

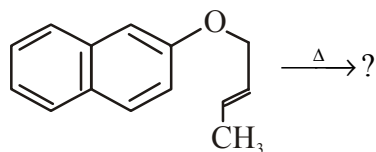
2021
CHEMISTRY
[HONOURS]
Paper : V

Full Marks : 75

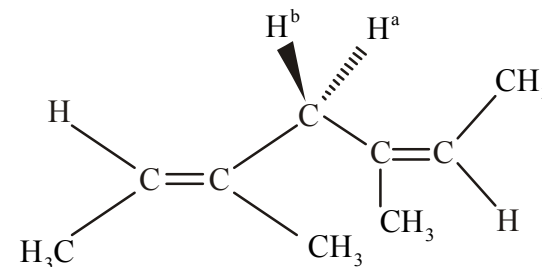
Time : 4 Hours

*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-37 $\frac{1}{2}$)**

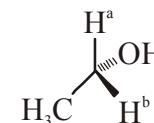
1. Answer any **three** of the following: $1 \times 3 = 3$
- a) Predict the major product of the following reaction:



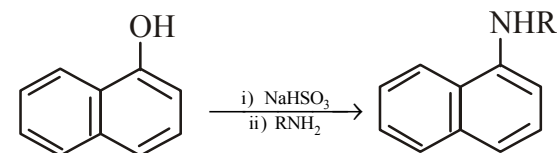
- b) Identify the 'pro-R' and 'pro-S' hydrogen atoms (marked) in the following molecule:



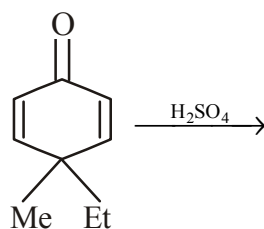
- c) Write the structure of the epoxide obtained from the reaction between (S)-I-bromo-2-methylbutan-2-ol with NaOH.
- d) Identify H^a and H^b in the following compound as 'pro-R' and 'pro-S':



2. Answer any **three** of the following: $2 \times 3 = 6$
- a) Explain the formation of the product in the following transformation:



b) Predict the product with suitable mechanism:



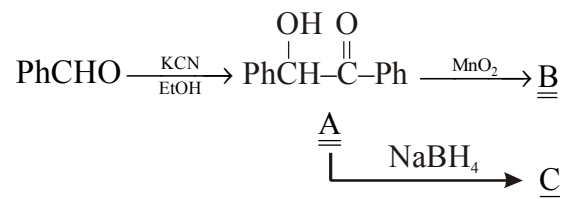
c) Chloral (Cl₃CCHO) is difficult to obtain in the pure form but its hydrate is easily obtained. Why?

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

e) Bromine addition takes place to the Re-Re face of fumaric acid. What will be the absolute configuration of the produced 2,3-dibromoderivative?

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

a) Consider the following sequence of events and the questions:



2(Sc)

[3]

[Turn over]

i) Write a suitable mechanism for the formation of A and also indicate the stereoisomeric forms.

ii) Identify B and write its most stable conformation.

iii) Write the stereo-structures of all possible isomers of C.

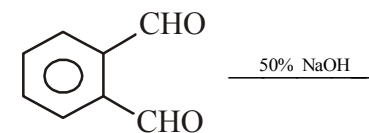
$$2 \frac{1}{2} + 1 \frac{1}{2} + 2 = 6$$

b) i) Write down the mechanism of

hydrolysis of the ester $\text{Me}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^{18}-\text{Bu}^t$ with ordinary water and indicate the distribution of O¹⁸ in the product. 2

ii) What happens when m-bromoanisole is treated with NaNH₂ in liquid ammonia? 1

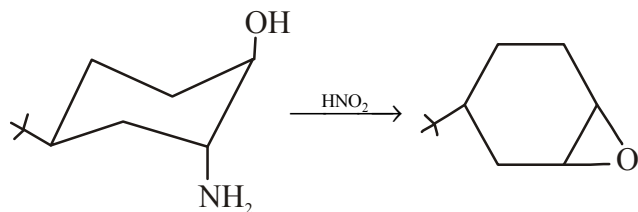
iii) Predict the product of the following reaction: $1 \frac{1}{2}$



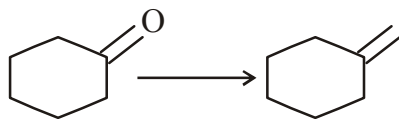
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[4]

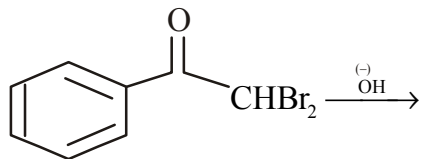
- iv) Explain the outcome of the following reaction: 1 $\frac{1}{2}$



- c) i) PhCHO on treatment with aluminium ethoxide or NaOH solution separately behaves differently. Explain.
 ii) Perform the following transformation with plausible mechanism.



