Roll No. 2131182300020 Exam Code : J-22

Subject Code—56816

B.Sc. EXAMINATION

(Main & Reappear) (Batch 2018 Onwards)

(Second Semester)

CHEMISTRY

CCL-205

Organic Chemistry-II

Functional Group Organic Chemistry

Time : 3 *Hours* *Maximum Marks* : 80

Note : Q. No. **1** is compulsory. Out of remaining eight questions (divided in 4 Units), attempt *four* questions by selecting Either one question from each Unit Or by selecting *two* questions from any one Unit and remaining *two* questions from two different Units out of remaining three Units.

(Compulsory Question)

1. (a) In organic synthesis, why is Friedel-Crafts acylation preferred over Friedel-Crafts alkylation ? **2**

(b) Write the structures of all the isomers of bromoalkane C_4H_9Br and arrange them in order of decreasing reactivity towards S_N2 reactions. **2**

(c) For each pair predict the cmpound which will act as a better nucleophile in the S_N2 reaction (using alcohol as the solvent). Also explain your prediction. **2**

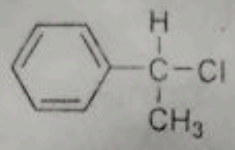
(i) NH_3 or PH_3

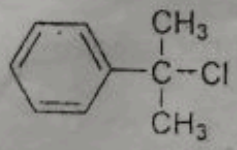
(ii) $(CH_3)_3N$ or $(CH_3)_2NH$

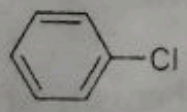
(iii) $(CH_3)_3N$ or $(CH_3)_2O$

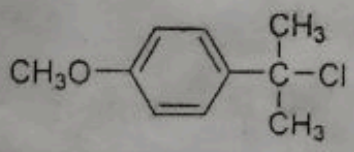
(iv) I^- or Cl^-

(d) Predict the order of relative reactivities of the following compounds in S_N1 solvolysis reactions, and explain your answer carefully : 2

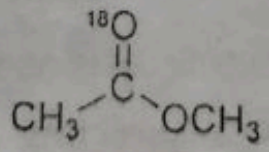
(i) 

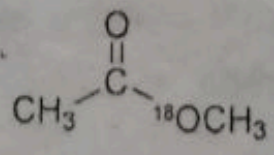
(ii) 

(iii) 

(iv) 

(e) Give the products obtained by the base catalyzed hydrolysis of the following isotopically labelled esters : 2

(i) 

(ii) 

(f) Explain, why ethers are cleaved only by acids and not by bases ? 2

(g) Explain why aldehydes undergo nucleophilic addition reactions more readily than ketones ? 2

(h) Show how resonance explains the enhanced electrophilicity of the carbonyl group upon protonation. 2

Unit I

2. (a) Discuss the mechanism of sulfonation of benzene. 6

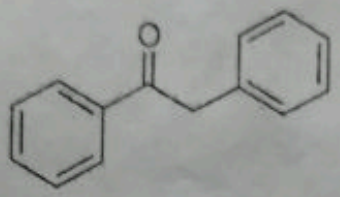
(b) Explain the following : 6

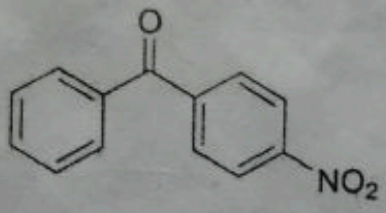
(i) Compared to aniline ($C_6H_5NH_2$), acetanilide ($C_6H_5NHCOCH_3$) is somewhat deactivated towards electrophilic aromatic substitution.

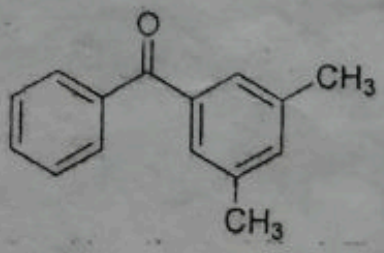
(ii) Alkoxy group acts as activating and *ortho-para* directing even though the oxygen is more electronegative than carbon.

