T(I)-Chemistry – H-1A

# 2021

# **CHEMISTRY**—HONOURS

# **First Paper**

# (Group - A)

## Full Marks : 50

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

#### CHT-12a

#### Unit - I

Answer any three questions.

1. (a) Give R / S configurational descriptor of the following compounds. Mention the priority of the ligands around the chiral centre.



- (b) Write the Fischer projection formula of *meso*-tartaric acid and represent it in Newman and Sawhorse projection formula.
  3+2
- 2. (a) Identify H<sub>A</sub> and H<sub>B</sub> in each of the following compounds as homotopic, enantiotopic or diastereotopic and explain.



- (b) Contrary to ClCH<sub>2</sub> CH<sub>2</sub>Cl, in FCH<sub>2</sub> CH<sub>2</sub>F gauche conformer is the more stable conformer. Explain the fact. 3+2
- 3. (a) Draw the energy profile diagram for rotation around C C bond of  $HO CH_2 CH_2 OH$  with proper labelling.
  - (b) Active phenyl sec-butyl ketone undergoes easy racemization in aqueous sodium hydroxide solution— Explain. 3+2

## **Please Turn Over**

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- **4.** (a) All chiral centres are stereogenic centres but all stereogenic centres are not chiral centres.— Explain.
  - (b) Give example/write down the structure of the following :
    - (i) A chiral molecule having  $C_2$  axis.
    - (ii) 2R, 3r\*, 4R 1, 2, 3, 4, 5-penta bromopentane.
- (a) Specific rotation of an enantiomeric mixture is (+)20° and that of pure laevorotatory enantiomer is (-)60°. Find out the optical purity of the sample and also the percentage composition of the enantiomers.
  - (b) Indicate symmetry elements present in (i)  $\stackrel{\bigcirc}{CH}_3$  (ii)  $H C \equiv C H$  3+2

### Unit - II

#### Answer any two questions.

- 6. (a) Draw the molecular orbital pictures of (i) allene and (ii)  $CH_3 CH = CH CN$  (*trans*), starting the state of hybridisation of each concerned atom.
  - (b) Compare the dipole moment of the following compounds.



3+2



7. (a) Classify the following compounds as aromatic, antiaromatic or homoaromatic and Justify.



(b) Predict the product, if any and explain.



- 8. (a) "Heat of combustion and not heat of hydrogenation is more suitable to compare the stabilities of 1butene, 2-butene and isobutene".— Justify with the help of an energy diagram.

(3)

(b) Write down all  $\pi$ -MOs for 1, 3-butadiene and ethylene. Compare their relative energy of HOMOs. 3+2

# CHT-12b

## Unit - I

#### Answer any three questions.

9. (a) Arrange the following compounds in increasing order of acid strength and explain.



(b) Which one is more stable in each following pairs and why?



10. (a) Arrange the following in the increasing order of enol content. Give reasons.



(ii) MeCOCH<sub>2</sub>COMe and MeCOCH<sub>2</sub>COOEt

(b) Explain the stability of an isopropyl cation with respect to ethyl cation.

3+2

**Please Turn Over** 

3+2

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11. (a) Compare the rate of decomposition of the following azo compounds. Suggest a reason for this.



- (ii)  $Me_3C N = N CMe_3$ ,
- (iii)  $MeCH_2 N = N CH_2Me$ .
- (b) Cite a suitable example to show intramolecular nature of rearrangement.

**12.** (a) 
$$CH_3COCH_3 + Br_2 \xrightarrow[K_H]{OH} Br - CH_2COCH_3$$

$$CD_{3}COCD_{3} + Br_{2} \xrightarrow[K_{D}]{\bigcirc} BrCD_{2} - \overset{O}{\overset{\parallel}{C}} - CD_{3},$$
  
Given  $\overset{K_{H}}{/}_{K_{D}} \approx 7.0$ .

Explain the above reaction indicating the rate determining step.

 (b) Which one of the following is more basic and why?

 ethylamine and guanidine.

 3+2

3+2

- 13. (a) 'Intramolecular reactions are thermodynamically more favourable than intermolecular reaction.'
   Comment with proper illustration.
  - (b) What are electrophilic and nucleophilic carbenes? Give one example of each. 3+2

#### Unit - II

#### Answer any two questions.

14. (a) Identify [A], [B] and [C] in the following reaction sequence :

$$Me \xrightarrow{Pn} OH \xrightarrow{Me \longrightarrow SO_2Cl} [A] \xrightarrow{CH_3COONa} [B] \xrightarrow{\bigcirc} OH [C]$$

(b) The reaction rate of  $CH_3I$  with  $N_3^{\ominus}$  at 0°C is increased  $4.5 \times 10^4$  fold on change of solvent from methanol to DMF. 3+2

(4)

- 15. (a) Compare the nucleophilicity and basicity order of EtO and <sup>t</sup>BuO with proper justification.
  - (b) Explain the following observation (where \* represents radioactive carbon) :



16. (a) Explain the following transformation with mechanism.



 (b) Compare the rate of hydrolysis of the following compounds with proper reason. MeCOCl, MeCONH<sub>2</sub>, MeCOOEt

3+2

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