- iii) How would you perform the following conversion?
 $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CH}_2\text{COOH}$
 iv) Write the product with mechanism of the following reaction:



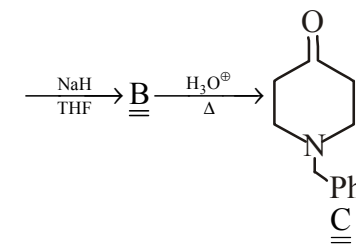
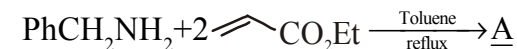
$$1 \frac{1}{2} + 1 \frac{1}{2} + 1 \frac{1}{2} + 1 \frac{1}{2} = 6$$

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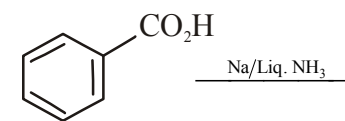
[5]

[Turn over]

- d) i) Identify the intermediates A and B in the following reaction and also explain the formation of C 1+1+1=3



- ii) Salicylic acid on treatment with excess bromine produces 2,4,6-tribromophenol. Explain the outcome. 2
 iii) Predict the product of the following reaction 1



- e) i) What is Bayer's strain theory? Discuss with examples. 3
 ii) Draw stable conformation of *cis*- and *trans*-1,2-cyclohexanediol. Which one will readily form ketal with acetone? 2+1

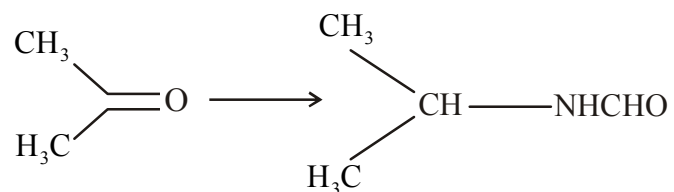
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[6]

4. Answer any **one** of the following: $10 \times 1 = 10$

a) i) How can you prepare the primary amine attached to a tertiary carbon atom?

ii) Carry out the following transformation:



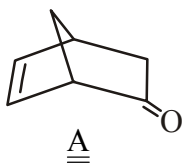
iii) How can you synthesize $\text{PhCOCH}_2\text{CH}_3$ from PhCOCH_3 ?

iv) What happens when isopropyl magnesium bromide is added to di-isopropyl ketone?

v) Phenol does not react with NH_2OH but phloroglucinol does. Explain.

$2+2+2+2=10$

b) i)



When compound A is treated with alkaline hydrogen peroxide it undergoes

Baeyer-Villiger oxidation to produce a lactone B. Identify B and show mechanism for its formation. $1+1$

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

$2+1$

iii) Describe three synthetic applications of Grignard reagents. 3

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

(General proficiency : $\frac{1}{2}$)

GROUP-B

(Marks-37½)

5. Answer any **three** questions of the following:
1×3=3
- a) Why KCl is chosen as salt bridge materials?
 - b) On which factors does the course of coagulation depend?
 - c) What is unit of equivalent conductance?
 - d) For a given reaction rate is independent of concentration; will it go to completion?
 - e) Why electrodes of a conductivity cell are platinised platinum?
6. Answer any **three** questions of the following:
2×3=6
- a) Physisorption must be exothermic– Explain.
 - b) If a very small amount of AlCl₃ is added to gold sol, the gold flocculates, but if a large quantity of AlCl₃ is added to gold sol, there is no flocculation– Explain.
 - c) Why not a voltameter but a potentiometer is used in measuring E.M.F. of a cell?
 - d) A zero order reaction can not be a single-step reaction– Justify.
 - e) In aqueous solution velocity of Li⁺ ion is less than Na⁺, however in organo-aqueous media velocity of Li⁺ is higher than Na⁺. Explain.

2(Sc)

[9]

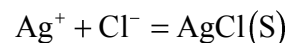
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7. Answer any **three** questions: 6×3=18
- a) i) Explain relaxation effect and electrophoretic effect found in strong electrolyte. 3
 - ii) Discuss the curve obtained by conductometric titration of a weak acid with strong base and a strong acid with a weak base. 3
 - b) i) What is meant by space lattice and unit cell of a crystal? What are Miller indices? 3
 - ii) Aluminium crystallizes with a face centred cubic lattice. The inter-ionic distance (shortest) in a unit cell of Aluminium is 2.86 Å. Calculate the density of Aluminium. (Atomic weight of Al=27). 3
 - c) i) Derive the Nernst equation for measuring the e.m.f. of a cell. 3
 - ii) The e.m.f. of a Weston standard cell is 1.01530 V at 20°C and 1.01807 V at 25°C. Calculate ΔG, ΔH and ΔS for the cell reaction at 25°C. 3

2(Sc)

[10]

- d) i) Discuss the principle behind the osmometric method for the determination of molecular weight of polymers. 3
- ii) Write the B.E.T. equation. Explain the meaning of various terms involved. Under what condition it is converted to Langmuir equation? 3
- e) i) On raising the temperature from 27°C to 37°C, the rate of reaction is doubled. Calculate the activation energy. 3
- ii) Construct cells where the following reactions occur:



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

- a) i) Discuss the primary salt effect in ionic reactions. How the velocity constant of reactions between ions of like charge and unlike charge depend upon the ionic strength? 4
- ii) How will you determine solubility and solubility product of a sparingly soluble salt from EMF measurement? 3

2(Sc)

[11]

[Turn over]

- iii) 10 c.c. of 0.2(N) NaOH is added to 30 c.c. of 0.1(N) CH₃COOH. Calculate the pH of the resulting solution. K_a for CH₃COOH = 1.80×10⁻⁵. 3
- b) i) Derive an expression for the rate constant of second order reaction involving two different reactants with different initial concentration. 4
- ii) Discuss the principle for the determination of transport numbers of ions by moving boundary method. 3
- iii) Half-life of decomposition of a compound was found to be 50 min. When the initial concentration was halved, the half-life becomes 100 min. What is the order of the reaction? 3

(General proficiency : $\frac{1}{2}$)

2(Sc)

[12]