B.Sc. 2nd Semester (Honours) Examination, 2019 (CBCS)

Subject : Chemistry

Paper : CC-IV

Time: 2 Hours **Full Marks: 40**

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: 2×5=10

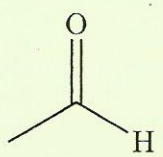
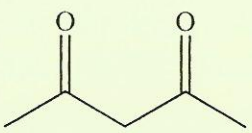
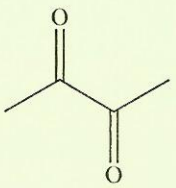
(a) Why does $CH_2 = CHCHBrCH_3$ undergo solvolysis much more rapidly than 2-bromobutane?

(b) Give two criteria of chirality of an organic molecule other than a chiral centre.

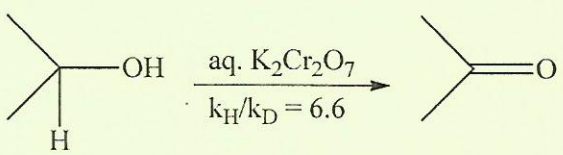
(c) Mark the hydrogens (in bold) of $CH_3\mathbf{CH_2}COC\mathbf{H_3}$ as kinetically or thermodynamically acidic.

(d) What are ambident nucleophiles? Give one example of such nucleophile showing its nucleophilic centres.

(e) Arrange the following compounds in order of increasing enol content in neat samples:

(i) 
(ii) 
(iii) 
(iv) 

(f) The value of k_H/k_D in the order of 6.6 was associated with the following oxidation reaction. Name the effect. What change in the value of k_H/k_D do you expect when the transformation is carried out at an elevated temperature?

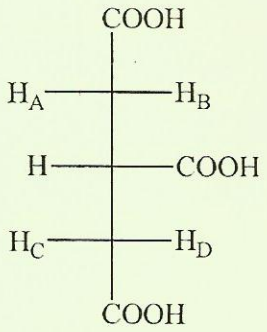


(g) Predict the major organic product in each case when 2-bromobutane and 1-bromobutane is separately treated with alcoholic KOH.

(h) Arrange the *syn*-clinal, *anti*-periplanar, *anti*-clinal and *syn*-periplanar conformers of n-butane in order of increasing energy.

2. Answer *any two* questions from the following: 5×2=10

(a) (i) Citric acid is a unique molecule where the diastereotopic and enantiotopic ligands coexist. Find out the prochiral relationship of the following pairs of homomorphic hydrogens of citric acid —H_A & H_B, H_B & H_C and H_A & H_C.



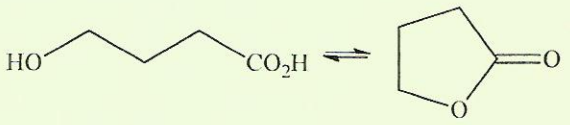
Citric Acid

(ii) What is the difference between the order and molecularity of a reaction? Give an example of first order (overall) bimolecular reaction. 3+2=5

(b) (i) Draw the Newmann projections for preferred conformations of the diastereomers of RCHOHCHOHR, where R is an alkyl group.

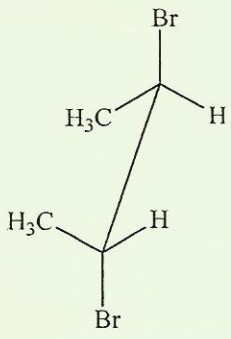
(ii) Which of the following two reactions carried out at identical reaction condition and at same temperature is expected to have a larger value of equilibrium constant and why? 3+2=5

(A) $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3\,COO\,CH_2\,CH_3 + H_2O$

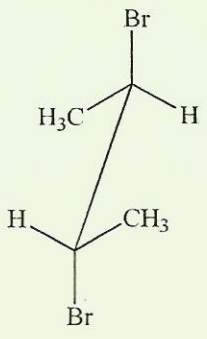
(B) 

(c) (i) Define and explain 'nucleophilic catalysis' by taking a nucleophile of your choice.