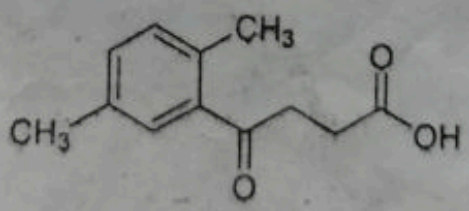
3. (a)

(c) What combination of arene and acyl chloride or acid anhydride would you choose to prepare each of the following compounds by Friedel-Crafts acylation ? 4

(i) 

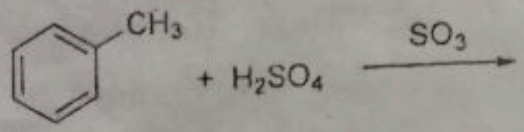
(ii) 

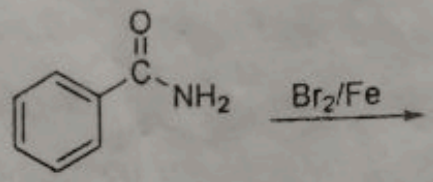
(iii) 

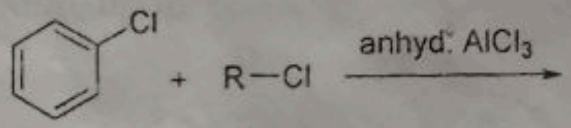
(iv) 

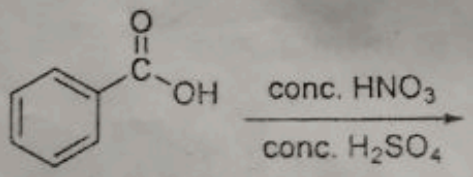
3. (a) Discuss the mechanism of chlorination of benzene. 6

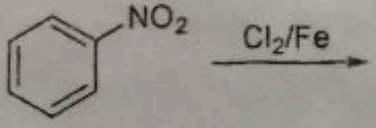
(b) Predict the major product(s) in the following reactions : 6

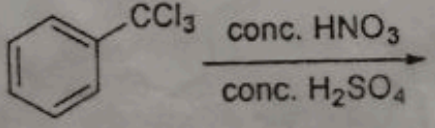
(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi) 

(c) Write the mechanism for the decarboxylation of sodium benzoate. 4

Unit II

4. (a) Taking the example of reaction of alcohols with thionyl chloride, explain the mechanism of S_Ni (substitution, nucleophilic, internal) reaction. 6

(b) Discuss the mechanism of S_N1 reaction. Also give its potential energy diagram. 6

(c) Which solvent favour S_N1 reactions and which favour S_N2 reactions ? Explain your choice ? 4

(i) CH_3OH

(ii) CH_3COOH

(iii) CH_3CN

(iv) CH_3COCH_3

5. (a) Explain each of the following statements : 6

(i) The reactions of cyanide ion with alkyl halides are slow in protic solvents such as water or alcohols but they are considerably accelerated in polar aprotic solvents such as DMSO, DMF, acetone etc.

(ii) Reactions of primary alkyl halides with NaCN give cyanides as the major product but with AgCN give isocyanides as the major product.

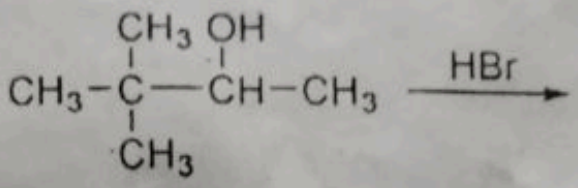
(b) Discuss addition-elimination mechanism or bimolecular displacement mechanism for nucleophilic aromatic substitution. **6**

