2021

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** (compulsory) and ***any eight*** questions from the rest (***question nos.* 2 to 13**)

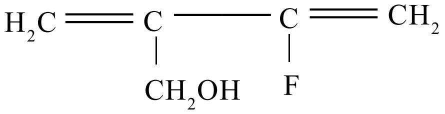
1. Answer ***any ten*** questions : 1×10

(a) Write in increasing order of nucleophilicity of the following :
$Et\overset{\ominus}{O}$, $Ph\overset{\ominus}{O}$, $t\mathrm{Bu}\overset{\ominus}{O}$, $CH_3CO\overset{\ominus}{O}$

(b) Why is the enol content of a cyclic–1, 2–diketone more compared to an acyclic 1, 2-diketone?

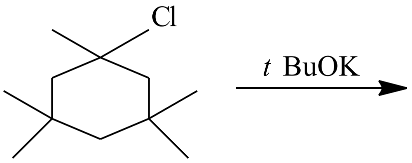
(c) Represent 2-butenoic acid in *Re* – *Re* face.

(d) Write down the stable conformer of the following compound and designate it as either *s-cis* or *s-trans*.



$H_2C{=}C(CH_2OH){-}C(F){=}CH_2$

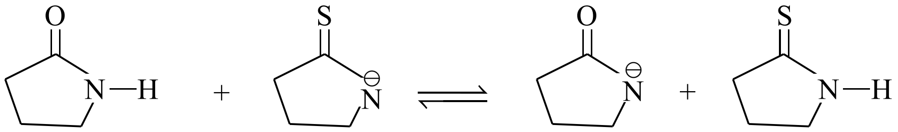
(e) Write down the major product of the following reaction :



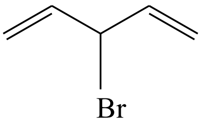
(f) Which one is a better nucleophile? $\overset{\ominus}{O}H$ or $\overset{\ominus}{O}OH$? Explain.

(g) Give an example of ring-chain tautomerism.

(h) Predict the position of equilibrium for the following acid base reaction. Give reason.



(i) Which one of the following undergoes silver ion assisted hydrolysis? Give reason.



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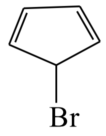
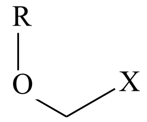


(j) Draw the structure of the most stable conformer in Newman formula for FCH_2CH_2F.

(k) Which one is the better substrate for S_N1 reaction of the following compounds? Give reason.



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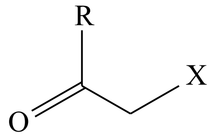
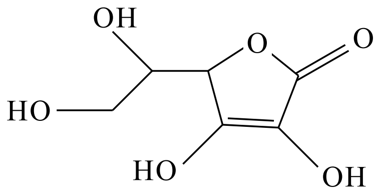
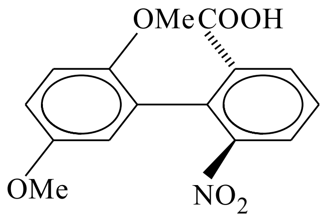


(l) Identify the most acidic proton and explain your choice.

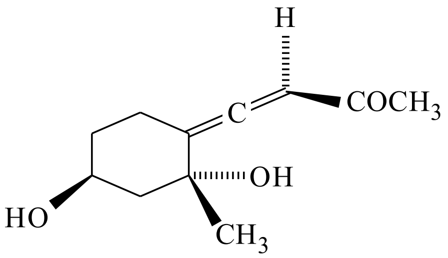


2. (a) Designate *R*/*S* in the following compound showing the priority of ligands.

