

2023

CHEMISTRY — HONOURS

Paper : CC-3

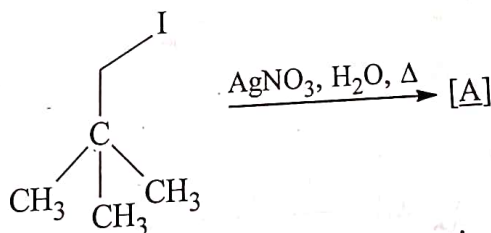
(Organic Chemistry - 2)

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.*Answer **question no. 1** and **any eight** questions from the rest.1. Answer **any ten** questions :

1×10

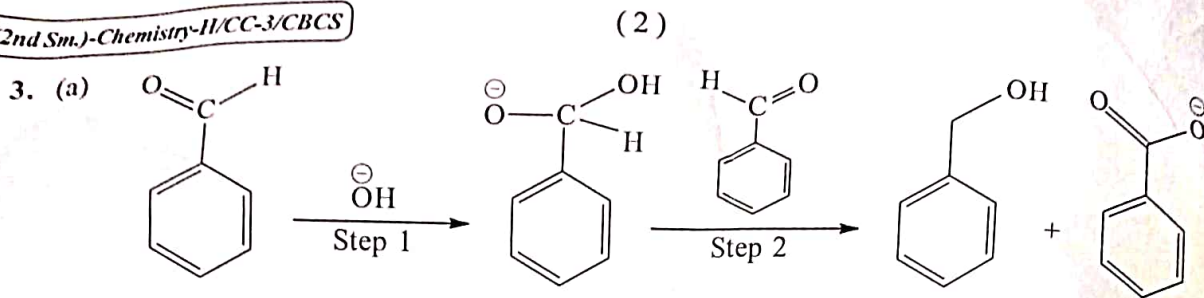
- (a) Draw the staggered conformation of *erythro*-3-aminopentan-2-ol.
- (b) 1,2-cyclopentadione exists almost exclusively in the enol form. Explain.
- (c) Give an example of ambident nucleophile.
- (d) Draw the anti-conformation of butanoic acid when rotated through C₂-C₃ bond.
- (e) Give an example of ring-chain tautomerism.
- (f) What type of reaction is halogenation of alkanes?
- (g) Represent but-2-ene by its *Re-Si* face.
- (h) Draw the tautomeric form of (CH₃)₂CH - N = O.
- (i) Which reaction S_N1 or S_N2 is favoured in α-halocarbonyl compounds?
- (j) Give a mathematical relationship between standard free energy of a reaction with the equilibrium constant.
- (k) What factors favour TCP?
- (l) Arrange the following anions in order of increasing nucleophilicity : R₂N[⊖], R₃C[⊖], F[⊖], RO[⊖].
- (m) Give chemical structure of a proton sponge.
2. (a) Draw the structure of (*R*)-2,2'-dichloro-6,6'-dinitrobiphenyl system. Comment on the chirality of 2,2',6,6'-tetra-bromobiphenyl.



Draw the structure of [A] and show mechanism of its formation.

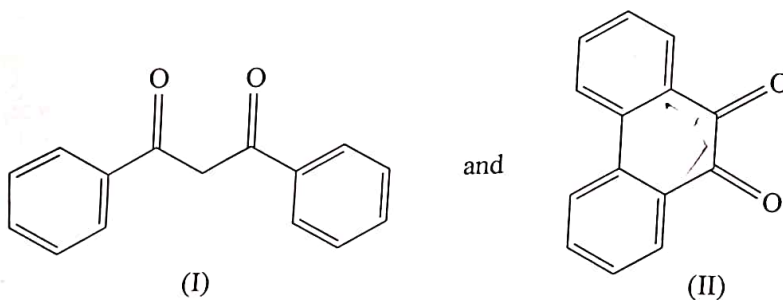
3+2

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Information : The above reaction shows PKIE.

- What is meant by PKIE?
 - How is PKIE measured?
 - From the above information, indicate r.d.s of the above reaction.
- (b) Comment on the relative enol content of



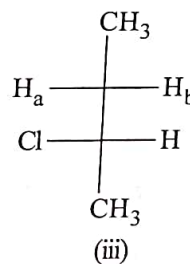
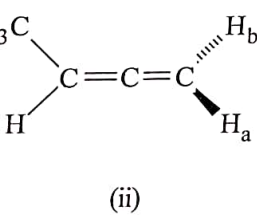
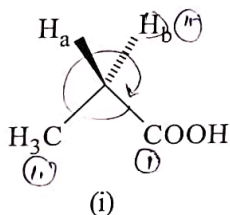
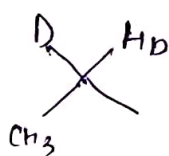
3+2

4. (a) 2,4,6-trinitro-N,N-dimethylaniline is 40,000 times stronger base than 2,4,6-trinitroaniline. Explain.