(ii) Show the structure of alkenes which could be obtained from each of the isomers A and B, respectively, upon one mole HBr elimination. Which isomer would readily eliminate further to 2-butyne? 2+3=5



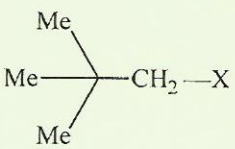
A



B

(d) (i) What happens when a solution of ethylacetoacetate in methanol is rapidly added with an excess solution of bromine in methanol followed by destruction of excess bromine by methanolic β-napthol? Explain the reactions involved with reasons.

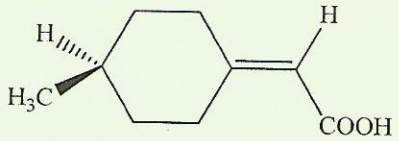
(ii) Neopentyl halide (A) is extremely reluctant to nucleophilic substitution reaction. — Justify or Criticize. (1+2)+2=5

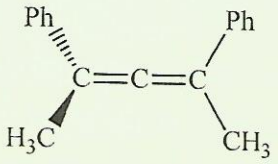


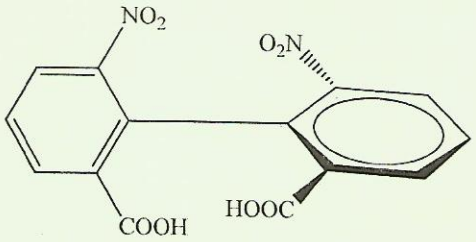
(A)

3. Answer *any two* questions from the following: 10×2=20

(a) (i) Provide the R_a, S_a descriptors for following chiral molecules.



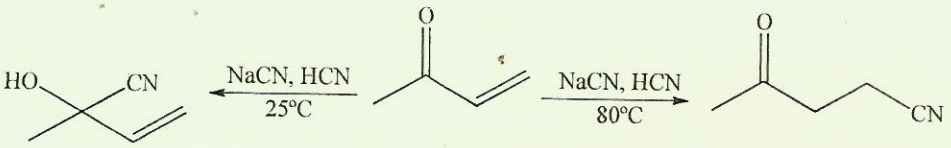




(ii) The observed nucleophilicity order of the halides in polar protic solvents is given below. The order is reversed in polar aprotic solvents.— Explain.

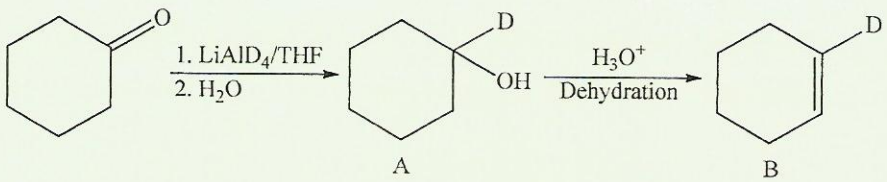
$$\overset{\ominus}{Cl} < \overset{\ominus}{Br} < \overset{\ominus}{I} \quad \text{(in polar protic solvents)}$$

(iii) Identify the thermodynamically controlled product (TCP) and kinetically controlled product of the following reactions and also provide justification in favour of your choice.

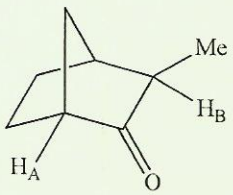


(iv) In pyrolytic elimination of acetates and xanthates are essentially *syn*. Draw the transition state of such reactions. 3+2+3+2=10

(b) (i) Suggest reasons why the synthesis of compound B, outlined below is considered as a bad choice. Propose an alternative pathway to synthesize B from A.



