

UG/2nd Sem/H/20(CBCS)

2020

## CHEMISTRY (Honours)

Paper : CEMH - DC - T4

[Organic - II]

(CBCS)

Full Marks : 25

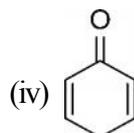
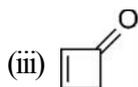
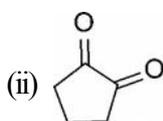
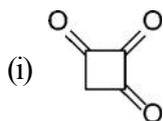
Time : Two Hours

*The figures in the margin indicate full marks.*

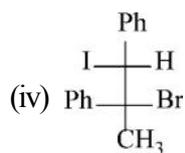
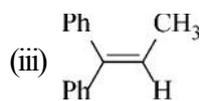
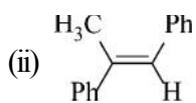
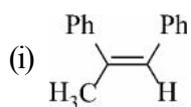
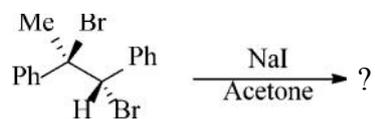
1. Answer any *five* questions from the following :

1×5=5

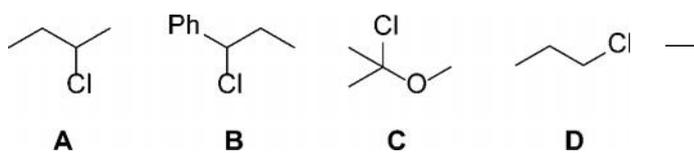
(a) Which of the following has the most unstable enol form?



(b) The major product in the following reaction is —



(c) The correct order of reactivity in  $S_N1$  reaction for the following compounds is :



(i)  $A > B > C > D$

(ii)  $B > A > C > D$

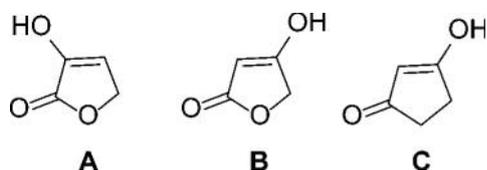
(iii)  $C > B > A > D$

(iv)  $D > C > B > A$

(d)  $\text{MeCH}=\text{C}=\text{C}=\text{CHPh}$  and  $\text{MeCH}=\text{C}=\text{C}=\text{C}=\text{CHPh}$  exhibit —

- (i) Enantiomerism
- (ii) Diastereomerism
- (iii) Enantiomerism and diastereomerism respectively
- (iv) Diastereomerism and enantiomerism respectively

(e) Which of the following orders is correct for the acid strength of the given compounds ?



- (i)  $A > B > C$
- (ii)  $B > A > C$
- (iii)  $C > B > A$
- (iv)  $C > A > B$

(f) Reaction of (R)-2-butanol with *p*-toluenesulfonyl chloride in pyridine followed by reaction with LiBr gives —

- (i) (R)-2-butylbromide
- (ii) (S)-2-butyltosylate
- (iii) (R)-2-butyltosylate
- (iv) (S)-2-butylbromide

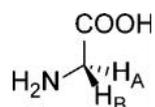
(g) Number of chiral conformers for *meso*-2, 3-dibromobutane is —

- (i) Two
- (ii) Three
- (iii) Six
- (iv) Five

- (h) Which of the following statement is the most appropriate in case of a catalyzed reaction ?
- (i) Catalyst alters the entropy change of the reaction
  - (ii) Catalyst raises the activation energy
  - (iii) Catalyst lowers the activation energy
  - (iv) Catalyst alters the enthalpy change of the reaction

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

- (a) The rate of reaction of  $\text{Ph}_2\text{CHCl}$  in aqueous EtOH with KF to give  $\text{Ph}_2\text{CHF}$  is retarded by the addition of NaCl. Explain.
- (b) The reaction of MeI with  $\text{N}_3^-$  is accelerated by  $4.5 \times 10^4$  fold on changing the solvent from methanol to dimethyl formamide (DMF) — Explain the observation.
- (c)  $(\text{Me}_3\text{CCO})_3\text{CH}$  exists almost exclusively in the keto form. Explain.
- (d) Arrange 2-hydroxybenzoic acid, 4-hydroxybenzoic acid and 2, 6-dihydroxybenzoic acid in the order of their decreasing acid strength. Explain your answer.
- (e) When methane is chlorinated in presence of sunlight traces of ethane are found among the products? Explain.
- (f) Identify the *pro*-R and *pro*-S hydrogen atoms in the following compound.

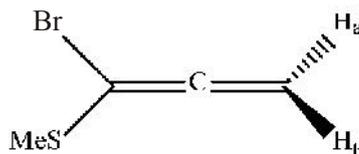
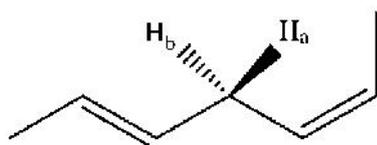


- (g) Draw energy profile for a reaction in which the free energy of activation for the first step is higher than that of the second step but the second step is the rate determining step. Explain your answer briefly.
- (h) Draw (+) sc and (–) ac conformations of 2-methyl butane. Can you represent them in Fischer projection ? Justify your answer.

3. Answer any two questions :

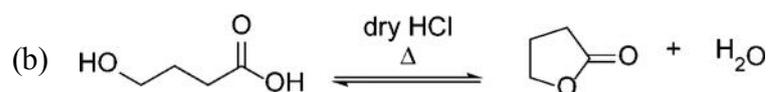
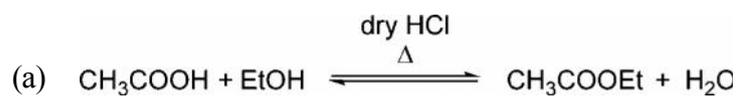
6×2=12

- (a) (i) Find out the topic relationships between  $H_a$  &  $H_b$  in each of the following compounds. 2



- (ii) One of the diastereomers of  $\text{PhCH(D)CH(OAc)Ph}$  loses deuterium on heating but the other doesn't. Explain with mechanism. 4
- (b) (i) Heating of (R)-2-bromopropanoic acid with conc. NaOH gives the sodium salt of (S)-2-hydroxypropanoic acid but use of dilute NaOH in the same reaction furnishes the sodium salt of (R)-2-hydroxypropanoic acid. Explain. 3
- (ii) For  $S_N2$  reactions only "backside" attack of the nucleophile is possible but for  $S_E2$  reactions nucleophile can approach both from the front and the backside. Explain in terms of elementary molecular orbital theory. 2
- (iii) Give one example of nucleophilic catalysis. 1
- (c) (i) Draw the potential energy diagram of 2-Methylbutane for rotation around  $C_2-C_3$  bond. Designate the conformers in terms of Klyne Prelog terminology. 4
- (ii) Ethoxide induced dehydrohalogenation of  $\text{MeCH}_2\text{CH}_2\text{CH(X)Me}$  gives higher 1-alkene to 2-alkene ratio for  $X=\text{F}$  than for  $X=\text{I}$ . Explain. 2
- (d) (i) Aniline is about two times weaker base than *N,N*-dimethyl aniline whereas 2,4,6-trinitro aniline is nearly 40,000 times weaker base than the corresponding *N,N*-dimethyl compound. Explain. 2

- (ii) Heat of formation,  $\Delta H$  of the following two reactions is almost the same, but the second reaction is more facile. Why? 2



- (iii) Molecules with enantiotopic ligands are not only prostereogenic but also prochiral. Explain with a suitable example. 2
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