U.G. 1st Semester Examination - 2021

CHEMISTRY

[HONOURS]

Course Code : CHEM-H-CC-T-02

Full Marks : 40 Time : $2\frac{1}{2}$ 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.

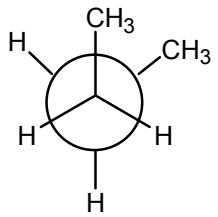
1. Answer any **five** questions: 2×5=10

a) State which of the four types of bonds shown below has the highest and which one the lowest bond energy. Give reasons.

C═O, C=C, C≡N, C—I

b) Why $C_2 - C_3$ bond distance in propene is shorter than C–C bond in propane?

c) The following conformer of butane is chiral, then why is butane optically inactive?



d) Cyclooctatetraene becomes planar on addition of two electrons to it– Explain.

e) Compare the dipole moments of each of the following pairs with reasons:

i) EtCN and EtNC

ii) 1,2- dibromo ethane and 1,2- dihydroxy ethane

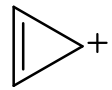
f) Boiling point of *n*-butanol is higher than that of *tert*-butanol. Give reason.

g) Draw the Fischer projection formula of each of the following:

i) 2R, 3R-2, 3-dihydroxy-3-methyl-pentanoic acid

ii) S-2, 3-Dihydroxypropanal

h) Arrange the following in the order of increasing stability:

$CH_3\overset{+}{C}HCH_3$ $CH_3\overset{+}{C}=CH_2$ $CH_2=CH\overset{+}{C}H_2$ 

2. Answer any **two** questions: 5×2=10

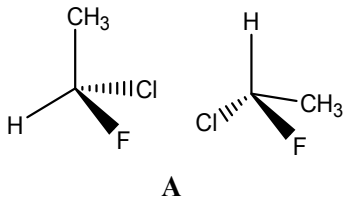
a) i) Why cyclopropenone is a stable compound while cyclopentadienone has not been prepared?

ii) Give one example for each of the following:

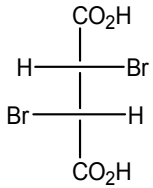
A) An optically active compound possessing a C_2 axis.

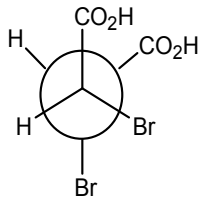
B) An optically inactive compound possessing a twofold alternating axis of symmetry. 2+3=5

b) i) Identify whether the following pairs of compounds represent homomers, enantiomers or diastereoisomers:

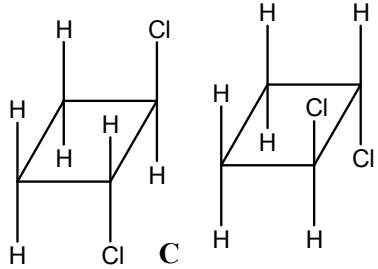


A





B



C

ii) A solution of 22 mg of an optically active compound in 1 cc methanol showed an optical rotation of -4.4^{o} in a 10 cm long polarimeter cell. What is the specific rotation of the compound? 3+2=5

c) i) The optical rotation of lactic acid disappears on treatment with a base. – Explain.

ii) The structure of both CH_3 radical and cation is similar but those of CF_3 radical and cation are different.– Explain with reason. 2+3=5

d) i) What is resonance energy? Calculate resonance energy of 1,3- butadiene, if its heat of hydrogenation is 57 kcal / mole and that of 1-butene is 30.3 kcal/mole.

ii) How carbene is formed? What is the shape, bond angle and state of hybridization of triplet carbene? 3+2=5

3. Answer any **two** questions: 10×2=20

a) i) Define the terms 'stereogenic centre' and 'chiral centre'. Are centres of stereogenicity always centres of chirality? Explain with suitable examples.

ii) α–Hydrogen of (R)-α-chloropropionic acid is substituted by bromine with retention of configuration. Write the structure of the product.

iii) How would you show that all hydrogen atoms of cyclopentadienyl anion are equivalent?

iv) Chiral acetic acid is a compound in which two hydrogen atoms of methyl group are replaced by deuterium (D) and tritium (T). Write down the three-dimensional formulae for

(R)- and (S)- HDTC-C(=O)-OH

4+2+2+2=10

b) i) Distinguish the terms with suitable examples in each of the following cases:

A) Asymmetric and dissymmetric compounds

B) Racemic modification and racemisation

ii) Benzyl chloride gives a precipitate with alcoholic silver nitrate solution but none of o-, m-, p-tolyl chlorides does not – explain.

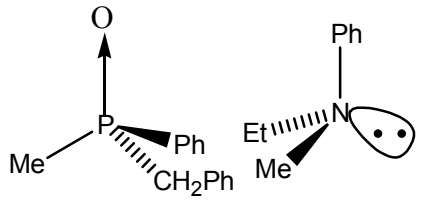
iii) Why the dipole moment of chlorobenzene is greater than fluorobenzene even though fluorine is more electronegative than chlorine?

iv) How does the inductive effect differ from the field effect? 4+2+2+2=10

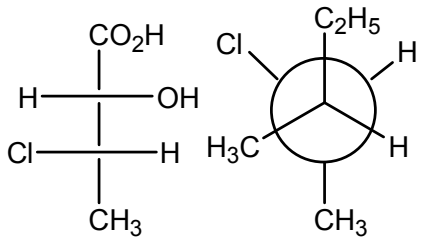
c) i) Draw the π molecular orbitals of HOMO and LUMO of (2E,4Z,6E)-octa-2,4,6-triene in the ground state.

ii) How heat of hydrogenation is related to the stabilities of alkenes? Compare the stabilities of 1-pentene, *cis*- and *trans*-2- pentene and 2-methyl-2-butene in terms of heats of hydrogenations.

iii) Explain whether the following compounds are resolvable or not. Give R, S- descriptors wherever possible:



iv) Reproduce the Fischer structure **A** as a staggered Sawhorse and the Newman structure **B** as a Fischer structure:

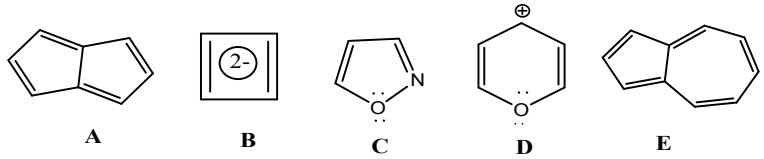


A **B**

2+3+3+2=10

d) i) Draw the Fischer projection formulas of all dichlorinated compounds resulting from free radical chlorination of (R) -2-methyl-3-chlorobutane and comment on their optical activity with proper stereochemical assignments.

ii) State Huckel's rule for aromaticity. By this rule which of the following species should be aromatic?



A **B** **C** **D** **E**

iii) Butadiene is more reactive than ethylene towards nucleophilic and electrophilic addition reactions. Explain in terms of molecular orbital theory.

(3+2)+(1+2)+2=10

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