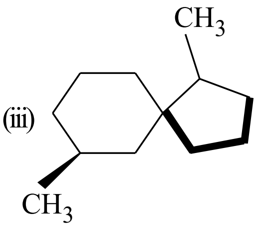
(i)



; (ii)

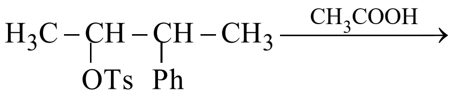


; (iii)



(b) The rotational energy barriers in CH_3CH_2X (X = F, Cl, Br, I) are remarkably similar in magnitude (around 14-15 kJ/mol) despite considerable difference in the size of halogens. How do you explain for the fact? 3+2

3. (a) Predict the products in the following reactions with mechanism. Offer explanation.



$$H_3C-\underset{OTs}{CH}-\underset{Ph}{CH}-CH_3 \xrightarrow{CH_3COOH}$$

(Both *threo*- and *erythro*-forms)

(b) Arrange three classes of aliphatic amines in increasing order of basicity in polar protic medium with explanation. 3+2

4. (a) Give an example of a molecule with enantiomorphic groups along with pro-*R* and pro-*S* hydrogen atoms on a pro-pseudoasymmetric centre.

(b) Between *p*-chlorophenol and *p*-fluorophenol which one is a stronger acid and why? 3+2

5. (a) Consider the following reaction sequence :

$$\mathbf{A} \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \mathbf{B} \xrightarrow{K_2} \mathbf{C}$$

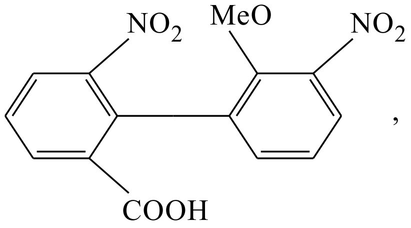
"**C**" has lower free energy that "**A**" and $K_2 >> K_{-1} >> K_1$.

Draw an energy profile diagram indicating transition states and rate determining step.

(b) Draw the structure (showing stereochemistry) of the product formed when $\overset{\ominus}{\mathrm{CN}}$ attacks from the *Re*-face of acetaldehyde. Determine the absolute configuration of the product. 3+2

6. (a) Draw the staggered conformation of 1-chlorobutane for rotation about C-1/C-2 bond and also about C-2/C-3 bond. Comment on the relative stabilities of the conformers.

(b) Compare the ease of racemisation of the following compounds with proper justification. 3+2



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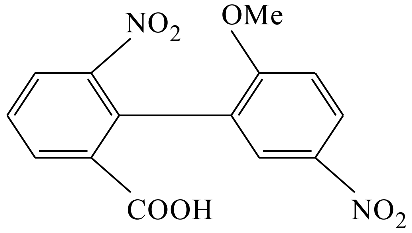
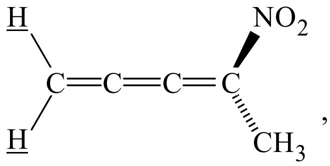
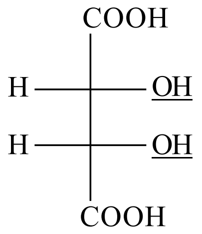


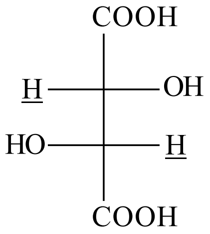
7. (a) Identify the underlined atoms and groups as homotopic, enantiotopic or diastereotopic with explanation.



(i)

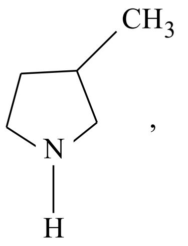


(ii)

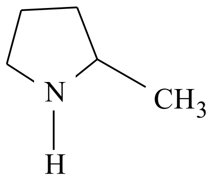


(iii)

(b) Using elimination reaction as a tool, identify the following isomeric compounds. 3+2



(i)



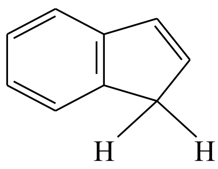
(ii)

8. (a) The ${}^{K_1}\!/\!{}_{K_2}$ ratio of fumaric acid is 23·17, while the value for maleic acid becomes 20·168. How would you explain this observation?

