

**2020**  
**CHEMISTRY**  
**[HONOURS]**  
**Paper : V**

Full Marks : 75

Time : 4 Hours

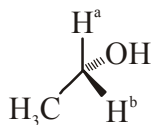
*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.*

**Write the answers to questions of each Group in separate answer script.**

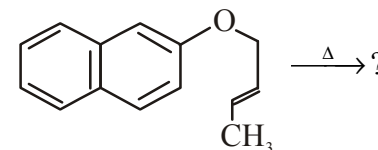
**GROUP-A**

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

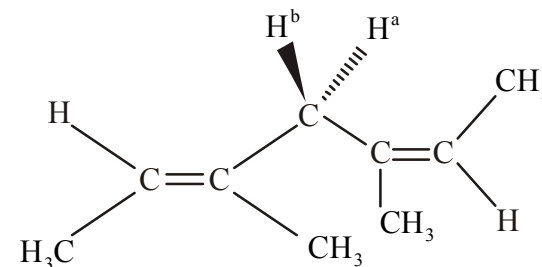
1. Answer any **three** of the following: 1×3=3
- a) Write the structure of the epoxide obtained from the reaction between (S)-I-bromo-2-methylbutan-2-ol with NaOH.
- b) Identify H<sup>a</sup> and H<sup>b</sup> in the following compound as 'pro-R' and 'pro-S':



- c) Predict the major product of the following reaction:

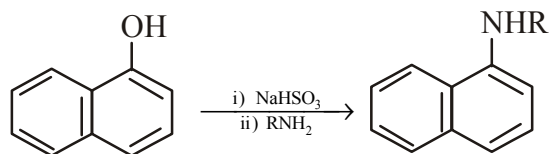


- d) Identify the 'pro-R' and 'pro-S' hydrogen atoms (marked) in the following molecule:

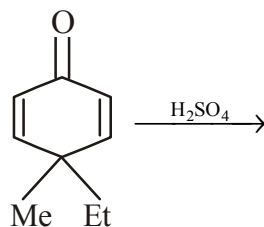


2. Answer any **three** of the following: 2×3=6
- a) Diazotisation of 2-aminophenol produces a heterocyclic compound. Write a possible structure of the product and explain its formation.
- b) Bromine addition takes place to the Re-Re face of fumaric acid. What will be the absolute configuration of the produced 2,3-dibromoderivative?

- c) Explain the formation of the product in the following transformation:



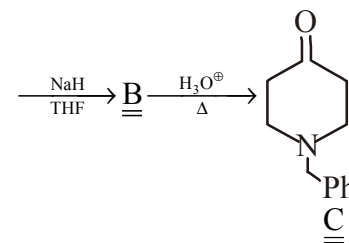
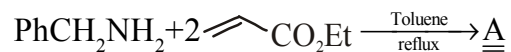
- d) Predict the product with suitable mechanism:



- e) Chloral (Cl<sub>3</sub>CCHO) is difficult to obtain in the pure form but its hydrate is easily obtained. Why?

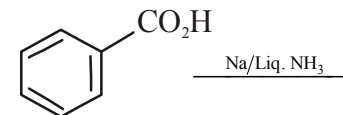
3. Answer any **three** of the following: 6×3=18

- a) 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

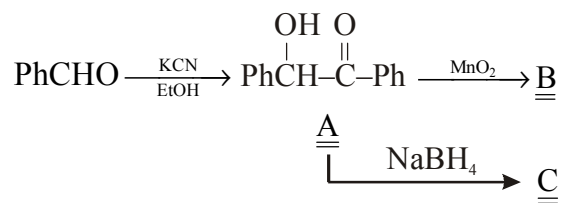
- iii) Predict the product of the following reaction 1



- b) 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

- c) Consider the following sequence of events and the questions:



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.

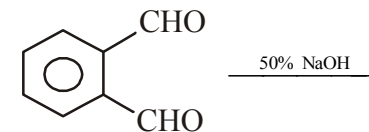
$$2 \frac{1}{2} + 1 \frac{1}{2} + 2 = 6$$

d) i) Write down the mechanism of

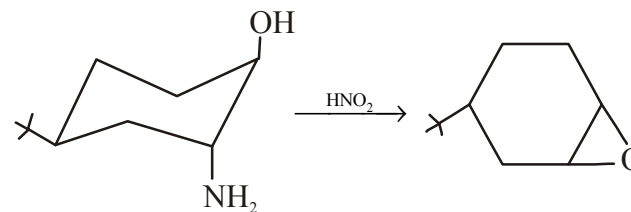
hydrolysis of the ester  $\text{Me}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^{18}-\text{Bu}^t$  with ordinary water and indicate the distribution of  $\text{O}^{18}$  in the product. 2

ii) What happens when m-bromoanisole is treated with  $\text{NaNH}_2$  in liquid ammonia? 1

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

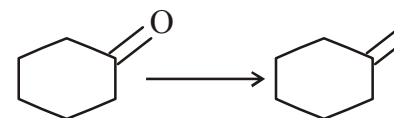


iv) Explain the outcome of the following reaction:  $1 \frac{1}{2}$

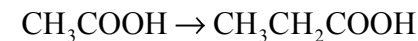


e) i) PhCHO on treatment with aluminium ethoxide or NaOH solution separately behaves differently. Explain.

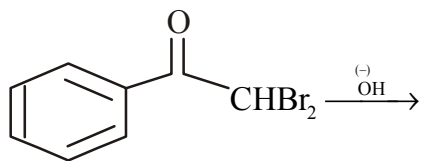
ii) Perform the following transformation with plausible mechanism.



iii) How would you perform the following conversion?



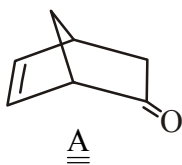
iv) Write the product with mechanism of the following reaction:



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

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

a) 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.

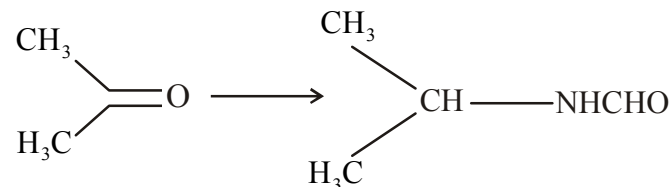
$2+1$

iii) Describe three synthetic applications of Grignard reagents.  $3$

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

b) 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  $\text{PhCOCH}_3$ ?

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

v) Phenol does not react with  $\text{NH}_2\text{OH}$  but phloroglucinol does. Explain.

$2+2+2+2=10$

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

**GROUP-B**  
**(Marks-37½)**

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

7. Answer any **three** questions: 6×3=18
- a) 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
  - b) 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:  
$$\text{Ag}^+ + \text{Cl}^- = \text{AgCl(S)}$$
$$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O} \quad 3$$
  - c) 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

- d) 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  $2.86 \text{ \AA}$ . Calculate the density of Aluminium. (Atomic weight of Al=27). 3
- e) 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  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the cell reaction at 25°C. 3

8. Answer any **one** question:  $10 \times 1 = 10$

- a) 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
- b) 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
- iii) 10 c.c. of 0.2(N) NaOH is added to 30 c.c. of 0.1(N)  $\text{CH}_3\text{COOH}$ . Calculate the pH of the resulting solution.  $K_a$  for  $\text{CH}_3\text{COOH} = 1.80 \times 10^{-5}$ . 3

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