

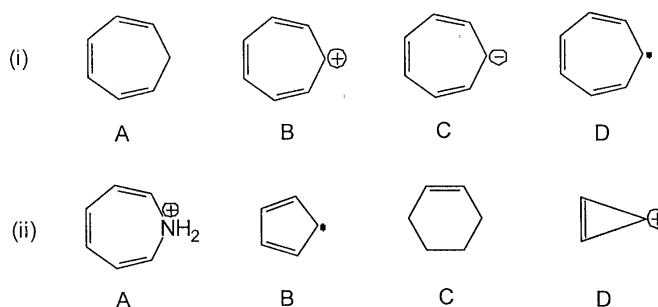
NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
END OF SEMESTER EXAMINATIONS – DECEMBER 2002
ORGANIC CHEMISTRY II – SCH 1202
TIME – (3) THREE HOURS

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) From each of the lists below, choose the species which is/are aromatic.



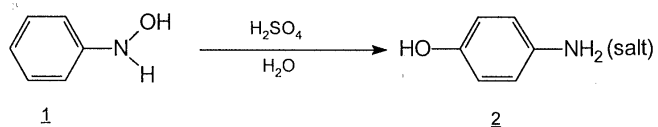
(4 marks)

- (b) Which of the statements from each of the lists below is generally true of aromatic compounds?

- (i)
- A. Electrophilic addition is a common reaction type.
 - B. Reactions forming aromatic compounds occur relatively readily.
 - C. Aromatic compounds have relatively large heats of hydrogenation.
 - D. The H/D isotope effect is large for ring substitution reactions.
- (ii)
- A. Nucleophilic addition is a common reaction type.
 - B. Reactions forming aromatic compounds are relatively difficult.
 - C. Aromatic compounds have relatively small heats of hydrogenation.
 - D. The H/D isotope effect is large for ring substitution reactions.

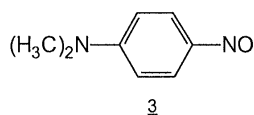
(4 marks)

- (c) Phenylhydroxylamine 1 is unstable in dilute H_2SO_4 . It is isomerized, under these conditions, to 4-hydroxylamine 2.



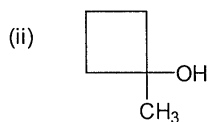
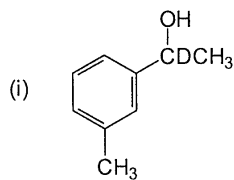
Suggest a mechanism for this transformation. (4 marks)

- (d) *p*-Nitroso-*N,N*-dimethylaniline 3 is a solid. Unlike unsubstituted nitrosobenzene, this compound exists as a monomer in the solid state. This suggests that *p*-nitroso-*N,N*-dimethylaniline is more stable than nitrosobenzene. Account for the stability of 3.



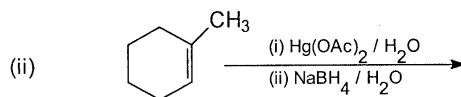
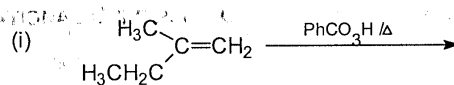
(4 marks)

- (e) For each reaction, give the Grignard reagent and carbonyl compound which would react to give each of the following compounds.



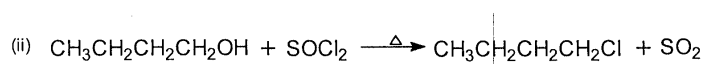
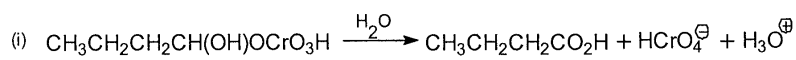
(4 marks)

(f) Give the major product of each of the following reactions.



