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CHEMISTRY

(Major)

Paper : 2-2

(Organic Chemistry)

Full Marks : 60

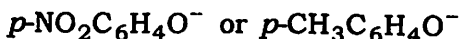
Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

1. Answer any seven questions : 1×7=7

(a) Explain, why β -keto acids like $\text{RCOCH}_2\text{CO}_2\text{H}$ readily decarboxylate on heating.

(b) Indicate which reagent is expected to be more nucleophilic toward CH_3Br in ethanol and why :



(c) Predict the major product :



(d) How would the pK_a values of ammonium ions change if they were determined in a solvent less polar than water?

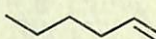
(2)

- (e) Arrange the following classes of compounds in decreasing order of boiling point considering that they have same number of carbon atoms :

Carboxylic acids, Amides,
Ketones, Nitriles

- (f) Semicarbazide has two NH_2 groups, but only one of them forms an imine. Explain.
- (g) Which tautomeric form of 2,4-pentanedione is more stable in—
(i) water;
(ii) hexane?
- (h) The reaction of an alkene with Br_2 does not require a Lewis acid but the reaction of benzene does. Why?

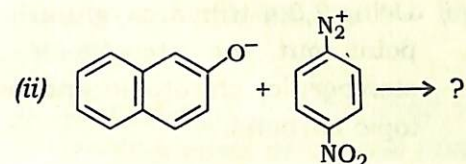
2. Answer any four questions : $2 \times 4 = 8$

- (a) With the help of an example, bring out the difference between a chiral centre and a stereogenic centre.
- (b) Ketones do not undergo Knoevenagel reaction with malonic acid or its esters. Why?
- (c) What products would you expect from the following reactions? $1 \times 2 = 2$
- (i)  + NBS $\xrightarrow{\text{peroxide}}$?

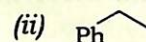
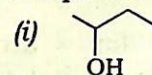
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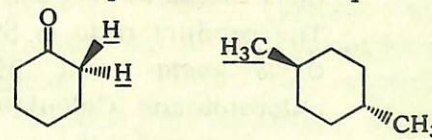


- (d) Account for the fact that acetals are stable to bases but are readily hydrolyzed by acids. 2
- (e) How would you employ organometallic reagents to make the following compounds? $1 \times 2 = 2$



3. Answer any two from (a), (b) and (c) and any one from (d) and (e) : $5 \times 3 = 15$

- (a) Compare the relative stabilities of chair, boat and twist-boat conformations of cyclohexane. 5
- (b) (i) Indicate whether the underlined atoms or groups are homotopic, enantiotopic or diastereotopic : 2



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(Turn Over)

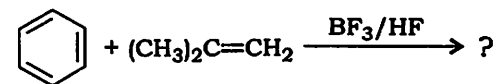
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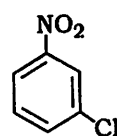
- (ii) Using 2,3,4-trihydroxyglutaric acid, point out the stereogenic, non-stereogenic, chirotopic and achirotopic carbons. 3
- (c) (i) Which conformer is favoured in ethylene glycol and why? $1\frac{1}{2}$
- (ii) Which conformer is favoured in 1,2-dibromoethane and why? $1\frac{1}{2}$
- (iii) Butane has chiral conformers, yet it is optically inactive. Explain. 2
- (d) Provide evidences for aromatic electrophilic substitutions involving—
- (i) π -complex;
- (ii) σ -complex.
- Draw the energy profile diagram for both the mechanisms. 4+1
- (e) (i) What do you mean by partial rate factor? How is it calculated? $1+1=2$
- (ii) The chlorination of toluene by using chlorine in aqueous acetic acid takes place 344 times faster than does the same reaction of benzene. The product ratio is 59.9% *ortho*-, 0.3% *meta*- and 39.8% *para*-chlorotoluene. Calculate the partial rate factors for the reaction. 3

(5)

