U.G. 2nd Semester Examinations 2022

CHEMISTRY (Honours)

Paper Code : CEMH DC-T4

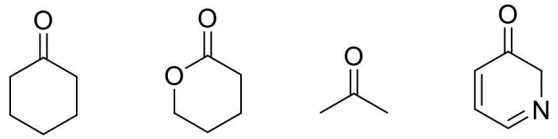
[CBCS]

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 decreasing order of enol content for the following set of compounds is —



I II III IV

(i) III>II>IV>I

(ii) IV>I>III>II

(iii) IV>II>I>III

(iv) IV>III>II>I

(b) pK_a values of acetic acid in three different solvents were measured as **4.76**, **9.63,** and **12.3**. If these three solvents are Methanol, Water, & DMSO, then point out which of the following matching set [Solvent (**pK_a**)] is correct

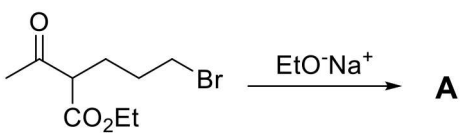
(i) Methanol (**4.76),** Water (**9.63),** and DMSO (**12.3**)

(ii) DMSO (**4.76),** Water (**9.63),** and Methanol (**12.3**)

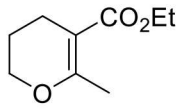
(iii) Water (**4.76),** Methanol (**9.63),** and DMSO (**12.3**)

(iv) Water (**4.76),** DMSO (**9.63),** and Methanol (**12.3**)

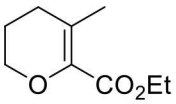
(c) Consider the following reaction.



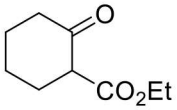
The structure of the product "**A**" is



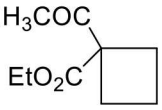
(ii)



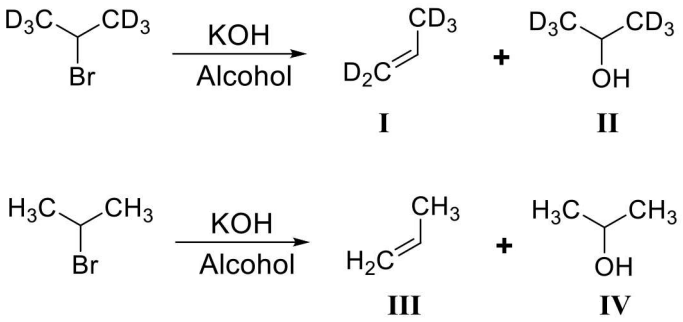
(iii)



(iv)



(d) Which of the following statements is incorrect for the given reaction?



(i) Rate of formation of **II** and **IV** would be identical

(ii) Rate of formation of **I** would be slower than that of **III**

(iii) Formation of **I** would show primary isotope effect

(iv) Formation of **III** involves E1 reaction

(e) During base catalysed dehydrobromination of diastereoisomeric 1-bromo-1,2-diphenylpropanes give alkenes. During the reaction —

(i) The *erythro* isomer react in faster rate through *trans* elimination process.

(ii) The *erythro* isomer react in faster rate through *syn* elimination process.

(iii) The *threo* isomer react in faster rate through *trans* elimination process.

(iv) The *threo* isomer react in faster rate through *syn* elimination process.

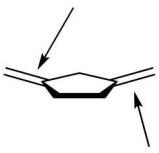
(f) In the following molecule the indicated faces are —

(i) Homotopic

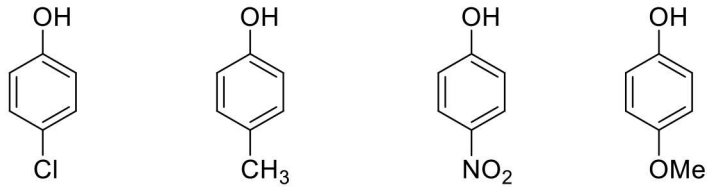
(ii) Diastereotopic

(iii) Enantiotopic

(iv) None of them



(g) Arrange the following compounds in the order of decreasing acidity.



