B.Sc. 2nd Semester (Honours) Examination, 2023 (CBCS)

Subject : Chemistry

Course : CC-IV

(Organic Chemistry-II)

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: 2×5=10

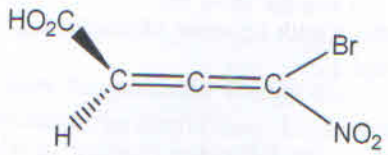
(a) α-Chlorocarbonyl compounds ($RCOCH_2Cl$) are very good substrates for S_N2 reactions, explain.

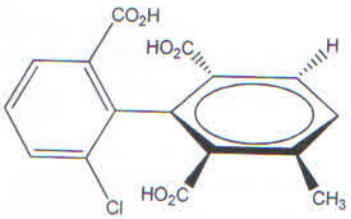
(b) CH_3–$CH(OH)CH_2$–SEt and CH_3–$CH(SEt)CH_2$–OH give same product when treated with dry HCl, explain.

(c) Between *p*-chlorophenol and *p*-fluorophenol which one is a stronger acid and why?

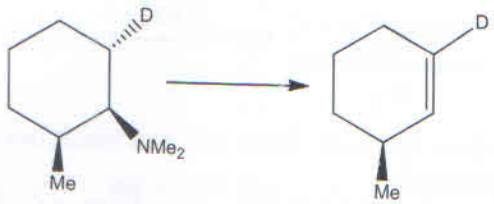
(d) Acetylacetone shows 15% enol content in H_2O whereas 92% enol content in *n*-hexane, explain.

(e) Assign R/S nomenclature of the following compounds:





(f) Carry out the following conversion with appropriate reagents.



(g) Can neopentylbromide udergo S_N2 reaction? Give argument for the fact.

(h) Draw the most stable conformer of 1,2-difluoroethane with proper explanation.

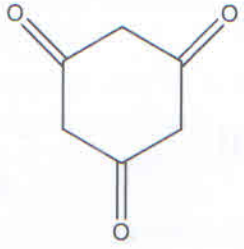
2. Answer *any two* questions. 5×2=10

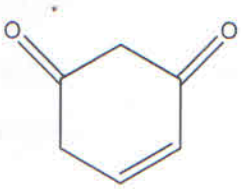
(a) (i) Compare the rates of the given reactions indicating the rate determining step.

$$CH_3-CO-CH_3 + Br_2 \xrightarrow[K_H]{\ominus OH} Br-CH_2-CO-CH_3$$

$$CD_3-CO-CD_3 + Br_2 \xrightarrow[K_D]{\ominus OH} Br-CD_2-CO-CD_3$$

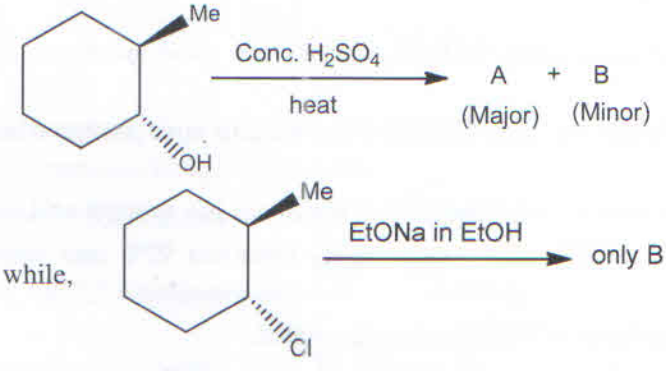
(ii) Which of the following has higher enol content? Give reason for your answer.





2½+2½

(b) (i) Account for the following observation:



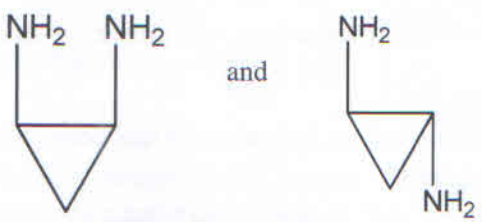
(ii) Alkyl halides produces mainly cyanides with aqueous ethanolic KCN, whereas mainly isocyanides with ethanolic AgCN, explain.

3+2

(c) (i) Draw a reaction coordinate diagram for the following reaction in which C is the most stable and B is the least one and the transition state going from A to B is more stable than from B to C:

Also predict which one is the faster step and which one is the rate determining step in the forward direction?

(ii) Between the following which one is a stronger base? Explain.

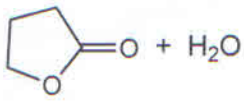


3+2

(d) (i) Explain with mechanism and the stereochemistry of the products formed when the threo-diastereomer of PhCHMe-CHMeOTs is treated with acetic acid in NaOAc solution.

(ii) The following two reactions are carried out at identical condition. Now predict which one is expected to have a larger value of equilibrium constant and why?

$$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

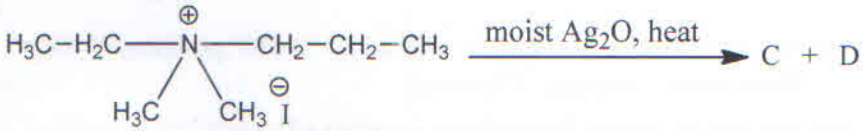
$$HOCH_2CH_2CH_2CO_2H \rightleftharpoons \text{  } + H_2O$$

2½+2½

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

(a) (i) 1,2-dichloroethane has a very low dipole moment while 1,2-ethanediol has a considerable moment, explain.