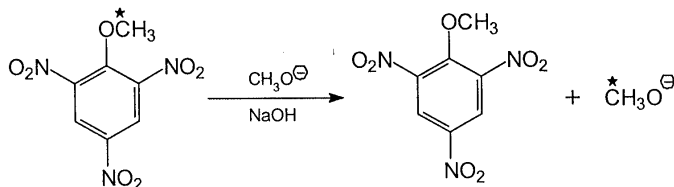
(4 marks)

(g) Give a mechanism that accounts for each of the following transformations.



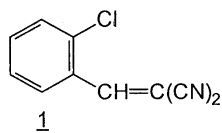
(4 marks)

(h) When 2,4,6-trinitro[methyl- ^{14}C]anisole **1** is treated with methanolic sodium methoxide at room temperature, the radioactive label is transferred from the starting material to the solvent. Give a mechanism together with resonance structures of the intermediate, that explains this transfer of label.



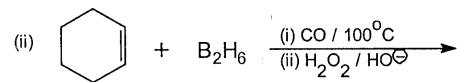
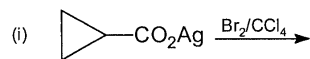
(4 marks)

- (i) CS 1 is a riot control agent which is formed by reacting a monosubstituted aldehyde with malononitrile [CH₂(CN)₂]. Give a mechanism for the formation of CS from the aldehyde.



(4 marks)

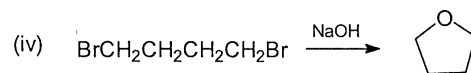
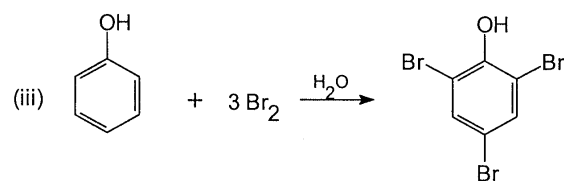
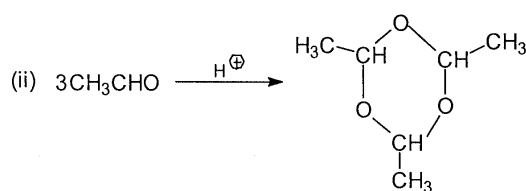
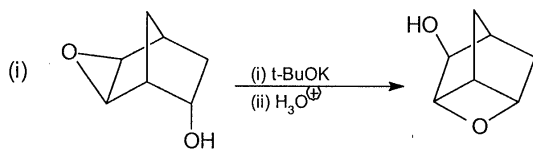
- (j) Give the product of each of the following reactions:



(4 marks)

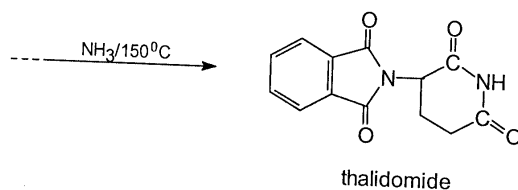
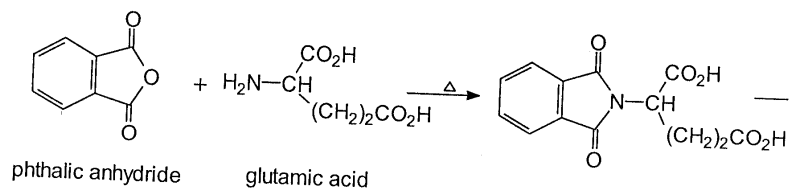
SECTION B

2. (a) Give a mechanism that accounts for each of the following reactions:



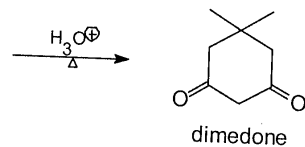
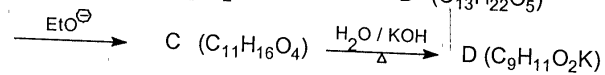
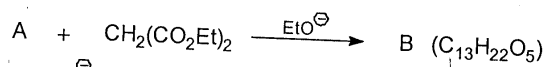
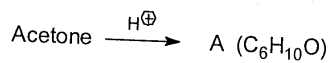
(4x3 marks)

- (b) Thalidomide, the sedative and sleep-producer that led to many deformed babies in the 1960s is synthesized as shown below. Suggest mechanisms for these transformations.



