2020

CHEMISTRY

[HONOURS]

Paper : V

[SUPPLEMENTARY]
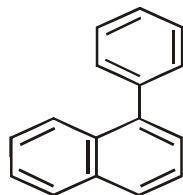
Full Marks : 75   Time : 4 Hours

The figures in the right-hand margin indicate marks.
Candidates are required to give their answers in
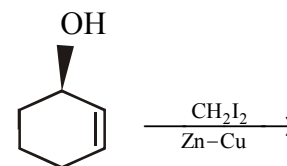*their own words as far as practicable.*
Write the answers to questions of each Group in
separate answer script.

GROUP - A

(Marks - 37½)

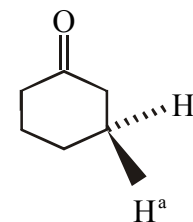1. Answer any **three** questions: 1×3=3

    a) Write down the major product of mono-
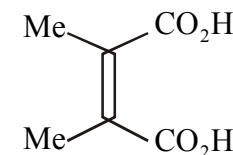   nitration of the following compound:

b) Predict the major product of the following
    reaction:

c) Designate H^a and H^b of the following molecule
   as pro-R or pro-S:

d) Give Re-Si descriptor to each ethylenic carbon
    face of the following molecule when viewed
    from top:

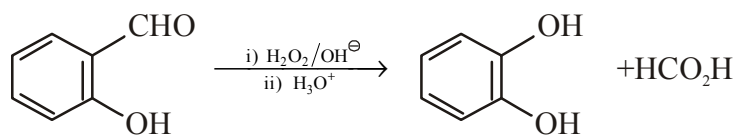2. Answer any **three** of the following: 2×3=6

    a) Between cyclopentanone and cyclopropanone,
        which one is more reactive towards $NaBH_4$ and
        why?

b) Diazotisation of 2-aminophenol produces a heterocyclic compound. Write a possible structure of the product and explain its formation.

c) Explain the formation of the product in the following transformation:
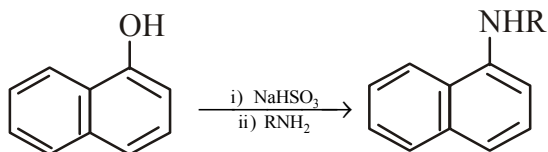
d) Bromine addition takes place to the Re-Re face of fumaric acid. What will be the absolute configuration of the produced 2,3-dibro-derivative?

e) Write down plausible mechanism of the following transformation:

3. Answer any **three** of the following: $6 \times 3 = 18$

a) i) Attempted esterification of 2, 4, 6-triphenylbenzoic acid with conc. H_2SO_4 and methanol resulted in the formation of a ketone instead of the expected methyl ester. Identify the product and suggest a mechanism of its formation.

2

ii) Which of the two diastereomers of the following oxime would undergo Beckmann rearrangement faster and why? Identify the product also. 2
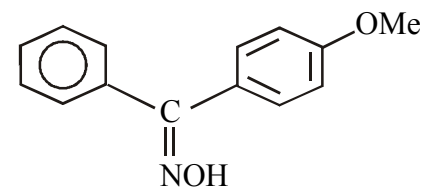

iii) When naphthalene is hydrogenated under high pressure two diastereomeric decahydronaphthalene are formed. Write the stereo-structure of the products and comment on their optical activity. 2

b) i) Write a note on Arndt-Eistert reaction.
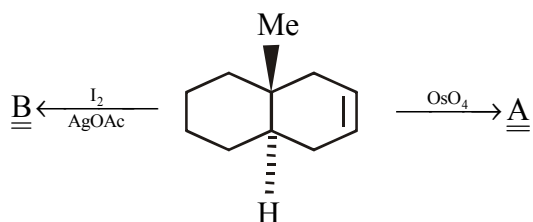
2

ii) Describe in brief, Gabriel phthalimide synthesis of primary amines. How can the phthalimido group be deprotected under neutral conditions? 2+1

iii) Explain the formation of the product in the following reaction: 1
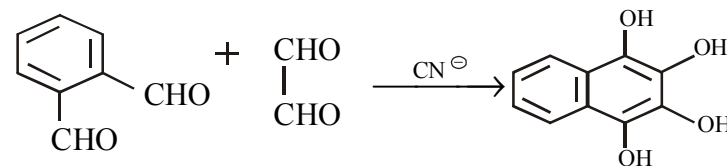
c) i) Draw all possible conformations of *cis*- and *trans*-1, 3-dimethylcyclohexane. Comment on their relative stability. Are these compounds resolvable? 2+1+1

ii) Draw the stereostructure of each of the two enantiomers of 6, 6′-dinitrobiphenyl-2, 2′-dicarboxylic acid and designate R/S-descriptor to each of these.   2

d) i) Comment on the optical activity of the product of mono-decarboxylation of each of two diastereomers of 2, 5-dimethylcyclopentane-1, 1-dicarboxylic acid.   2

ii) Identify $\underline{A}$ and $\underline{B}$ in the following transformations: 2

$$\underline{B} \xleftarrow[\text{AgOAc}]{\text{I}_2} \quad \text{(bicyclic structure with Me and H)} \quad \xrightarrow{\text{OsO}_4} \underline{A}$$

Me

H

iii) Write the major product of the following reaction: 2

NMe$_2$

$$\xrightarrow[\text{ii) H}_3\text{O}^+]{\text{i) Li, NH}_3}$$

CH$_3$

e) i) Identify $\underline{A}$ and $\underline{B}$ in the following transformations: 2