(b) S_N2 reaction always leads to inversion of absolute configuration. Justify/Criticise the statement. 3+2

9. (a) Optically pure PhCH(Me)Cl shows 98% racemisation while $C_6H_{13}CH(Me)Cl$ shows only 34% racemisation when treated with water : acetone (1:4) solvent. Explain the observation.

(b) Arrange the following compounds in order of increasing acidity.



(i)

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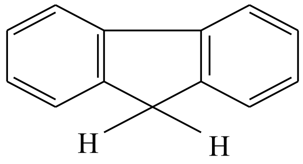


(ii)

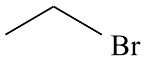
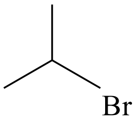
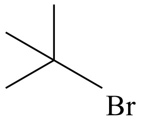
Give explanation in favour of your answer. 3+2

10. (a) The following reaction normally does not take place. What you should add to the reaction mixture to make it a feasible one? Explain your answer.

$$R-X \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{NaCN (Aqueous)}} R-CN$$

(b) When benzenethiol is first treated with an excess of sodium ethoxide followed by 1, 2–dibromoethane, the main product is phenylthioethene. Explain this reaction with plausible mechanism. 3+2

11. (a) Relative rate constants for solvolysis of three bromoalkanes in 60% EtOH–H_2O and in H_2O are as follows :

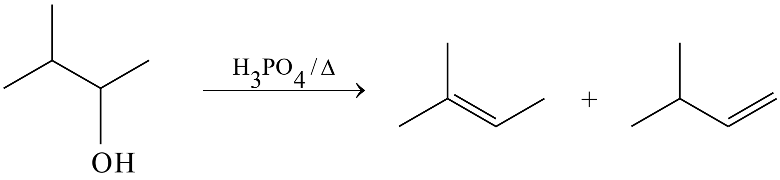
			
1. 60% EtOH-H_2O (55°C)	1·00	1·78	$2{\cdot}41\times10^4$
2. H_2O (50°C)	1·00	11·60	$1{\cdot}2\times10^6$

(i) Explain why 2–bromo–2–methylpropane undergoes solvolysis more than 10^4 times faster than bromoethane and 2–bromopropane in both solvents.

(ii) Explain why the relative solvolytic reactivity of 2–bromopropane is significantly larger in H_2O than in 60% EtOH – H_2O as solvent.

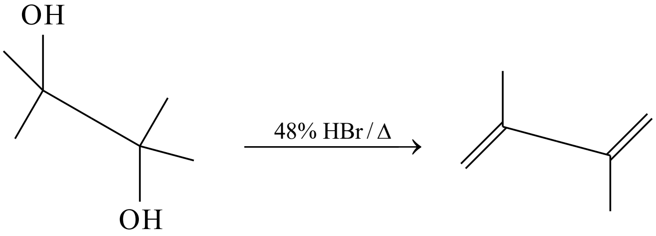
(b) Suggest mechanisms for the following elimination reactions. Why does the first reaction yield a mixture of products but the second one gives a single product?

(i)



(Yield = 64% in 4:1 ratio)

(ii)



3+2

12. (a) Bromination of isobutane (Br_2/127°C, light) gives 1% isobutyl bromide and 99% *t*-butyl bromide but chlorination of isobutane (Cl_2/25°C, light) gives 67% isobutyl chloride and 33% *t*-butyl chloride. Explain the above observation.

(b) Compare the basicities of 2, 6–ditertiarybutylpyridine and pyridine in aqueous medium. 3+2

13. (a) $CH_3CH(OH)CH_2SEt$ and $CH_3CH(SEt)CH_2OH$ gives the same product when treated with dry HCl. Give the structure of the product and explain its formation.

(b) When *n*-butyl bromide is treated with NaI in ethanol, the concentration of iodide ion decreases quickly but then slowly returns to its original concentration. Identify the major product of this reaction with explanation. 3+2