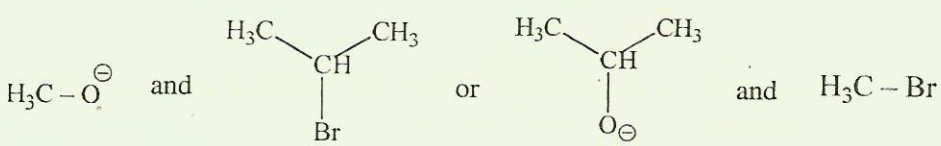
(ii) Which of the marked hydrogens of the following compound show D/H exchange with $NaOD/D_2O$ and why?



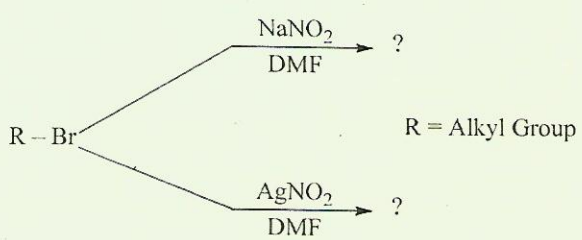
(iii) In halogenation of alkanes regioselectivity in bromination is found to be more than chlorination. Draw the corresponding energy profile diagrams of both the reactions taking 2-methylbutane as the starting material and explain this phenomenon according to reactivity-selectivity principle. Also comment on the corresponding enthalpies (ΔH).

(1.5+1.5)+(1+1)+(2+2+1)=10

(c) (i) Which combination of reactants would be the best to prepare $CH_3OCH(CH_3)_2$ by an S_N^2 reaction and why?



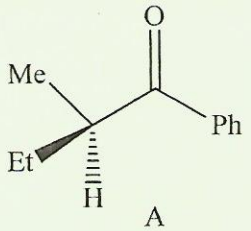
(ii) Complete and explain:



(iii) CH_3—CH(OH) CH_2 SEt & CH_3—CH(SEt) CH_2OH gives same product when treated with dil. HCl, respectively. Give the product and explain the observation.

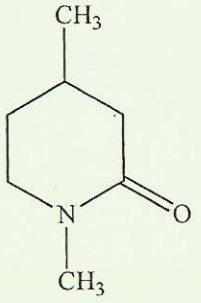
(iv) Mark the stereoheterotopic faces of the compound A drawn below with appropriate descriptors. What is the relation between them— diastereotopic *or* enantiotopic?

2+(2+2)+2+2=10

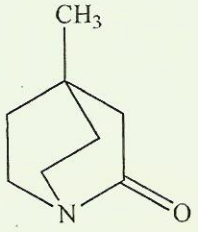


A

(d) (i) The amide B is soluble in dilute HCl while the amide A is neutral.— Explain.

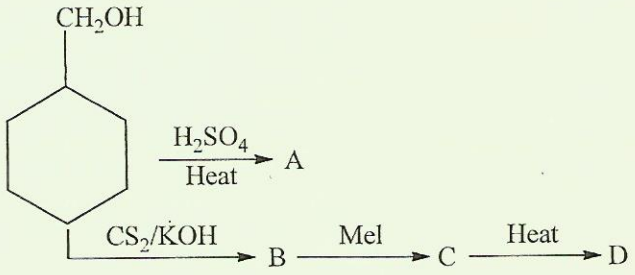


A

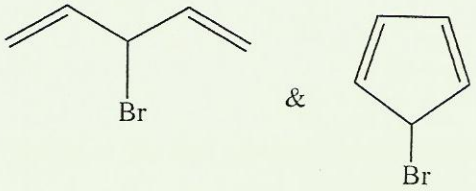


B

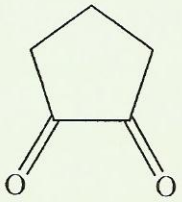
(ii) Identify the compounds A-D in the following reaction sequence (mechanism not required):



(iii) Which of the following two monobromo compounds would undergo silver ion assisted hydrolysis at a faster rate? Give reason.



(iv) The following compound A exist as 100% enol form.— Explain. 2+4+2+2=10



A