(ii) Identify the major product between C and D in the following reaction with proper explanation.



(iii) Find out the configuration of the final product when,

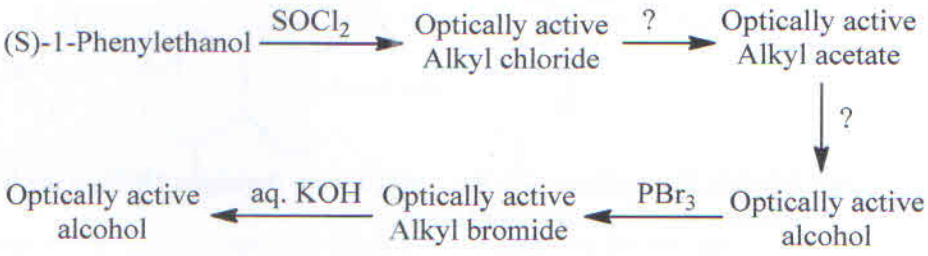
(A) *pro*-R hydrogen of propionic acid is substituted by ethyl group.

(B) Hydride is allowed to attack on the *re*-face of ethyl methyl ketone.

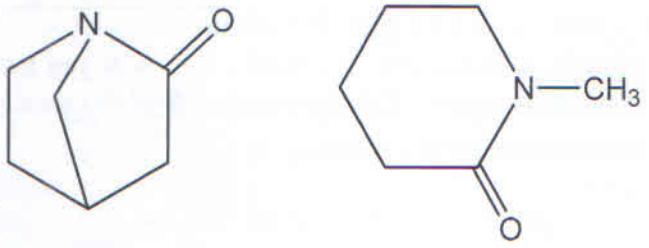
(iv) Write down the *s-cis* conformer of $CH_2=C(CH_2OH)-CF=CH_2$ and compare its stability with the *s-trans* conformer. 2+3+3+2

(b) (i) Draw the potential energy diagram of 2,3-butanediol for rotation around C_2-C_3 bond showing the conformers. Explain the relative stabilities of the conformer.

(ii) For the following inter-conversions show appropriate three dimensional formula of the product in each step.



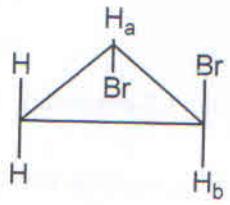
(iii) Which of the following is more basic and why?

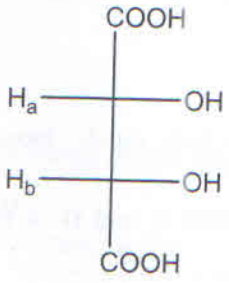


3+5+2

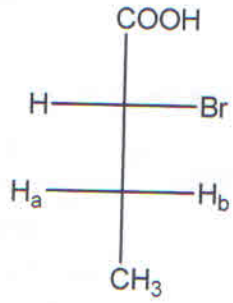
(c) (i) Draw the Fischer projection formula of all possible stereoisomers of 2,3,4-trihydroxypentane. Comment on the stereogenecity of C-3 centre in the *active* and *meso* forms.

(ii) Identify H_a and H_b in each of the following structures as homotopic, enantiotopic or diastereotopic ligands.

(a) 

(b) 

(c) 

(d) 

(iii) On esterification, (-)-Lactic acid with CH_3OH produces (+)-Methyllactate. Has the configuration changed? Comment.

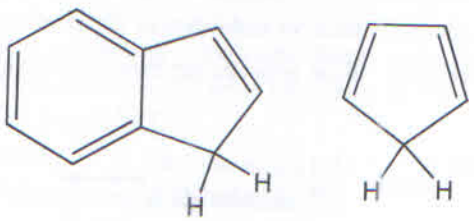
(iv) Identify the product with proper mechanism.

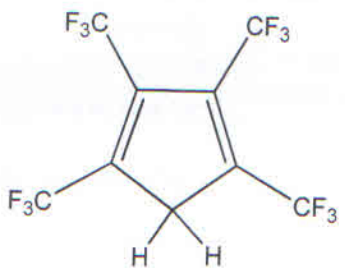
2R, 3R-2,3-dibromobutane $\xrightarrow{\text{Zn in AcOH}}$ E

3+4+1+2

(d) (i) Hydrolysis of methyl bromide becomes faster in presence of catalytic amount of KI, explain this observation with proper energy profile diagram.

(ii) Arrange the following compounds in order of decreasing acidity and explain.





(iii) Identify the products with the configuration descriptor (R/S) in the following reactions. Explain their formation mechanistically.

(2R)-2-Bromopropionic acid $\xrightarrow{\text{Conc. NaOH}}$ F

(2R)-2-Bromopropionic acid $\xrightarrow{\text{Dil. NaOH}}$ G

(iv) $KMnO_4$ is immiscible in benzene. How will you make it soluble in benzene using appropriate reagent? Comment on the role of this reagent.

(v) Give an example of a proton sponge.

2+2+3+2+1