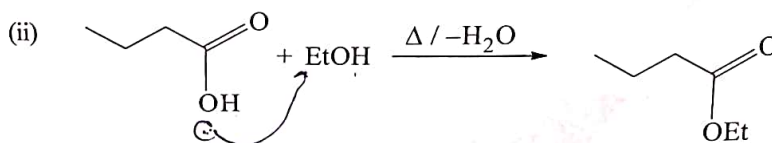
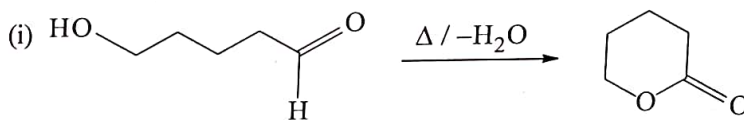
(b) The torsional barriers in fluoroethane and iodoethane are remarkably similar (3.3–3.5 kcal mol⁻¹). Why?

3+2

5. (a) Pick out the pro-S hydrogen in the given molecules.



(b) Which of the following two reactions will have higher equilibrium constant and why?

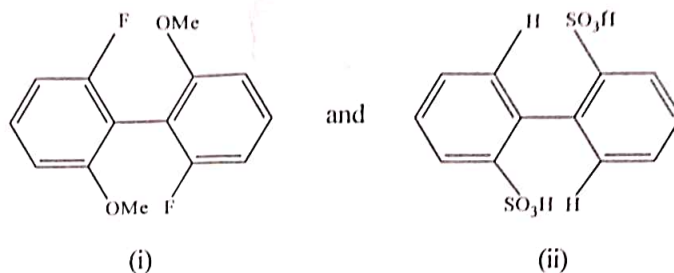


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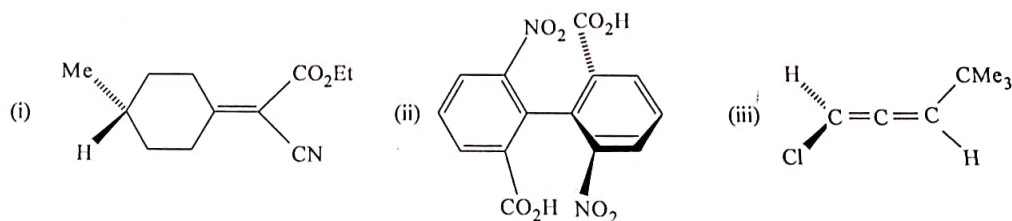
(3)

Z(2nd Sm.)-Chemistry-II/CC-3/CBCS

6. (a) State the criteria for a chiral biphenyl system to be resolvable. Which of the following molecules is resolvable and why?



- (b) Name one (i) polar protic solvent, (ii) polar aprotic solvent. 3+2
7. (a) Write down the products obtained when butane-1,3-diene is subjected to bromination at (i) low temperature and (ii) high temperature. Draw the corresponding energy profile diagram. 3+2
- (b) Which one is a better nucleophile in acetone— Br^\ominus or I^\ominus ? Explain. 3+2
8. (a) Only one of the two diastereoisomers of stilbene dichloride $[\text{PhCH}(\text{Cl})-\text{CH}(\text{Cl})\text{Ph}]$ undergoes dehydrohalogenation with pyridine at 200°C . Identify the diastereoisomer. Explain why the other does not undergo such elimination. 3+2
- (b) With respect to chlorination of alkane, fill in the blanks shown below :
- (i) The transition state closely resembles to _____ (reactant / intermediate)
- (ii) Transition state appears _____ (earlier / later) in the reaction. 3+2
9. (a) Compare $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$ between fumaric and maleic acids. 3+2
- (b) Give an application of nucleophilic catalysis in organic reactions. 3+2
10. (a) Comment on the optical properties of the product(s) in the following reaction ;
- threo*-3-phenyl-2-butyl tosylate $\xrightarrow{\text{acetic acid}}$
- (b) Explain the fact that *o*-hydroxybenzoic acid is more acidic compared to *o*-methoxybenzoic acid. 3+2
11. (a) Designate *R/S* in the following compounds showing the priority of the ligands.



- (b) If bromine is added to the *Re* - *Re* face of fumaric acid, what will be the absolute configurations of the chiral centres formed? 3+2

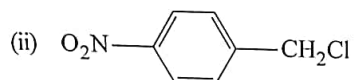
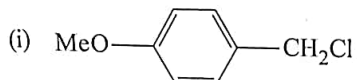
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12. (a) Draw the energy profile diagram arising out of rotation around C – C bond in ethylene glycol. Label maxima and minima with appropriate conformation.

(b) Draw the preferred conformer of 1-bromopropane with appropriate reason. 3+2

13. (a) Neopentyl chloride cannot be prepared from neopentyl alcohol. Explain the observation.

(b) Which mechanism, S_N1 or S_N2 is favourable for the following compounds? Explain.



