

NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
END OF SEMESTER EXAMINATION – MAY/JUNE 2004
ORGANIC CHEMISTRY II – SCH1202
TIME – (3) HOURS

INSTRUCTIONS TO CANDIDATES:

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.

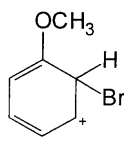
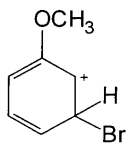
Section A

1(a) Account for the aromaticity of the following:

- (i) Cyclopentadienyl anion
- (ii) Cyclopropenyl carbonium ion

(4marks)

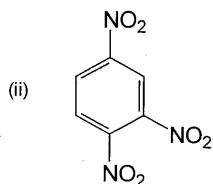
(b) Explain which of the cations **A** or **B** should be more stable



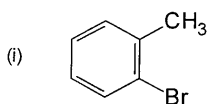
(4marks)

(c) How many isomers of a disubstituted benzene of the type C_6H_4XY are possible. Draw the structures. (4marks)

(d) What is wrong with each of the following names? Provide a correct name for the structure.



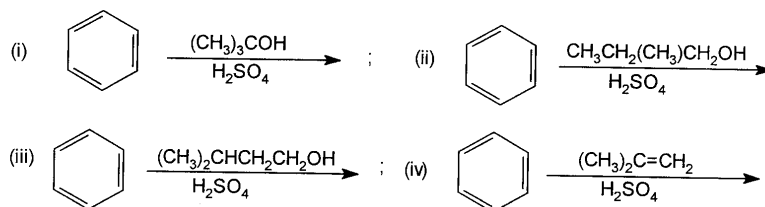
1,3,4-trinitrobenzene



o-bromomethylbenzene

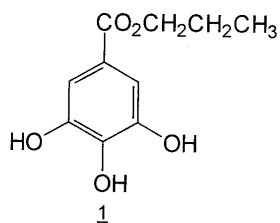
(4 marks)

(e) Which of the following pathways would produce t-butyl benzene? With appropriate mechanisms explain your answer.



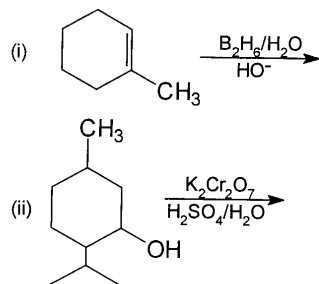
(4marks)

(f) Propylgallate **1** is used as a preservative in many products, including foodstuffs. Suggest a synthesis of this compound starting from gallic acid i.e. 3,4,5-trihydroxybenzoic acid.



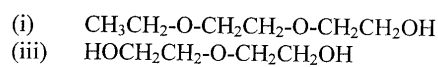
(4marks)

(g) Give the major product of each of the following reactions:



(4marks)

(h) The following compounds are commercially available for use as water-soluble solvents. Outline methods for their preparation.



(4marks)

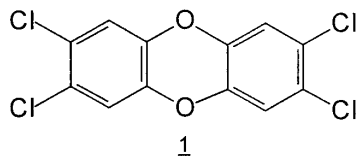
(i) With mechanistic details, show all the steps involved in the acid-catalysed hydrolysis of ethylene oxide by S_N1 mechanism.

(4marks)

(j) Dioxin **1** is reported to be a **teratogenic** agent.

(i) Show how this compound is formed from 2,4,5-trichlorophenol

(ii) In your own words explain what you understand by 'teratogenic agent'.



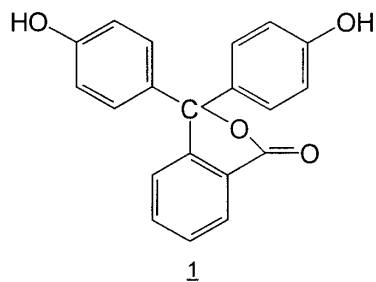
(4marks)

Section B

2. (a) Phenolphthalein **1** is a colourless solid which under basic conditions forms a dianion that is red in colour.

