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 C_2-C_3 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 $(CH_3)_2CH-N=O$.

(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.

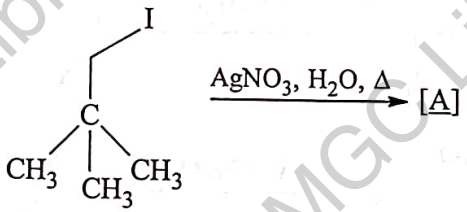
(k) What factors favour TCP?

(l) Arrange the following anions in order of increasing nucleophilicity : $\overset{\ominus}{R_2N}$, $\overset{\ominus}{R_3C}$, $\overset{\ominus}{F}$, $\overset{\ominus}{RO}$.

(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.

(b)



Draw the structure of [A] and show mechanism of its formation. 3+2

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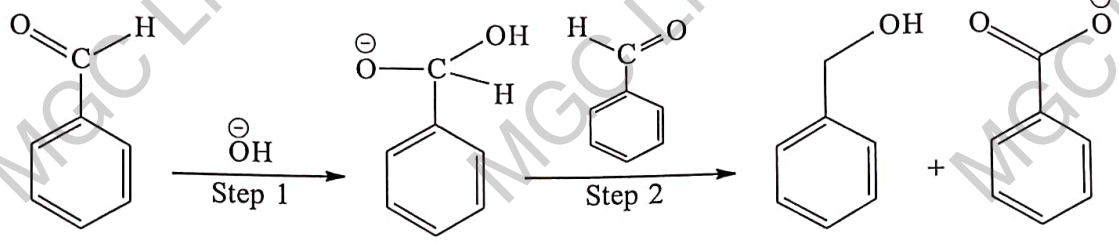
3. (a)



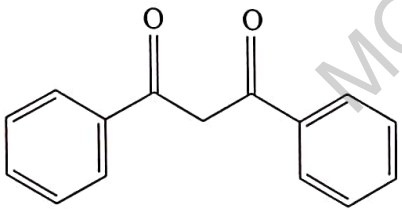
Information : The above reaction shows PKIE.

(i) What is meant by PKIE?

(ii) How is PKIE measured?

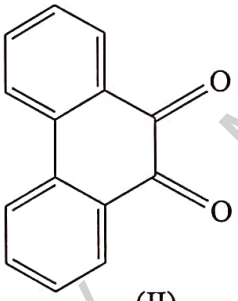
(iii) From the above information, indicate r.d.s of the above reaction.

(b) Comment on the relative enol content of



(I)

and



(II)

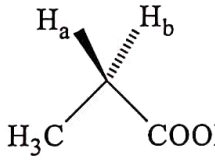
3+2

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

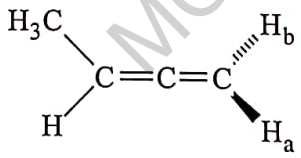
(b) The torsional barriers in fluoroethane and iodoethane are remarkably similar (3.3–3.5 k cal mol^{-1}). Why?

3+2

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



(i)



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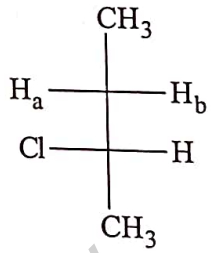
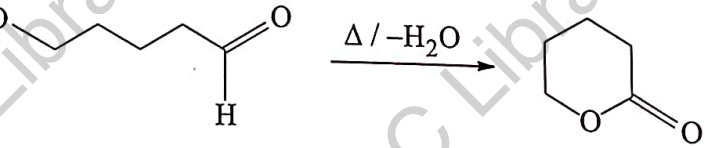


(iii)

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

(i)



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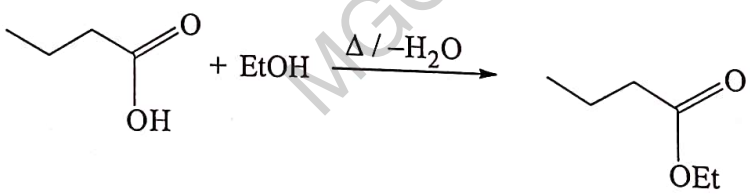
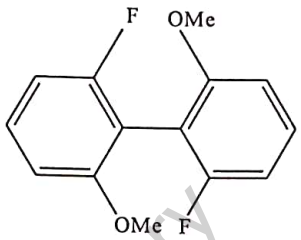


3+2

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



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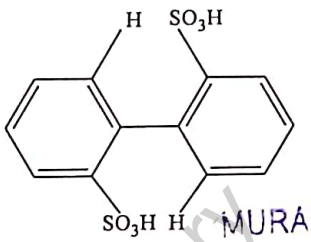


(i) (ii)

(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.

(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 [PhCH(Cl)—CH(Cl)Ph] undergoes dehydrohalogenation with pyridine at 200°C. Identify the diastereoisomer. Explain why the other does not undergo such elimination.

(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 pK_{a1} and pK_{a2} between fumaric and maleic acids.

(b) Give an application of nucleophilic catalysis in organic reactions. 3+2

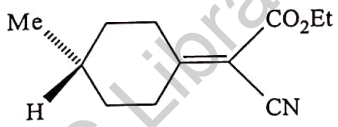
10. (a) Comment on the optical properties of the product(s) in the following reaction :

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 <u>*R*</u>/<u>*S*</u> in the following compounds showing the priority of the ligands.

(i)



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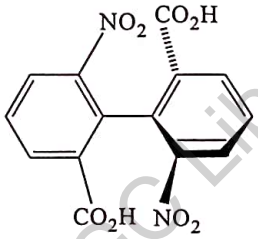
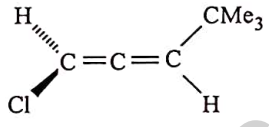


(iii)



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

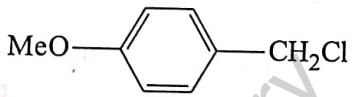
Please Turn Over

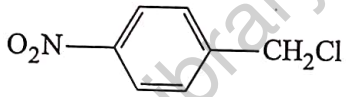
12. (a) Draw the energy profile diagram arising out of rotation around C – C bond in ethylene glycol. Label maxima and minima with appropriate conformation.

(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.

(i) 

(ii) 

3+2