I II III IV

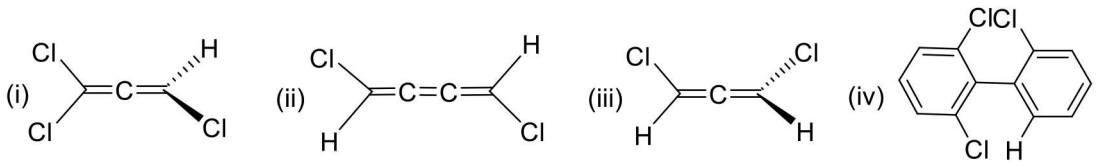
(i) II>IV>I>III

(ii) II>I>III>IV

(iii) III>I>II>IV

(iv) III>I>IV>II

(h) Which one of the following molecules is chiral?



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

(a) The hydrolysis of n-BuCl in aqueous ethanol is accelerated in the presence of NaI. Explain the reaction.

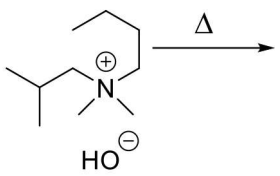
(b) What is Buttressing effect? Explain with example.

(c) "**S_N1** reaction between *t*-Butyl alcohol and HBr acid does not follow the 1st order kinetics" — Justify with the help of an energy profile diagram.

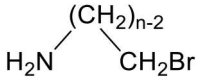
(d) Using Hammond's Postulate, demonstrate that reagent's reactivity and selectivity are inversely related.

(e) Which of the cyclohexane 1,3,5-trione and cyclohexane 1,3-dione has the larger enol content, and why?

(f) Explain the formation of major and minor product from the following reaction :



(g) Explain, in light of "enthalpy and entropy factor," why the formation of a four-membered ring is energetically less favourable than that of a five-membered ring. The following information is provided as a sample.

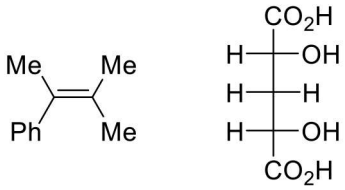


n	4	5
$k_{relative}$	0.002	100

(h) Draw the most stable conformer of $HO\text{-}CH_2\text{-}CH_2\text{-}F$. Give reason.

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

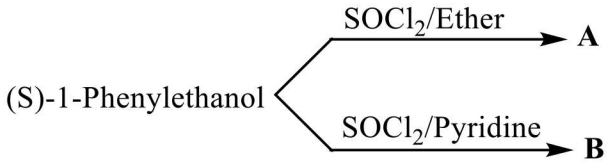
(a) (i) Find out pro-pseudoasymmetric and/or pro-stereogenic centres in the following two molecules. Designate the diastereotopic ligands that are connected with these centres. 4½



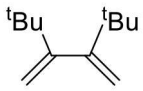
(ii) Which one between HS^- and HO^- is stronger nucleophile in water and why? 1½

(b) (i) $PhCH_2Cl$ in 50% aqueous ethanol follows a mixed kinetics but in water follows the 1st order kinetics only. Explain. 3

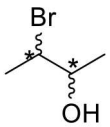
(ii) Explain the following reactions with plausible mechanism and give the structures **A** and **B**. 3



(c) (i) Draw the unstable and preferred conformations of the following molecule in Newman Projection. Justify your answer. 2



(ii) The following compound on treatment with HBr loses its optical activity. How will you explain this observation? 4



(d) (i) Between guanidine and urea which one is more basic and why? 2

(ii) Reaction between KCN and EtI in water is greatly accelerated tetrabutyl ammonium bromide. Explain why? 2

(iii) Bromine with ether is a more effective reagent than free bromine for the following conversion. How will you account for this observation? 2