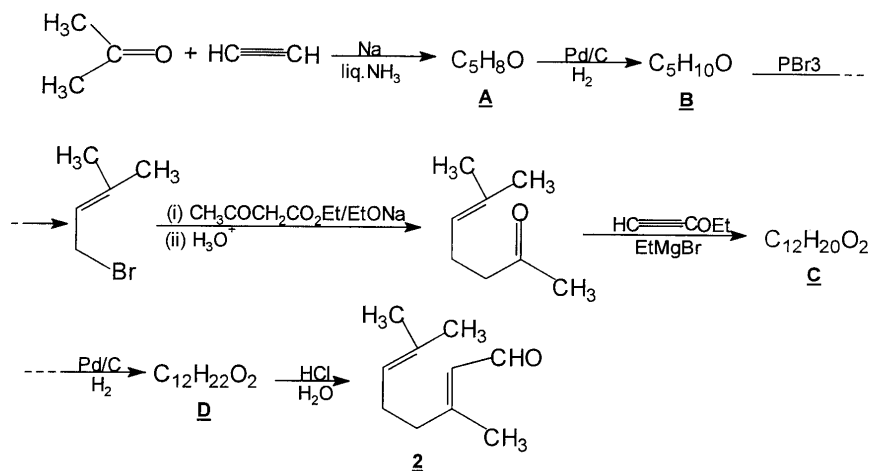
(i) Draw all the resonance structures of phenolphthalate anion

(ii) What is the structure of the degradation product of the dianion



(8marks)

(b) An important intermediate in the synthesis of β -carotene is citral **2**. For the following sequence of reactions give the structures of intermediates **A** to **D**.

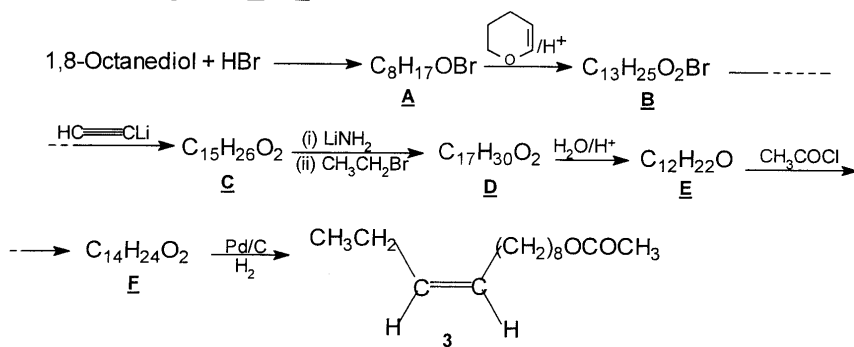


(8marks)

(c) Give two examples of reactions which illustrate the limitations of Friedel-Crafts alkylation reactions.

(4marks)

3. (a) An insect pheromone **3** has been prepared using the procedure shown below. Using the structure of the pheromone **3** and the given starting material as guides, give all the intermediate compounds **A** to **F**.



(12marks)

(iii) For maximum biological activity, there should be present at least 4% of its geometrical isomer. How could you modify the above procedure to obtain this isomer?

(2marks)

3 (b) Arrange the compounds of each set in order of decreasing reactivity toward bromine:

- (i) anisole (methoxybenzene), chlorobenzene, nitrobenzene and phenol
- (ii) anisole, *m*-hydroxyanisole, *o*-methylanisole and *m*-methylaniline
- (iii) *p*-C₆H₄(OH)₂, *p*-CH₃OC₆H₄OH and *p*-C₆H₄(OCH₃)₂

(6marks)

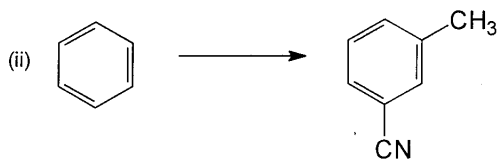
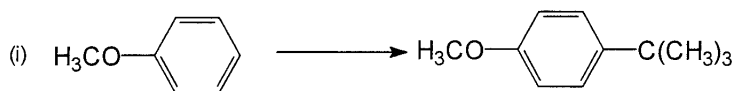
4(a) Two moles of aromatic aldehydes could be condensed together in the presence of cyanide to give α -hydroxy ketones.

- (i) Give a comprehensive mechanistic account of this reaction in the formation of benzoin. (10marks)
- (ii) List three key roles that are played by cyanide in this reaction. (6marks)

(b) Give two starting materials that would react together to give 2-ClPhCHC(CN)₂. (4marks)

5 (a) Explain in detail why Friedel-Crafts reactions of benzene with 1-chloropropane and 2-chloropropane both give isopropylbenzene as the only product. (6marks)

(b) Give a comprehensive account for each of the following transformations:

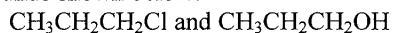


(6marks)

(c) Propylene oxide can be converted into 1,2-propanediol by the action of either dilute acid or dilute base. When optically active propylene oxide is used, the 1,2-diol obtained from the acid hydrolysis has a rotation opposite to that obtained from alkaline hydrolysis. What is the most likely interpretation of these observations?

(6marks)

(d) Describe a simple chemical test, which would distinguish between the two compounds shown below:



(2marks)

END OF PAPER

