

NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF APPLIED CHEMISTRY

SECOND SEMESTER EXAMINATIONS - MAY 2001

ORGANIC CHEMISTRY II-SCH 1202

TIME - 3 HOURS

LIBRARY USE ONLY

INSTRUCTIONS TO CANDIDATES

The paper is divided into TWO Sections, A and B. You are advised to answer **ALL** questions from Section A and **ANY THREE** questions from Section B. Section A carries 40 marks and each question in Section B carries 20 marks. Marks distribution within questions is as indicated.

TOTAL 100 Marks

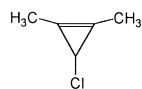
The Question Paper consists of 5 printed pages, including the top page.

SECTION A

1. (a) With the aid of an appropriate structure, define the term "aromatic" and show how it is related to Huckel's rule.

(5 marks)

- (b) Explain why compounds 1 and 2 are not aromatic.



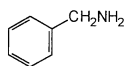
(1)



(2)

(2 x 2 1/2 marks)

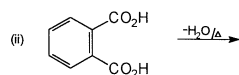
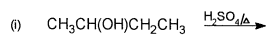
- (c) Outline a synthetic route to the compound shown below:



starting from benzene and any other reagents of your choice.

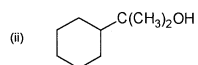
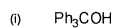
(5 marks)

- (d) Give the major product of each of the following reactions:



(2x2 1/2 marks)

- (e) Give the Grignard reagent and the ester or carbonyl compound, which are precursors for each of the following products.

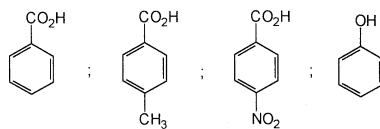


(2x2 ½ marks)

- (f) Given that D-erythrose is 2,3,4-trihydroxybutanal and that D-erythrose is epimeric with D-threose; draw a structure for threose. (5 marks)
- (g) With the aid of appropriate diagrams, distinguish between epimers and anomers. (5 marks)
- (h) The self-condensation of acetone (2-propanone) under basic conditions gives mesityl oxide (4-methyl-3-pentene-2-one). Mechanistically account for the formation of the product. (5 marks)

SECTION B

2. (a) Using the carbonium-ion stability approach, show all the possible resonance structures for the nitration of phenol i.e. *ortho*, *meta* and *para* and hence explain why the -OH group is *o/p*-directing with activation. (15 marks)
- (b) With brief explanations, arrange the following compounds in order of increasing acidity:



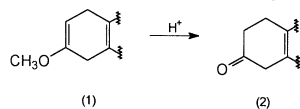
(5 marks))

- 3 (a) While 2,2-dimethoxypropane can be viewed as an ether, it is rapidly hydrolysed to methanol and acetone in dilute aqueous acid. However, diethyl ether and 1,2-dimethoxypropane are stable in this medium. Account for this difference and provide a mechanism for the acid-catalysed hydrolysis of 2,2-dimethoxypropane. (10 marks)

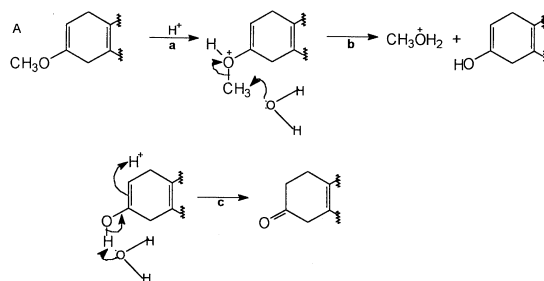
- (b) From the list given below, pick out the substituents, which are:
 (i) α/p -directing with activation
 (ii) α/p -directing with deactivation
 (iii) m -directing with deactivation
 with respect to electrophilic substitution reactions in benzene derivatives.
 $-\text{Cl}$; $-\text{NH}_2$; $-\text{OH}$; $-\text{OCH}_3$; $-\text{NO}_2$;
 $-\text{CHO}$; $-\text{CO}_2\text{H}$; $-\text{CBr}_3$; $-\text{Br}$; $-\text{I}$.

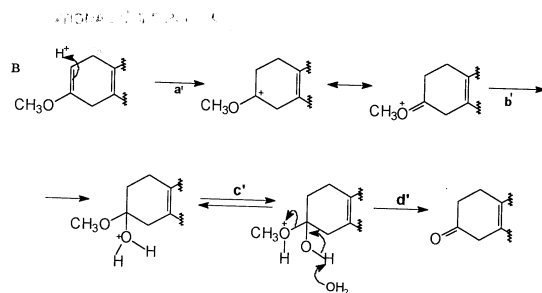
(10 marks)

- 4 (a) The following step shows the first step in the preparation of ring A of a steroid.



Below are presented two alternative mechanisms A and B for this step.





Study these mechanisms and with detailed explanations state which of the two seems more plausible.

(10 marks)

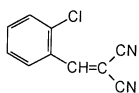
- (b) With specific examples for each state the major difference(s) between Friedel-Crafts alkylation and Friedel-Crafts acylation reactions.

(10 marks)

- (a) Nitriles usually react with carbonyl compounds to form cyanohydrins; however aromatic aldehydes behave differently. With detailed mechanism outline a route to the synthesis of benzoin, $\text{PhCOCH}(\text{OH})\text{Ph}$, starting from benzaldehyde and any other reagents of your choice.

(15 marks)

- (b) CS is a compound, which is used as a riot control agent. Outline a synthetic pathway for the preparation of CS.



CS

(5 marks)

END OF QUESTION PAPER!