2019

CHEMISTRY — HONOURS

Paper : CC – 3

(Organic Chemistry – 2)

Full Marks : 50

The figures in the margin indicate full marks.

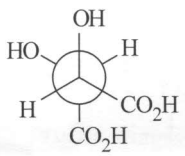
Candidates are required to give their answers in their own words as far as practicable.

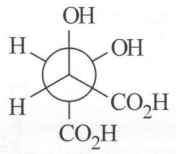
Answer ***question no.*** **1** and ***any eight*** from ***question no.*** **2** to ***question no.*** **11**.

1. Answer ***any ten*** questions : 1×10

(a) Give one example of axially chiral molecule indicating its chiral axis.

(b) Designate as P- or M- conformation for the following conformers :





(c) Draw the most stable conformer of $HO-CH_2-CH_2-F$. Give reasons.

(d) Cyclopentane–1,2-dione is present almost in enol form. Explain.

(e) Triphenylamine is not at all basic in nature.— Explain.

(f) Pro-R chlorine of 2,2-dichlorobutane is replaced by 'H' atom. Draw the structure of the product and assign its configuration.

(g) Write down the structure of 12-Crown-4 ether and its binding selectivity towards Li^+, Na^+ and K^+.

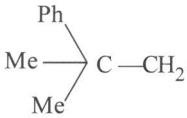
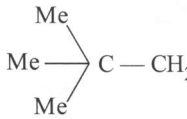
(h) Which one between HS^- and $\bar{O}H$ is stronger nucleophile in water and why?

(i) Which of the following reactions is/are stereospecific?
S_N1, S_N2, E^1 and E^2.

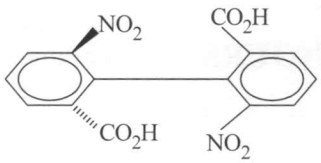
(j) The reaction rate of MeI with $N_3^{\ominus}$ will increase by $4{\cdot}5\times10^4$ fold on changing the solvent from methanol to dimethyl formamide— explain the observation.

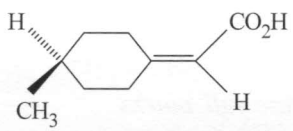
(k) Which of the following is more basic and why?
aniline and p-toluidine.

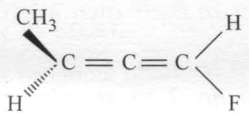
(l) Vinyl halides are very unreactive towards nucleophiles. Explain it.

(m) Between  and  , which will undergo solvolysis at a faster rate and why?

2. (a) Designate as R/S for the following compounds mentioning priority sequence :

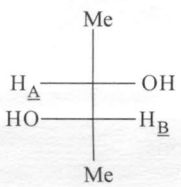
(i) 

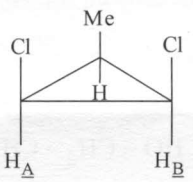
(ii) 

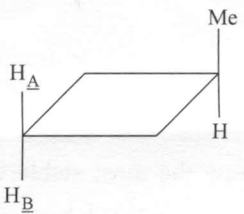
(iii) 

(b) Write down the (–) sc conformation of active butane-2,3-diol. Propose the other conformers of it and indicate their relative stability. 3+2

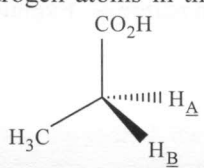
3. (a) State whether the marked hydrogens $H_{\underline{A}}$ and $H_{\underline{B}}$ are homotopic, enantiotopic or diastereotopic in each example given below :



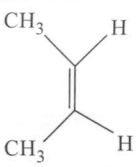


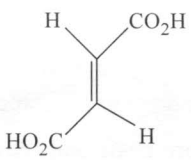


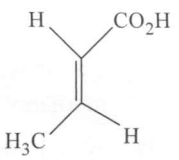
(b) Identify the Pro-R and Pro-S hydrogen atoms in the following compound : 3+2



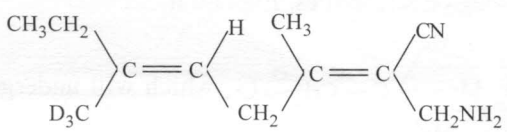
4. (a) Identify the Re – Re or Re – Si/Si/Re or Si – Si faces of the following compounds when viewed from the top face :

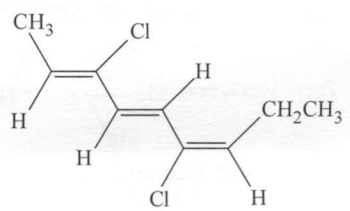
(i) 

(ii) 

(iii) 

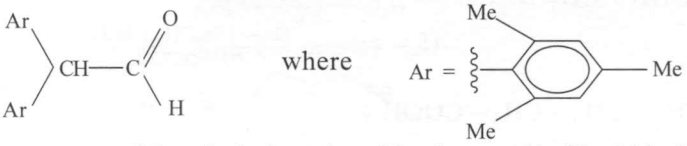
(b) Assign E/Z configuration of the following compounds : 3+2

(i) 

(ii) 

5. (a) Draw the energy profile diagram arising out of rotation around C – C bond in 1,2-dibromoethane. Label all maxima and minima with appropriate conformation. Indicate the most stable conformation.

