2018

CHEMISTRY

(Major)

Paper : 2·2

(Organic Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

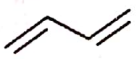
1. Answer any *seven* questions : $1\times7=7$

(a) Explain, why β-keto acids like $RCOCH_2CO_2H$ readily decarboxylate on heating.

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

p-$NO_2C_6H_4O^-$ or p-$CH_3C_6H_4O^-$

(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?

(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?

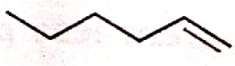
(h) The reaction of an alkene with Br_2 does not require a Lewis acid but the reaction of benzene does. Why?

2. Answer any *four* questions : 2×4=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? 1×2=2

(i)  + NBS $\xrightarrow{\text{peroxide}}$?

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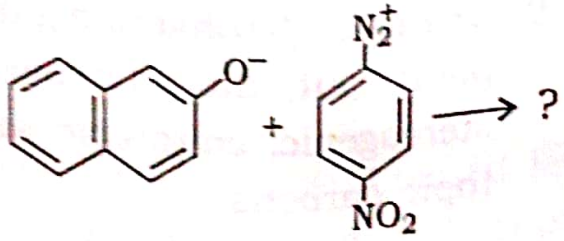
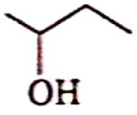
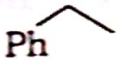
(ii) 

(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? 1×2=2

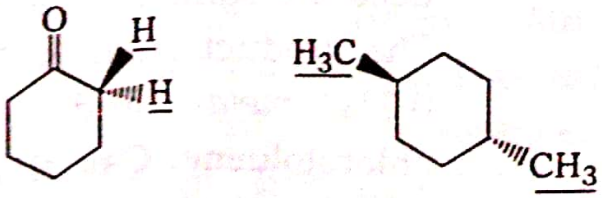
(i) 

(ii) 

3. Answer any *two* from *(a)*, *(b)* and *(c)* and any *one* from *(d)* and *(e)* : 5×3=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



(ii) Using 2,3,4-trihydroxyglutaric acid, point out the stereogenic, non-stereogenic, chirotopic and achiro-topic carbons. 3

(c) (i) Which conformer is favoured in ethylene glycol and why? 1½

(ii) Which conformer is favoured in 1,2-dibromoethane and why? 1½

(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

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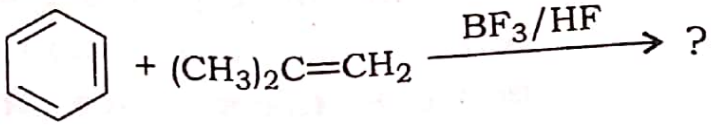
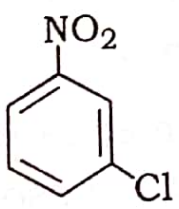
4. Answer either *(a)* or *(b)* and any *two* from *(c)*, *(d)*, *(e)* and *(f)* : 10×3=30

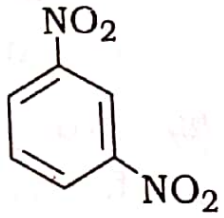
(a) *(i)* Write the product obtained for the reaction given below and propose a mechanism for the same : 1+3=4



(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





(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 decraboxylation of 2-methylbutanoic acid? 2

(Continued)

(iv) How can the compound $HOCH_2CH_2NH_2$ 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

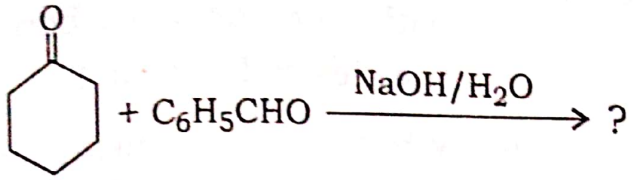
(ii) Compound *A* ($C_{10}H_{16}$) takes up 2 mols of hydrogen on catalytic hydrogenation. Ozonolysis gives two diketones, *B* ($C_6H_{10}O_2$) and *C* ($C_4H_6O_2$). Propose a reasonable structure (or structures) of *A*. 2

(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 C_3H_9N. 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*-phenylene-diamine is diazotized? Write the reaction. 2

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