HCHO \xrightarrow{OH^{\ominus}}$

(*iv*)  $\xrightarrow{Br_2/CCl_4}$

(*v*) $(CH_3)_3C-Cl \xrightarrow{OH^{\ominus}}$

(*vi*) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow[433\,K]{\text{Conc. } H_2SO_4}$

(*b*) Write the reactions involved in the reduction of nitrobenzene under acidic, neutral and alkaline conditions.

(*c*) What happens when toluene is treated with chromyl chloride? 6,6,2

2. Explain giving reasons why:

(*a*) Only α-hydrogen atoms in aldehyde and ketone are involved in aldol condensation.

(*b*) Alkynes undergo nucleophilic addition.

(*c*) Conjugated dienes are more stable than isolated dienes.

(*d*) Nitration of bromobenzene is much faster than bromination of nitrobenzene. $3\times4=12$

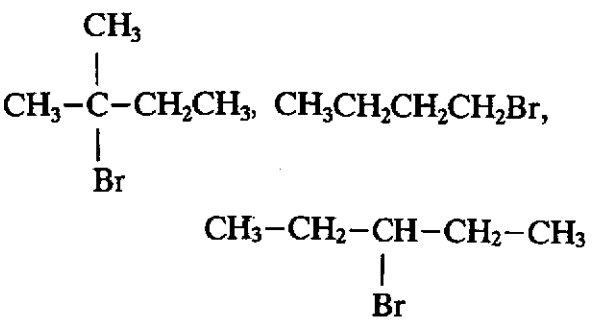
3. (*i*) Outline the mechanism of formation and structures of products from the reaction of HBr with—

(*a*) 3-methyl-1-butene

(*b*) 3,3-dimethyl-1-butene.

(*ii*) Giving reason arrange the following in increasing order of reactivity:

(*a*) Towards S_N1 reaction:



(*b*) Towards electrophilic substitution:

Phenol, benzene, toluene, nitrobenzene. 4,8

4. (*i*) Write the possible monosubstitution products that would be obtained by chlorination of isopentane at 300°C. Which isomer would you expect to predominate? Give mechanism.

(*ii*) How will you carry out the following conversion?

(*a*) 1-chloropentane to 1-bromopentane

(*b*) 1-chloropentane to 2-chloropentane

(*c*) 1-chloropentane to 1,2-dichloropentane

(*d*) Aniline to *p*-bromoaniline. 4,8

5. (*a*) Explain why a >C=O group of esters does not undergo nucleophilic addition reactions.

(*b*) How will you prepare 1-butanol and 2-butanol from 1-butene?

(*c*) Describe a mechanism for formation of benzyl chloride from toluene by photochlorination.

(*d*) Name one isomer of octane which on chlorination will give only one octyl chloride. 3,4,3,2

6. (*i*) Give the reactions which support the existence of ethyl acetoacetate in keto and enol form.

(*ii*) Give synthesis of 3-methyl uracil from ethyl aceto-acetate.

(*iii*) Outline the following rearrangement reactions: (*a*) pinacol-pinacolone, (*b*) Beckmann. 6,2,4

SECTION B

Marks : 25

(*Physical Chemistry*)

Attempt any two questions.

Calculator may be allowed.

R=8·314J/K/mol.

7. (*a*) Write short note on Kohlraush's Law of independent migration of ions. How does it help in determining the equivalent conductance at infinite dilution of weak electrolytes? 4

(*b*) The conductivity of a saturated solution of CaF_2 at 18°C was found to be $4{\cdot}2\times10^{-5}$ ohm^{-1} cm^{-1}. The conductivity of water used for making the solution was $2{\cdot}0\times10^{-6}$ ohm^{-1} cm^{-1}. The equivalent conductivities at infinite dilution of Ca^{2+} and F^- ions are 52·0 and 48·0 ohm^{-1} cm^2 equiv^{-1}, respectively. Calculate solubility product and solubility in gram/litre of CaF_2. 4 1/2

(*c*) At a certain temperature, the degree of dissociation of pure water is found to be $1{\cdot}81\times10^{-9}$. Calculate ionic product and dissociation constant of water at this temperature. 4

8. (*a*) What is emf of a cell? Describe the method of measuring emf of an electrochemical cell. 4

(*b*) How is *p*H of a solution determined by quinhydrone electrode and what are its limitations? 4

(*c*) Write the cathodic, anodic half cell reactions and the cell reaction for the following cell:

$Pt|H_{2(g)}$ NaOH satd. with $HgO_{(s)}|Hg_{(l)}|Pt$. 2 1/2

P. T. O.

(*d*) Write the expression for activities of $MgCl_2$ and $CuSO_4$ in terms of their molalities and mean ionic activity coefficients. 2

9. (*a*) Derive a relationship between K_p, K_c and K_x. State the condition for which $K_p = K_c = K_x$. 5

(*b*) Apply Le Chatelier's Principle to predict the effect of temperature and pressure on the following reactions:

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

$$\Delta H = -180 \cdot 5 \text{ kJ}$$

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$$

$$\Delta H = -113 \text{ kJ}$$

4

(*c*) 5 moles of HI were heated in a sealed bulb at 717 K till the equilibrium state was reached and it was found to be 20% dissociated at that time. Calculate the equilibrium constant for the dissociation of HI reaction. 3½

10. (*a*) For a reaction in equilibrium, derive that:

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}.$$

4

(*b*) *Derive the* expression for Gibb's phase rule and define the terms used in the final expression. 5

(*c*) For the reaction:

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

K_p at 673 K is $1{\cdot}64\times10^{-4}$ atm^{-2}. If heat of reaction is 165·21 kJ, find out the equilibrium constant at 773 K. $3_{1/2}$