

U.G. 1st Semester Examination - 2022

CHEMISTRY

[HONOURS]

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

Full Marks : 40

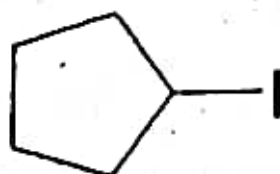
Time : 2½ Hours

*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

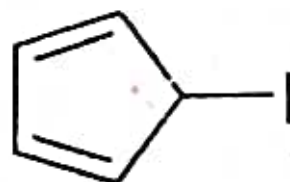
a) Arrange the following bonds in order of decreasing bond energy with proper reason:

C-O, C-S, C-Br, C-N

b) The compound (I) undergoes solvolysis when treated with silver perchlorate in propionic acid, but compound (II) does not. Explain.



(I)



(II)

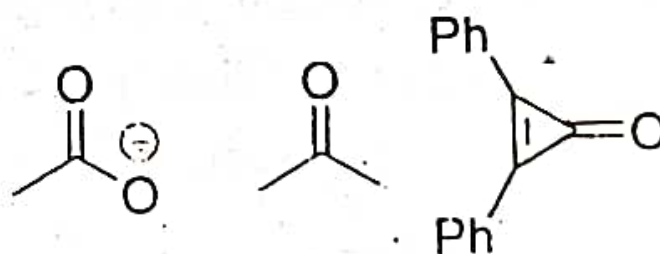
c) Draw the orbital picture of HOMO of allyl cation and anion.

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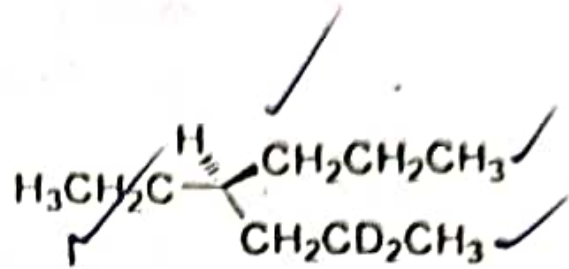
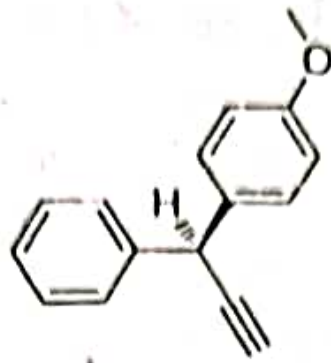
- d) (S)-2-Bromobutane undergoes racemization when treated with chlorine in the presence of sunlight. Explain.
- e) Which one between HS^- and HO^- is stronger nucleophile in water and why?
- f) Identify and write down the steps for generation of the reactive intermediate when chloroform is heated with an alkali.
- g) C-C bond distance in CCl_3CHO is 1.54\AA but in CH_3CHO is 1.5\AA — explain.
- h) Indicate the symmetry elements present in methylene dibromide and acetylene.

2. Answer any two questions: 5×2=10

- a) i) Compare C=O bond distance of the following molecules:



- ii) Assign the following compounds with R/S descriptor:



$$2+3=5$$

b) i) What are proton sponges? Explain with suitable example.

ii) Dextrorotatory EtCH(Me)COPh loses optical activity during deuteration with D₂O/NaOD. Explain.

iii) Give an example of captidative radical.

$$2+2+1=5$$

c) i) Boiling point of neopentane is lower than that of n-pentane but reverse is true for their melting points. Explain this observation.

ii) How nitrene can be generated from nitro compounds? Give one synthetic use of nitrene.

$$2+(2+1)=5$$

d) .i) Write structural formula of the most stable free radical having the formula C₅H₁₁. Justify your answer.

- ii) The dipole moment of butan-2,3-dione is very small, whereas that of cyclohex-3,5-diene-1,2-dione is very large.

$$3+2=5$$

3. Answer any two questions:

$$10 \times 2 = 20$$

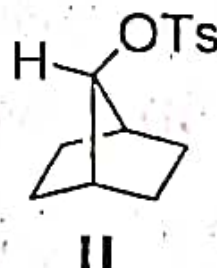
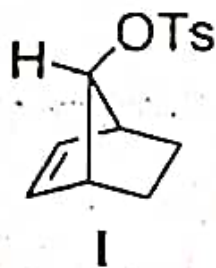
a) Explain the following observations:

i) Mesitoic acid does not undergo esterification under normal acid-catalyzed conditions.

ii) Ethyl methyl ether reacts with HI to give ethanol and methyl iodide, whereas *t*-butyl methyl ether is cleaved by HI to give methanol and *t*-butyl iodide.

iii) MeCl has higher dipole moment than MeF, though F is more electronegative than Cl.

iv) Compound I undergoes acetolysis at a rate 10^{11} times faster than compound II with retention of configuration.



v) (+)Ph CH(OH)CH₃ loses its optical activity when treated with dilute HCl.

$$2 \times 5 = 10$$

b) i) What do you mean by "Optical Purity"? Pure (-)-enantiomer of an optically active compound A has a specific rotation $[\alpha]^{20^\circ} = (-) - 51.3^\circ$. What would be the optical purity of a sample A, which shows a specific rotation of $(-) - 35.9^\circ$? How much of each enantiomer is present in the enantiomeric mixture?

ii) Give an example of 'internally compensated' optically inactive molecule.

iii) Draw the π molecular orbitals of 1,3-butadiene showing the nodes. Mention HOMO and LUMO in the ground state and excited state.

$$(2+3)+1+4=10$$

i) Draw all the possible stereoisomers of $\text{CH}_3\text{CH}(\text{Br})\text{CH}=\text{CHBr}$. Find out stereochemical relationship among them.

- ii) How does an asymmetric centre differ from a pseudo asymmetric centre?
- iii) $-\text{COOH}$ has $-I$ effect but $-\text{COO}^-$ has $+I$ effect— justify the statement.
- iv) Give example/write down the structures of the following:

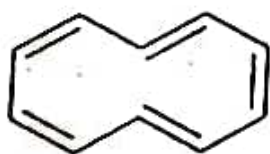
I) A chiral molecule with a C_2 axis $\text{CH}_2=\text{CH}_2$

II) $2R, 3R^*, 4S$ -1,2,3,4,5- pentachloropentane

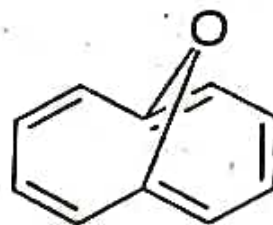
III) $2S, 3R$ -3-Amino butane-2-ol

$$3+2+2+3=10$$

- d) j) Of the following two structures which one is more stable? Give reason.

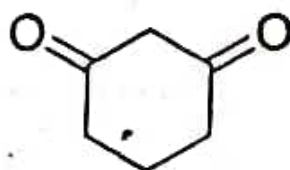


I



II

- ii) Compound I is readily soluble in alkali but compound II is not. Explain.



I



II

- iii) Discuss the solvation effect on nucleophilicity order of the halide ions.
- iv) When *cis*-2-butene and *trans*-2-butene separately react with CH_2I_2 in the presence of Zn-Cu couple, both *cis*- and *trans*- products are obtained. Predict the products with reason. $2+2+3+3=10$
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