

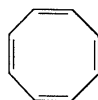
NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
END OF SEMESTER EXAMINATIONS – MAY 2002
ORGANIC CHEMISTRY II – SCH 1202
TIME – (3) THREE HOURS

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) Draw structures for all the isomeric dichlorotoluenes. (4 marks)
- (b) Account for the aromaticity of the cyclopentadienyl anion. (4 marks)
- (c) Which of the following compounds would you expect to show aromatic properties? Explain your answer.



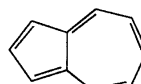
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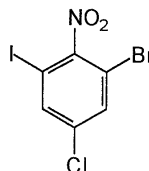
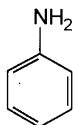
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(4 marks)

- (d) Give IUPAC names to each of the following compounds.



(4 marks)

- (e) Explain the following observations:
- (i) Treatment of benzene with excess fuming nitric acid and sulphuric acid yields *m*-dinitrobenzene but not the trinitrated product.
- (ii) Under the same conditions toluene yields 2,4,6-trinitrotoluene. (4 marks)

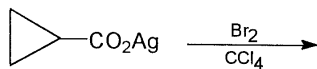
(f) Give a molecular-orbital representation of benzyne and state what factors are responsible for the instability of the molecule.

(4 marks)

(g) Explain why a completely random (i.e. statistical) attack on a monosubstituted benzene should lead to 40% *ortho* and 40% *meta* attack but only 20% *para* attack (Assume that the substituted carbon is not attacked).

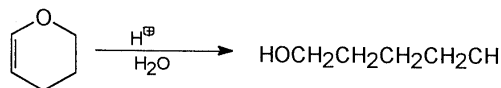
(4 marks)

(h) Give the major product for the following reaction:



(4 marks)

(i) Give a mechanism for the following transformation.



(4 marks)

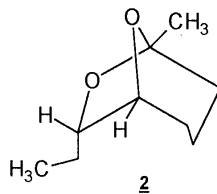
(j) Give the reactants which would react under basic conditions to give the compound shown below:



(4 marks)

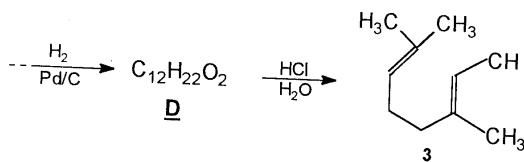
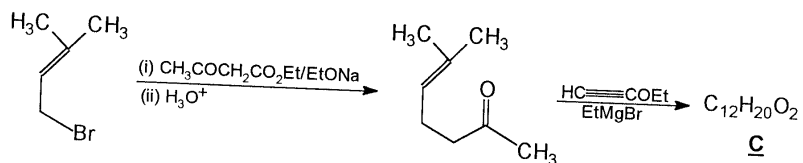
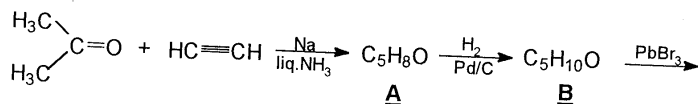
SECTION B

2 (a) Given $\text{EtC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ and any other inorganic reagents, devise a synthetic route to compound **2**, the sex attractant of the Western pine beetle.



(8 marks)

2. (b) An important intermediate in the synthesis of β -carotene is citral **3**, for the following sequence of reactions give the structures of the intermediates **A**



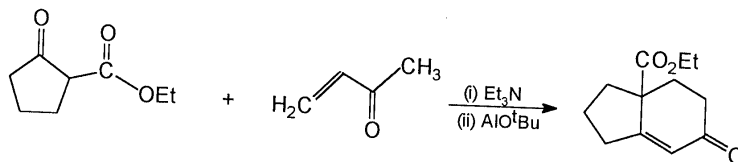
(8 marks)

- (c) The products of the mononitration of phenol can be separated from each other by steam distillation. A compound can only be steam-distilled only if it is relatively volatile and is appreciably insoluble in water.

- (i) Predict which nitrophenol will steam distil.
- (ii) Why do the isomers have such different properties.

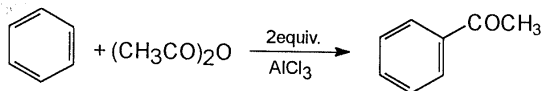
(4 marks)

3. (a) Give a comprehensive mechanism for the two step reaction shown below.



(6 marks)

3. (b) Anhydrides can be used in Friedel-Crafts acylation reactions in place of acid chlorides. Give a mechanism for the following reaction and explain why two equivalents of AlCl_3 must be used.



(6 marks)

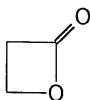
- (c) Devise syntheses for each of the following compounds:

- 1,2,3-trichlorobenzene starting from aniline and any other reagents of your choice.
- 2,6-dibromophenol starting from a monosubstituted benzene and any other reagents of your choice.

(2x4 marks)

4. (a) Given that hydrolysis of propiolactone **4** in H_2^{18}O gives $\text{H}^{18}\text{OCH}_2\text{CH}_2\text{CO}_2\text{H}$ when the reaction is catalysed by acid and $\text{HOCH}_2\text{CH}_2\text{CO}^{18}\text{OH}$ when it is catalysed by base; with mechanistic details, give the products of:

- acid-catalysed methanolysis and
- base-catalysed methanolysis



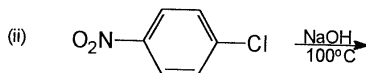
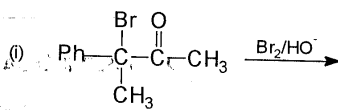
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(8 marks)

- (b) In aldol and Claisen reactions, a pair of carbonyl compounds react to yield a condensation product. The aldol is a reversible reaction that favours the formation of the product in many cases. The Claisen reaction strongly favours the starting materials. What stabilizing factor occurring only in the Claisen reaction can be cited to explain this difference.

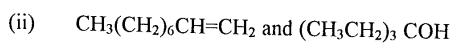
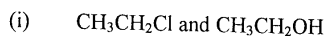
(4 marks)

- (c) With mechanistic details give the major product of each of the following reactions:



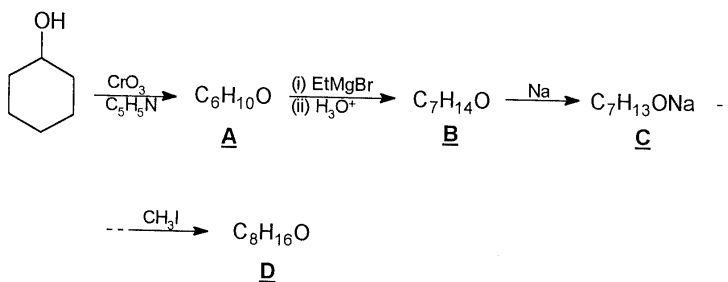
(2x4marks)

5. (a) Describe a simple chemical test which would distinguish between members of the following sets of compounds:



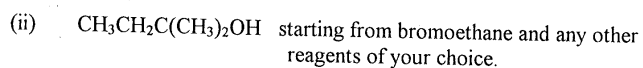
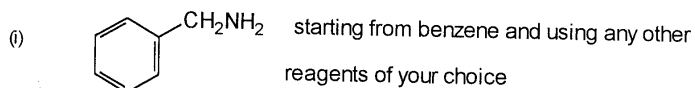
(2x4 marks)

- (b) In the following sequence of reactions, draw the structures of compounds A to D shown below:



(8 marks)

- (c) Suggest a synthetic route to each of the following (no mechanism required).



(4 marks)

END OF QUESTION PAPER.