

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

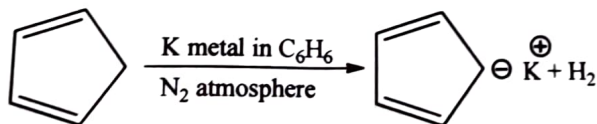
I. Answer any five questions.

2×5=10

- (a) BF_3 and NH_3 have same general formula AX_3 but they greatly differ in their dipole moments — why?
- (b) Calculate the specific rotation of the mixture of 3g of (+) form and 9g of (–) form of an optically active compound with the specific rotation of pure form being $+20^\circ$.
- (c) Between the two resonating forms of acyl carbocation shown below, which one is more stable and why? $\text{—C}^{\oplus}=\text{O} \longleftrightarrow \text{—C}\equiv\text{O}^{\oplus}$
- (d) Draw the orbital picture of methyl carbocation.
- (e) Which of the following compounds contain stereogenic centre and why?



- (f) By virtue of which physical property can you explain the evolution of hydrogen gas from cyclopentadiene as shown in the following reaction?



- (g) Arrange following free radicals according to the order of increasing stability:



- (h) Why the melting point of maleic acid is almost double as of fumaric acid?

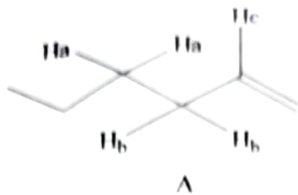
5×2=10

Answer any two questions:

- (a) (i) Between trifluoroacetic acid (CF_3COOH) and trichloroacetic acid (CCl_3COOH), which one have appreciably low boiling point and why?

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- (ii) During a free radical substitution of the following compound (A) by bromine radical which of the marked hydrogens will be preferably attacked? Write down the structures of the products. 2+3

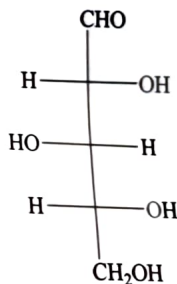
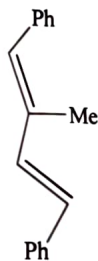
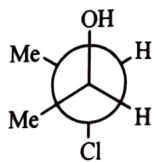
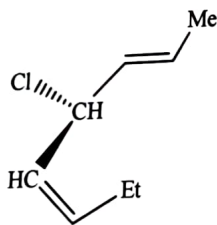


- (b) (i) Give an example of a nucleophile whose nucleophilicity is high despite its low basicity. Give reasons for such behaviour. 2+2+1
- (ii) Azulene, being a hydrocarbon have appreciably high dipole moment — explain.
- (iii) Draw the structure of the smallest aromatic compound. 2+3
- (c) (i) Cite two differences between hyper conjugation and resonance. 3+2
- (ii) How do bond angles and bond lengths vary with hybridization of the central carbon atom in an organic molecule? Explain with examples. 2+3
- (d) (i) How can you resolve (\pm) mandelic acid (PhCHOHCOOH)? 3+2
- (ii) Benzylic carbocations and carbanions are equally stable — explain. 3+2

3. Answer any two questions:

10×2=20

- (a) (i) Why [10] annulene is non-aromatic even though it contains Hückel number of electrons?
- (ii) Provide *R,S* or *E,Z* descriptor(s) for the following compounds wherever applicable (any three):

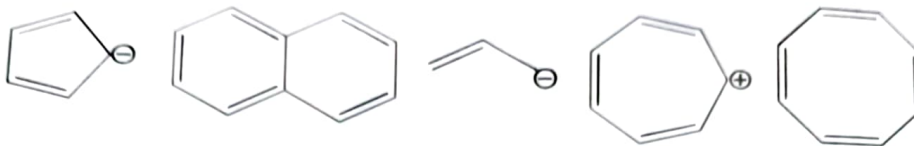


- (iii) What is bond energy? For which type of molecules 'bond energy' and 'bond dissociation energy' have same numerical value?
- (iv) Draw a clean labelled orbital diagram of allene and also mention the hybridization state of each carbon atom present in it. 2+3+2+3

- (b) (i) What do you mean by the term 'isovalent hyperconjugation'? Give one example.
- (ii) Give an example of 'internally compensated optically inactive' compound and draw its structure in Fischer projection.
- (iii) What is known as symmetry number? Find out the symmetry number of benzene. To which point group does the benzene molecule belongs?

(iv) Which type of carbene adds to *trans*-2-butene in stereospecific manner? Write the structure of the product formed.
2+2+(1+2+1)+(1+1)

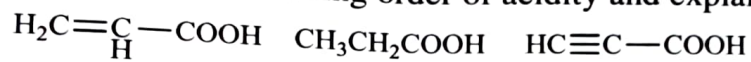
(c) (i) Mark the following species as aromatic, anti-aromatic or non-aromatic. (any four):



(ii) Calculate the double bond equivalent of the organic molecules having molecular formula $C_8H_{10}O_2$ and C_5H_5N respectively.

(iii) Calculate the formal charges of each atom present in CH_3O^\ominus and CH_3^\oplus ions.

(iv) Arrange the following in ascending order of acidity and explain:



(v) Which one of the following is more basic?



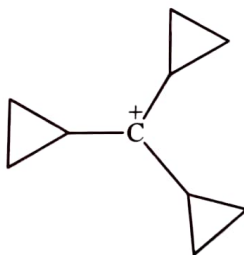
2+2+2+3+1

(d) (i) Cite one difference between asymmetric and dissymmetric molecule.

(ii) Draw the HOMO(s) of cyclopentadienyl anion and allyl cation.

(iii) Compare inductive effect and field effect with suitable examples.

(iv) Explain the unusual stability of the following carbocationic species:



(v) Draw a structure of organic molecule with pseudo-asymmetry in Fischer projection. Identify the stereogenic, chirotopic centres present in it. Also give its *R,S* nomenclature.
1+2+2+2+3