2021

CHEMISTRY

[HONOURS]

Paper : II

Full Marks : 75   Time : 4 Hours

The figures in the right-hand margin indicate marks.

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

Write the answers of each Group in separate answer scripts.

GROUP–A
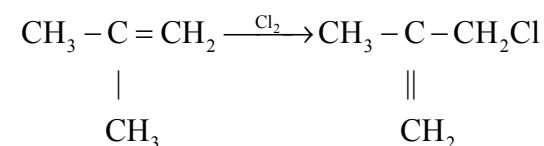
(Organic)

(Marks : $37\frac{1}{2}$)

1. Answer any **three** of the following: 1×3=3

    a) Explain the lack of reactivity of α-halocarbonyl compounds in S$_N$1 reaction.

    b) Draw the molecular orbital picture of acrylonitrile.

    c) Explain the relative order of basicity of the following amines.

    , $N(CH_2Et)_3$,
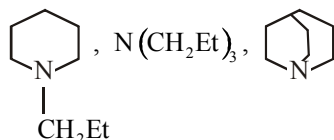
d) 18-Crown-6 ether greatly increases the rate of reaction where KCN is used as the source of cyanide ion. Account for the observation.

2. Answer any **three** of the following: 2×3=6

    a) Write down the structure of each of the following:

        i)   2$\underline{R}$,3$\underline{R}$ – 2,3- -dihydroxy-3-methyl-pentanoic acid

        ii) D-Glyceraldehyde

    b) Which compound in the following pair has the higher dipole moment and why : i) 1, 2-dibromoethane & (ii) 1, 2-dihydroxyethane.

    c) Write the structure of all the possible tautomers of acetyl acetone. Compare their relative stability.

   d) Account for the following change:

    $$CH_3 - C = CH_2 \xrightarrow{Cl_2} CH_3 - C - CH_2Cl$$
    $$\quad\quad\quad |\quad\quad\quad\quad\quad\quad\quad\quad\quad ||$$
    $$\quad\quad\quad CH_3\quad\quad\quad\quad\quad\quad\quad\quad CH_2$$

    e) Arrange the following in the increasing order: of basicity:

        OH^-, $C_2H_5O^-$, Me_3CO^-, $MeCO_2^-$.

        Give explanation.

3. Answer any **three** questions: 6×3=18

a) i) Write the A_{AC^2} and B_{AC^2} mechanism for the hydrolysis of methyl benzoate. It is observed that electron withdrawing substituents in the m-and p- positions enhance the rates of B_{AC^2} hydrolysis of substituted methyl benzoates while the effect is negligible for A_{AC^2} reactions. Explain.

ii) Treatment of alkyl iodide with AgCN yields alkyl isocyanides as the major product wheres alkyl iodides give alkyl cyanides mainly on treatment with KCN. Explain.   (2+2)+2=6

b) i) Discuss E1-E2-EIcB as the full spectrum of elimination reaction mechanism. Cite one example in each case.

ii) Discuss the factors which govern Elimination versus Substitution.   4+2=6

c) i) Bromine is separately added to maleic acid and fumaric acid. Discuss what will be the observation.

ii) Reaction of trans-2-butene with methylene (:CH$_2$) obtained from diazomethane occurs in a stereospecific manner, but the reaction in presence of nitrogen is not stereospecific. Why?   (2+2)+2=6

d) i) Explain the stereochemistry of the product(s) with suitable mechanism when the threo-diastereomer of PhCHMeCHMeOTs is treated with sodium acetate in acetic acid.

ii) What do you mean by conformational isomers and diastereomers? Give one example in each case.   3+3=6

e) i) Draw the energy profile diagram for the sulphonation of naphthalene. Account for the fact that at $40^{\circ}C$, the main product is naphthalene-1-sulphonic acid, while at $160^{\circ}C$, the main product is naphthalene-2-sulphonic acid.

ii) Discuss the stereochemistry of dehydrobromination of meso-1,2-dibromo-1,2-diphenylethane with NaOEt in EtOH. Write down the major product.   (1+2)+(2+1)=6
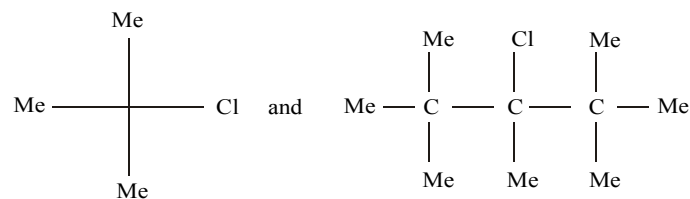
4. Answer any **one** of the following: $10 \times 1 = 10$

a) i) Write with suitable mechanism the major and minor products from the reaction of

$Me_2C(OH)C(OH)Ph_2$ with Conc. H_2SO_4. 2
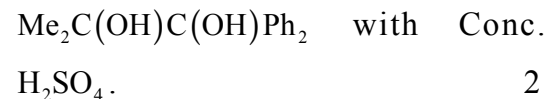
ii) The reaction of hydroxide ion at the marked carbon for the compound $\underline{A}$ is 10 times faster than that of the compound $\underline{B}$. Explain. 2

$\underline{\underline{A}}$ $\underline{\underline{B}}$
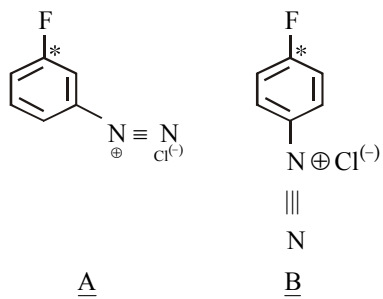
iii) Compare the ease of S_N1 reaction with explanation in the following pair:

2

iv) Compare the relative stability of the following compounds:

Diazomethane and ethyl diazoacetate.