(b) The following compound exists mainly in the enol form (~95%). Explain. 3+2



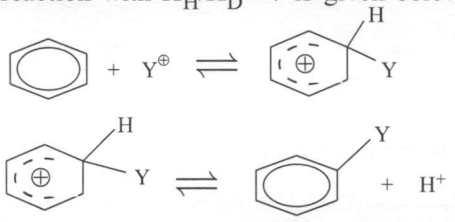
6. (a) Write down the structure of the alcohol produced by the attack of hydride (H^-) ion on 2-butanone from its Si-face and find its absolute configuration.

(b) Arrange the following ions in decreasing order of nucleophilicity in protic solvents :

$$Cl^{\ominus}\ ,\ Br^{\ominus}\ ,\ I^{\ominus}\ ,\ F^{\ominus}.$$ 3+2

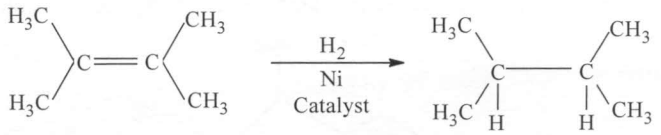
7. (a) A two step reaction with $K_H/K_D \approx 7$ is given below :

Step 1 :



Draw and explain energy profile diagram for the reaction showing the T.S.(s) and intermediate. Indicate the rate determining well.

(b) Calculate ΔH(Enthalpy change) for the following reaction : 3+2



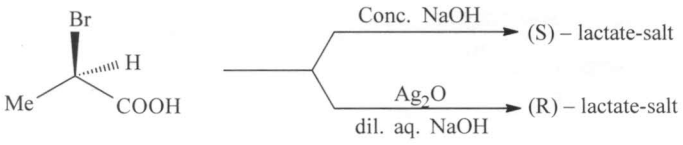
C = C bond energy = 145 kcal/mole

C – C bond energy = 83 kcal/mole

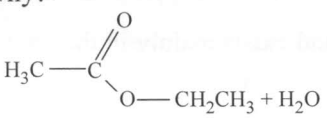
C – H bond energy = 99 kcal/mole

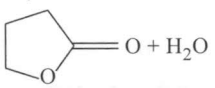
H – H bond energy = 103 kcal/mole

8. (a) Account for the following observations with mechanism :



(b) Which of the following two reactions conducted at same temperature is expected to have larger value of equilibrium constant and why? 3+2

(i) $CH_3COOH + CH_3CH_2OH \rightleftharpoons$ 

(ii) $HO-CH_2-CH_2-CH_2-COOH \rightleftharpoons$ 

9. (a) Discuss the stereochemistry of dehydrobromination of meso – 1,2-dibromo – 1,2-diphenyl ethane with NaOEt in EtOH. Write down the product.

(b) Indicate the products obtained from the following reactions showing the mechanism involved. 3+2

(i) $Me_2CH-CH(Br)-Me \xrightarrow[\Delta]{\ominus OH}$

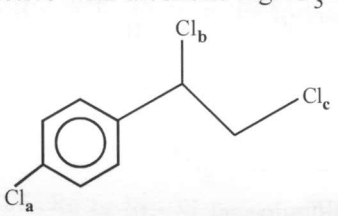
(ii) $Me_2CH-\underset{\overset{|}{\overset{\oplus}{N}Me_3}}{CH}-Me \xrightarrow[\Delta]{\ominus OH}$

10. (a) Explain the following observations with mechanism :

$(CH_3)_3CH \xrightarrow{Br_2,\ 127^\circ C} (CH_3)_3C\,Br + (CH_3)_2CH-CH_2Br$ (~98% : ~2%)

$(CH_3)_3CH \xrightarrow{Cl_2,\ 300^\circ C} (CH_3)_3C\,Cl + (CH_3)_2CH-CH_2Cl$ (~25% : ~75%)

(b) Which 'Cl' atom is more reactive with alcoholic $AgNO_3$ solution and why? 3+2

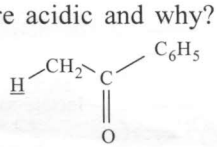


11. (a) Explain the following reactions with plausible mechanism and give the structures of A and B :

(S)–1–Phenylethanol $\xrightarrow[\text{ether}]{SOCl_2}$ A

(S)–1–Phenylethanol $\xrightarrow[\text{Pyridine}]{SOCl_2}$ B

(b) Which one is more acidic and why? 3+2



and