3+2

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CHEMISTRY — HONOURS

Paper : CC-4

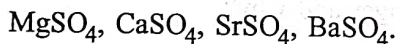
(Inorganic Chemistry - 2)

Full Marks : 50

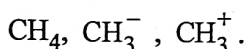
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1×10

(a) Arrange the following in order of increasing thermal stability :



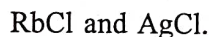
(b) Predict the increasing bond angle sequence of the following :



(c) Categorize the compounds with respect to Schottky and Frenkel defects : AgBr, ZnS, NaCl, KCl.

(d) Predict the structure of XeOF_4 indicating the hybridization of the central element.

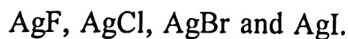
(e) Which of the following has greater melting point?

(f) Find the total number of lone pairs of electrons on the central atom of $\text{SF}_4.$ (g) Predict the unstable nuclei and write the mode of decay— ${}^{18}_9\text{F}$ and ${}^{18}_{10}\text{Ne}.$

(h) Write the number of unpaired electrons in the HOMO of NO.

(i) Find the O – O bond order in $\text{O}_2^{2-}.$

(j) Predict the order of solubility in water of the following :

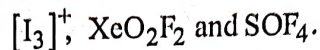


(k) Give an example of an isotope which is used in the treatment of human cancer.

(l) Write an example of an odd electron molecule.

Please Turn Over

2. (a) Predict the shapes of the following species and mention the type of hybrid orbitals on the central atom :



- (b) How and under what condition can an insulator be converted to a semiconductor? 3+2

3. (a) Write the Kapustinskii equation and explain how it is helpful in finding the lattice energy of an ionic solid, where the crystal structure is not known.

- (b) Find the minimum energy required to split an $^{16}_8O$ nucleus into 4_2He and $^{12}_6C$ nucleus. The binding energies of $^{16}_8O$, $^{12}_6C$ and 4_2He are 127.6, 92.1 and 28.3 MeV, respectively. 3+2

4. (a) Construct the MO energy level diagram of CO_2 and find the C-O bond order in the molecule.

- (b) The C-Cl distance in CH_3Cl and CF_3Cl are 1.78 Å and 1.75 Å, respectively. Explain. 3+2

5. (a) Compare the σ -donor and π -acceptor property of CN^- and NO^+ through MO approach.

- (b) Which hydrogen bond would you expect to be stronger and why?



3+2

6. (a) Calculate the electron affinity of iodine from the following data :

$$\text{Formation energy of NaI}(s) = -289 \text{ kJ mol}^{-1}$$

$$\text{Sublimation energy of Na}(s) = 108.8 \text{ kJ mol}^{-1}$$

$$\text{Dissociation energy of I}_2(g) = 214.2 \text{ kJ mol}^{-1}$$

$$\text{Ionization energy of Na}(g) = 497.3 \text{ kJ mol}^{-1}$$

$$\text{Lattice energy of NaI}(s) = -694.7 \text{ kJ mol}^{-1}$$

- (b) What do you mean by 'Fissile nucleus'? Name one of such nuclei with atomic and mass numbers. 3+2

7. (a) BF_3 , PF_3 and ClF_3 are AX_3 type of molecule, but their structures and bond angles are different. Explain.

- (b) From the radius ratio (r_+ / r_-) values, CdS (0.52) and HgS (0.55) are expected to adopt the NaCl structure but they actually crystallize in the ZnS structure. Explain. 3+2

8. (a) Explain the following :

(i) Li_3N can be formed while Na_3N is not.

(ii) The iodine atom in IF_5 sits slightly below the plane of the base of the square pyramid.

- (b) N_3^- is more resonance stabilized than HN_3 . Explain.

3+2

9. (a) Justify the following :
- (i) Methanol, CH_3OH , has a much higher boiling point than methyl mercaptan, CH_3SH .
 - (ii) Solubility of ortho-nitrophenol and para-nitrophenol in water are different.
- (b) The nucleus ^{23}Ne decays by β -emission. Write down the decay equation and determine the maximum kinetic energy of the electron emitted. (Ignore the mass of anti-neutrino)
- Mass of $^{23}\text{Ne} = 22.994466 \text{ u}$
Mass of $^{23}\text{Na} = 22.989770 \text{ u}$ 3+2
10. (a) ZnO and SnO_2 are white when cold but they look yellow when hot. Explain schematically the theory behind it.
- (b) AlCl_3 is covalent, but it behaves like an ionic compound on hydration. — Justify. 3+2
11. (a) Draw the Lewis structure of SO_2Cl_2 and find the formal charge on S and O.
- (b) Predict and justify the order of dipole moment of CH_3Cl and CHCl_3 . 3+2
12. (a) Explain the structure of PCl_3F_2 in the light of Bent's rule.
- (b) PbCl_2 is white while PbI_2 is coloured. — Justify. 3+2
13. (a) CH_3NCS is angular while SiH_3NCS is linear. — Explain.
- (b) What is radiocarbon dating? 3+2
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