2020

CHEMISTRY (Honours)

Paper : CEMH-DC-T1

(Organic Chemistry)

(CBCS)

Full Marks : 25 Time : Two Hours

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

1. Answer any *five* questions from the following : 1×5=5

(a) The correct order of stability of the following free radicals is —

(i) $\dot{C}H_3 > (CH_3)_2\dot{C}H > (CH_3)_2\dot{C}$

(ii) $(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > \dot{C}H_3$

(iii) $\dot{C}H_3 > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H$

(iv) $(CH_3)_3\dot{C} > \dot{C}H_3 > (CH_3)_2\dot{C}H$

(b) Difference between the number of stereoisomers of 2-bromo-3-chloorobutane and 2, 3-dibromobutane is —

(i) 1

(ii) 2

(iii) 0

(iv) None of the above

(c) For R and S designations of 1, 2-dichloro 3-methyl butane, priority sequence of the ligands is

(i) $(CH_3)_2CH > CH_2Cl > Cl > H$

(ii) $Cl > CH_2Cl > (CH_3)_2CH > H$

(iii) $Cl > (CH_3)_2CH > CH_2Cl > H$

(iv) $CH_2Cl > Cl > (CH_3)_2CH > H$

(d) The one among the compounds given below, with highest dipole moment is —

(i) naphthalene

(ii) phenanthrene

(iii) anthracene

(iv) azulene

(e) The positive carbon in phenyl carbocation

(i) Is sp^2 hybridised and has a vacant p orbital

(ii) Is sp^2 hybridised and has a vacant sp^2 orbital

(iii) Is sp hybridised and has a vacant sp orbital

(iv) Is sp hybridised and has a vacant p orbital

(f) Ground state LUMO of 1, 3, 5-hexatriene has

(i) One vertical node

(ii) Two vertical nodes

(iii) Zero vertical nodes

(iv) Three vertical nodes

(g) Which one of the following molecule belongs to C_{3v} point group?

(i) NH_3

(ii) HCN

(iii) H_2O

(iv) CH_4

(h) Between nucleophilicity and basicity which one is more susceptible to steric factors?

(i) Nucleophilicity

(ii) Basicity

(iii) Both nucleophilicity and basicity

(iv) Neither nucleophilicity nor basicity

2. Answer any *four* questions : 2×4=8

(a) Dipole moment of ethyl chloride is 2.05 D while that of vinyl chloride is 1.44 D. Explain.

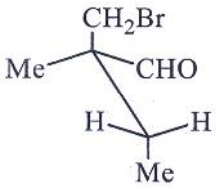
(b) *n*-Butyl alcohol has higher boiling point than *iso*-butyl alcohol. Explain.

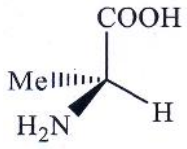
(c) Draw the orbital picture of $CH_2 = CHCN$ indicating the state of hybridization of all the carbon and nitrogen atoms.

(d) The concentration of compound *X* dissolved in solvent *Y* is 7.55 g per 100mL of solution. A portion of this solution in a 5-cm polarimeter tube causes an observed rotation of –1.35°. Calculate the specific rotation of compound *X*.

(e) *S*-1-phenyl ethyl chloride undergoes extensive racemisation when distilled. Offer an explanation.

(f) Designate the chiral centres of the following compounds as R-/S- notation by mentioning the priority order of ligands attached to the chiral centres.

(i) 

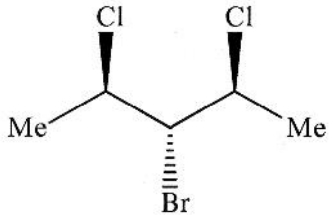
(ii) 

(g) Calculate double bond equivalent (DBE) for a compound having molecular formula C_3H_3N and suggest a structure for the compound.

(h) Tub-shaped cyclooctatetraene becomes planar when two electrons are added to it. Why?

3. Answer any *two* questions : 6×2=12

(a) (i) Indicate asymmetric and pseudo asymmetric centres in the following molecule. Is the molecule chiral? Explain. 2½



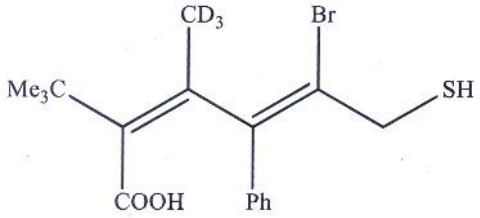
(ii) Dimethoxy carbene fails to react with isobutene. Explain. 1½

(iii) Compare the basicity and nucleophilicity of EtS^- and EtO^- with reasons. 2

(b) (i) Between *tert*-butyl radical and nitro methyl radical which one is nucleophilic and which one is electrophilic? Explain their electrophilicity and nucleophilicity in terms of elementary molecular orbital theory. 3

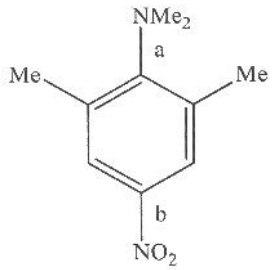
(ii) *F-C-F*, *F-C-H* and *H-C-H* angles in CH_2F_2 are 108°, 109.25° and 112° respectively. Explain. 3

(c) (i) Find out E/Z configurational descriptors for the following molecule. 2



(ii) *C-O* Bond is weaker than *C-C* bond but *C=O* bond is stronger than *C=C* bond. Explain. 2

(iii) Which *C-N* bond between *a* and *b* in the following molecule is longer? Explain your answer. 2



(d) (i) Between heat of hydrogenation and heat of combustion which is more reliable for comparison of stability of isomeric alkenes? Justify your choice. 2

(ii) Cyclopentadiene reacts with a base faster than cyclopropene. Explain. 2

(iii) A stereogenic centre need not be a centre of chirality. Explain with suitable examples. 2