O

$$\xrightarrow{\text{HNO}_3} \underline{A} \xrightarrow{\text{Ac}_2\text{O}} \underline{B}$$
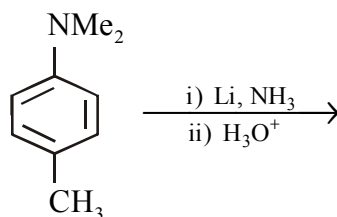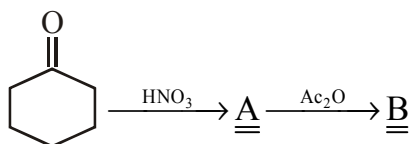
ii) Predict the major product of the following reaction: 1

OH

OH

$$\xrightarrow[\text{ii)} \quad \text{H}_3\text{O}^{\oplus}]{\text{i) POCl}_3 \text{/ DMF}}$$
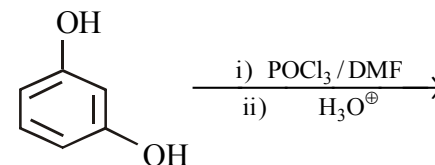
iii) Identify $\underline{C}$ and $\underline{D}$ in the following reaction: 2

$$\text{RCH}_2\text{NH}_2 \xrightarrow[\text{KOH}]{\text{CHCl}_3} \underline{C} \xrightarrow[\text{heat}]{\text{S}} \underline{D}$$
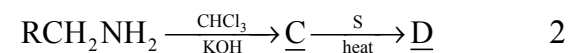
iv) Give one application of dissolving metal reduction.   1

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

a) i) Draw the energy profile diagram for the conformational isomerism in an *ortho*-disubstituted biphenyl derivative and describe the various conformations.

   2+1

ii) Describe three synthetic applications of Grignard reagents.   3

iii) Highlight the importance of Mannich reaction as a three-component reaction in organic synthesis.   2

iv) (bicyclic structure) O

$\underline{A}$

When compound $\underline{\underline{A}}$ is treated with alkaline hydrozen peroxide it undergoes Baeyer-Villiger oxidation to produce a lactone $\underline{\underline{B}}$. Identify $\underline{\underline{B}}$ and show mechanism for its formation. 1+1

b) i) Describe one method for the preparation of diazomethane and outline two of its synthetic applications. 1+2=3

ii) Explain mechanistically the difference in the pattern of coupling of benzenediazonium chloride with aniline and N,N-diethylaniline. 2

iii) Write a note on Reformatskii reaction. 2

iv) Give an example of transfer hydrogenation. 1

v) Write a plausible mechanism for the following transformation: 2
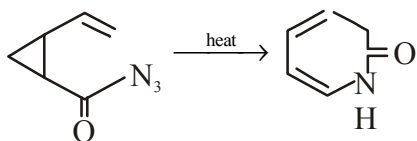
**(General proficiency : $\frac{1}{2}$)**

GROUP-B

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

5. Answer any **three** questions: 1×3=3

a) If a crystal plane makes intercepts in the ratio $2a:b:2c$ on the three axes (a, b, c being the standard intercepts), determine the Miller indices of the plane.

b) Distnguish between number average and weight average molecular weight for polymers.

c) Explain what is meant by $E^0_{Cu^{2+}/Cu} = 0.34\,V$.

d) Define half life of a reaction and write the expression for half life of a 1st order reaction.

6. Answer any **three** questions: 2×3=6

a) For the consecutive reaction $A \rightarrow B \rightarrow C$ draw the plot showing variation of the different components with time.

b) What is the relation between surface tension (γ) and surface excess (Γ). Explain briefly.

c) Distinguish between weight average and number average molecular weight.

d) λ^0 of HCl, NaCl and CH$_3$COONa are 426, 126 and 91 ohm^{-1} cm^2 eq^{-1} respectively at 25°C. Calculate λ^0 of CH$_3$COOH.

e) What is the distance between 111 planes in a simple cubic lattice? [Given unit cell edge length = x].

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

a) i) Discuss the working principle of the quinhydeone electrode.

ii) For the Daniell cell, $E^0_{cell} = 1.10\,V$. Calculate 'K' for the cell reaction

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$
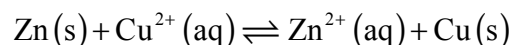
at $25^o C$. 4+2

b) i) A certain reaction is first order 540S after initiation of reaction, 32.5% of the reactant remains. What is the rate constant for this reaction? At what time after initition will 10% remain?

ii) Briefly discuss the isolation method for determination of rate constant.

$1\frac{1}{2}+1\frac{1}{2}+3$

c) Explain briefly the term "transport number" of an ion. In a transport experiment in 1(N) KCl solution, the boundary between KCl and BaCl$_2$ (following) solution was found to sweep through a volume of .15ml in 35 minutes with a current of 0.014 amp. Calculate the transport number of chloride ion. 2+4

d) Define surface excess. Define thermodynamically an expression to show the variation of surface excess of a dilute solution with the concentration of the solution. 1+5

e) The first order reflections from the 100, 110 and 111 planes of a given cubic crystal occurat angles 23.7^o, 34.7^o and 20.4^o respectively. To what type of cubic lattice does the crystal belong? Give an example of a compound that crystallises in this lattice form. 5+1

[Given $\sin 23.7^o = 0.4019$
$\sin 34.7^o = 0.5693$
$\sin 20.4^o = 0.3486$]

8. Answer any **one** question: 10×1=10

a) i) Discuss the principle of determination of molecular weight of a polymer by viscosity method. 4

ii) Discuss unimolecular reactions in the light of Lindemann theory. 6

b) i) For an enzyme catalyzed reaction derive an expression for reaction rate at low catalyst concentration. 4

ii) What is electrophoresis and what is its utility? How is it different from electroosmosis? 3

iii) Define the terms : buffer and buffer capacity. Give an example of a buffer used in the acidic pH region.   1+1+1

(*General Proficiency - $\frac{1}{2}$*)

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