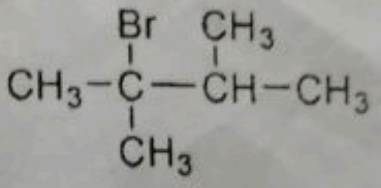
(c) Write two evidences in support of benzyne mechanism for nucleophilic aromatic substitution. **4**

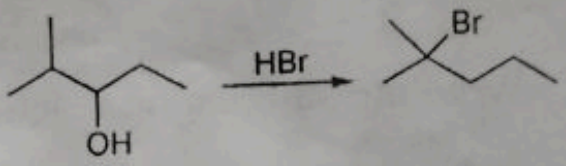
Unit III

6. (a) 3-Methylhexan-3-ol can be synthesized by three different combinations of a Grignard reagent and a ketone. Show each combination. **6**

(b) Propose a mechanism for the formation of rearranged products in the following reactions : **6**

(i) 



(ii) 

(c) Discuss the mechanism of pinacol-pinacolone rearrangement. 4

7. (a) Write the structures and reactions for the generation of electrophiles involved in the following reactions : 6

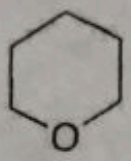
(i) Reimer-Tiemann reaction

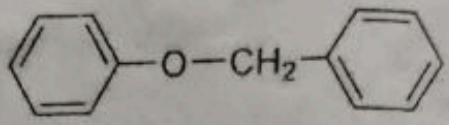
(ii) Gattermann reaction

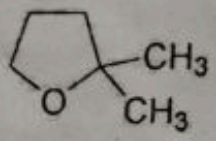
(iii) Houben-Hoesch reaction.

(b) Draw the major products obtained from heating each of the following ethers with one equivalent of HI : 6

(i) $CH_3 - CH_2 - O - CH = CH - CH_3$

(ii) 

(iii) 

(iv) 

(c) Write the sulfonation reactions of phenol and answer the following questions :

(i) Which sulfonation product is more stable, *ortho* or *para* ?

(ii) For which sulfonation product is the free energy of activation lower ?

4

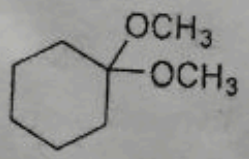
Unit IV

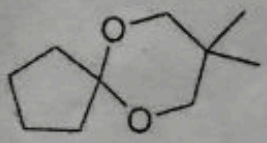
8. (a) Discuss the mechanisn of halogenation of aldehydes and ketones under basic conditions.

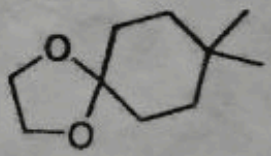
6

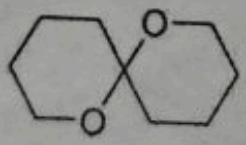
(b) Give the mechanism of Wolff-Kishner reduction. 6

(c) Each of these molecules is an acetal, that is, an compound made from an aldehyde or ketone and two alcohol groups. Which compounds were used to make these acetals ? 4

(i) 

(ii) 

(iii) 

(iv) 

9. (a) What is aldol addition reaction ? Give the mechanism for the acid-catalyzed aldol addition reactions. 6

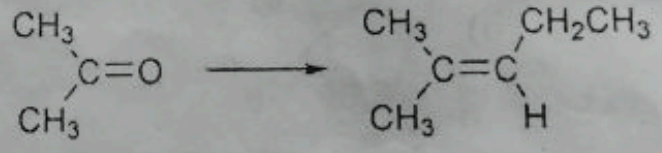
(b) Give the structure of a compound in each case with the formula C_4H_8O that satisfies the given criterion : **6**

(i) Gives a negative iodoform test but gives a 2,4-DNP derivative

(ii) Gives a positive iodoform test and a 2,4-DNP derivative

(iii) Gives a positive iodoform test but no 2,4-DNP derivative.

(c) Show how to bring about the following conversions using a Wittig reaction : **4**

(i) 

(ii)