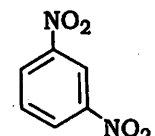
4. Answer either (a) or (b) and any two from (c), (d), (e) and (f) : $10 \times 3 = 30$

- (a) (i) Write the product obtained for the reaction given below and propose a mechanism for the same : $1+3=4$



- (ii) Nitration of *N,N*-dimethyl aniline gives mainly the *m*-nitro derivative when concentrated nitric and sulphuric acids are used but mainly the *o*- and *p*-nitro derivatives in less acidic conditions. Why? 2
- (iii) Indicate the position(s) of major monoelectrophilic substitution of each of the following compounds and account for the same : 2
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O=[N+]([O-])c1cccc(Cl)c1



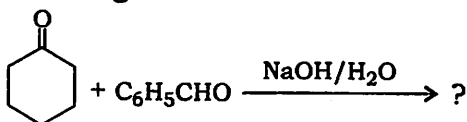
O=[N+]([O-])c1cccc([N+](=O)[O-])c1
- (iv) When nitrations of aromatic substrates are carried out, nitronium ion is said to act as an electrophile. Provide two evidences in support of formation of the nitronium ion. 2

- (b) (i) What happens when methyl picrate is allowed to react with potassium ethoxide? Propose a mechanism for the reaction and justify with evidences. 1+2+1=4
- (ii) Account for the observation that nucleophilic substitution of chlorobenzene takes place through a benzyne mechanism whereas nucleophilic substitution of chloronitrobenzenes proceeds via the addition-elimination sequence. 3
- (iii) Why is S_N1 mechanism common to diazonium compounds? Provide evidence in support of the reversible nature of the first step of the mechanism. 3
- (c) (i) Why is propene more reactive towards electrophilic addition than ethene? Explain. 2
- (ii) Propose a mechanism for the formation of *meso*-1,2-dibromostilbene by the addition of bromine to 2-stilbene in nitromethane. 3
- (iii) What is decarboxylation? What product(s) is/are formed by the decarboxylation of 2-methylbutanoic acid? 2

- (iv) How can the compound $\text{HOCH}_2\text{CH}_2\text{NH}_2$ be prepared, starting with a carbonyl compound with one fewer carbon atom than the desired product? 2
- (v) What do you mean by reductive amination? 1
- (d) (i) How can you convert cyclohexene to *trans*-1,2-cyclohexane diol? Propose a mechanism for the reaction. 3
- (ii) Compound A ($\text{C}_{10}\text{H}_{16}$) takes up 2 mols of hydrogen on catalytic hydrogenation. Ozonolysis gives two diketones, B ($\text{C}_6\text{H}_{10}\text{O}_2$) and C ($\text{C}_4\text{H}_6\text{O}_2$). Propose a reasonable structure (or structures) of A. 2
- (iii) Account for the fact that aliphatic α -chloroamines hydrolyse even more rapidly than the related α -chloroethers. 3
- (iv) How can you prepare pentan-1-ol from pentene? Write the reaction. 2
- (e) (i) Although an aryl group is usually found to be electron-withdrawing relative to alkyl, aromatic aldehydes tend to be less reactive than aliphatic aldehydes. Explain. 2

- (ii) Predict the major product and propose a mechanism for the reaction given below :

3



- (iii) Using the Hell-Volhard-Zelinsky reaction, propose a synthetic route for the preparation of alanine. 2
- (iv) Give a chemical method to distinguish three isomeric amines having the molecular formula $\text{C}_3\text{H}_9\text{N}$. 3
- (f) (i) Propose a mechanism for the benzoin condensation reaction. What role does cyanide ion play in this reaction? 3+1=4
- (ii) Grignard reagents fail to form addition compounds with olefins. Why? 2
- (iii) Distinguish between phenol and benzyl alcohol using chemical methods. 2
- (iv) Diazonium salts can be used to prepare heterocyclic compounds. What happens when *o*-phenylenediamine is diazotized? Write the reaction. 2

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