2

v) What would be the product composition if an equimolecular mixture of toluene and chlorobenzene is treated with 1 molar proportion of bromine in presence of iron powder? 2

b) i) Salicylic acid is a stronger acid than benzoic acid whereas *p*-hydroxy benzoic acid is weaker than benzoic acid. Explain. 2

ii) The following compound exists mainly in the enol form— Account. 2
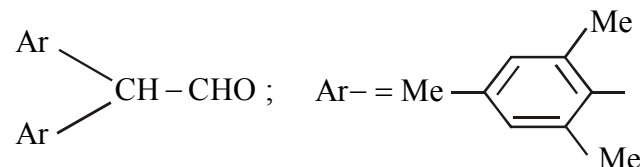
iii) Compare carbon-oxygen bond distance in $Me_2C = O$, $MeCO_2^-$ and

2
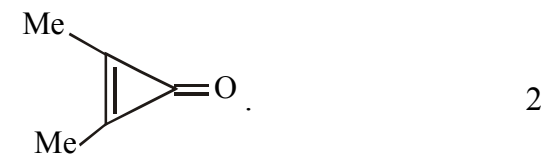
iv) Which has higher dipole moment and why–allyl bromide or vinyl bromide? 2

v) Carry out the following conversion: 2

$(\underline{R}) - MeCHPhOH \rightarrow (\underline{R}) - MeCHPhCl$

[General Proficiency : $\frac{1}{2}$]

GROUP-B

(Physical)

(Marks : $37\frac{1}{2}$)

5. Answer any **three** of the following: 1×3=3

a) Is it possible to have gaseous dissociation without the gas showing any abnormal vapour density?

b) Why does a piece of blotting paper soak water?

c) In cryoscopic study of solutions, which concentration unit is preferable molarity or molality? Why?

d) What is the unit and dimension of viscosity coefficient?

e) Arrange the following in order of increasing freezing point:

0.1(M) HCl, 0.1(M) CH_3COOH,

0.1(M) Sucrose solution

6. Answer any **three** of the following: 2×3=6

a) Joule-Thomson process is an isoentropic process– Comment. (Justify or Criticize)

b) Highly viscous liquids are less volatile. – Explain.

c) ΔH is a state function. (Justify or Criticize)

d) Using the principle of equipartition of energy, estimate the energy of

i) CO_2

ii) H_2O

e) What is heat of neutralisation? The heat of neutralisation of a strong acid by a strong alkali is always the same– Justify.

7. Answer any **three** of the following: 6×3=18

a) i) Write down the mathematical expression of Poiseuille equation explaining the symbols used. Show how the simple working formula of Ostwald viscometer is derived from this equation.

ii) How does the surface tension of a liquid vary with temperature? Explain.

4+2=6

b) i) State and formulate Raoult's laws of relative lowering of vapour pressure for a dilute solution. State its limitations.

ii) Human blood is isotonic with 0.1(N) NaCl solution. The Vant Hoff factor for

NaCl is 1.82. Calculate the osmotic pressure of Human blood at 37°C.

3+3=6

c) How does the equilibrium constant for the reaction $2A+3B \rightleftharpoons 4C+Q$ change when (i) the pressure is increased (ii) temperature is decreased (iii) a catalyst is added? Explain using mathematical equation.   2+2+2=6

d) i) State and explain Hess's law of constant heat of summation.

ii) The heat of combustion of $C_6H_6(l)$ is −781 kCal mole⁻¹. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are −94.3 kCal.mole⁻¹ and −68.3 kCal mole⁻¹ respectively. Calculate the heat of formation of benzene.   3+3=6

8. Answer any **one** of the following: 10×1=10

a) Calculate the heat of formation of Carbon disulphide. The heat of combustion of CS_2, S and C are −26.5 kcal, −94.3 k cal and −71.08 kcal respectively at 25°C.   (2+2+2)+4=10

b) i) What thermodynamic parameters will you able to calculate from a study of the equilibrium of different temperatures? Derive the equation required in this connection.

ii) Calculate the osmotic pressure of 0.01M KCl solution of 27°C.

iii) Describe the principle of capillary rise method for the determination of the surface tension of a liquid.

4+2+4=10

c) How would a carnot cycle look in a T−S diagram? Label the states and various processes involved. What does the enclosed area signify?

[General Proficiency : $\frac{1}{2}$]

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