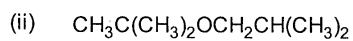
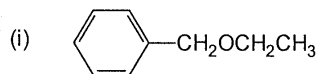
(8 marks)

3. (a) In the following sequence of reactions, identify the lettered compounds [no mechanism(s) required].



(12 marks)

- (b) Specify the two Williamson syntheses which could be used to prepare each of the following ethers.



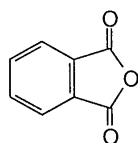
(4 marks)

- (c) When a mixture of *cis*-1,2-dihydrocyclopentane and acetone, containing a trace of mineral acid, is boiled in a Dean-Stark apparatus, a product with the molecular formula $\text{C}_8\text{H}_{14}\text{O}_2$ is formed.

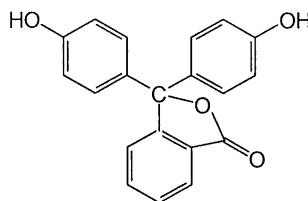
- (i) What is its structure?
(ii) Suggest why a similar reaction does not occur with *trans*-1,2-dihydrocyclopentane.

(4 marks)

4. (a) One of the most interesting Friedel-Crafts acylation reactions undergone by phenol with phthalic anhydride 1 is the formation of phenolphthalein 2 (under H_2SO_4 catalysis). Give a mechanism that accounts for the formation of this product.



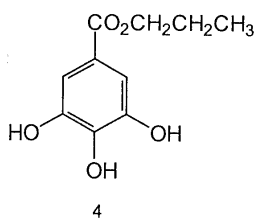
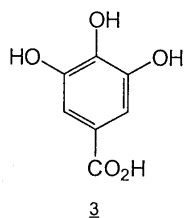
1



2

(8 marks)

- (b) Propyl gallate **4** is used as a preservative in a number of products, including foods. Suggest a synthesis of this compound, starting from gallic acid **3** and using any other reagents you may need.



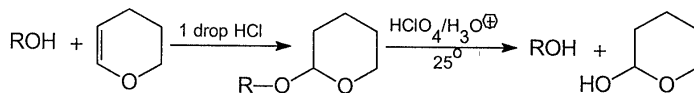
(4 marks)

- (c) Explain why:

- (i) *trans*-2-chlorocyclohexanol reacts, under basic conditions, to give cyclohexene oxide whereas the *cis*-isomer gives cyclohexanone.
 (ii) benzyl alcohol (PhCH₂OH) reacts instantly with the Lucas reagent even though it is only a primary alcohol.

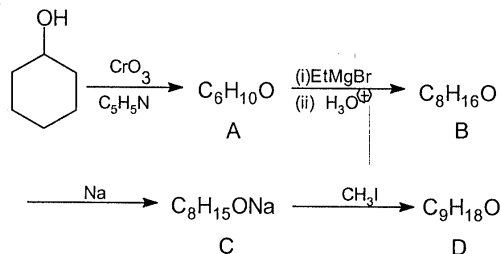
(2x4 marks)

5. (a) Provide detailed mechanisms for the following transformation:



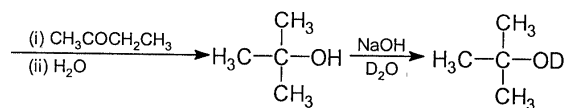
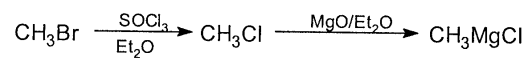
(4 marks)

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



(4 marks)

- (c) Identify the error(s) in each of the proposed syntheses. In each case, the final product shown is the desired product. Having identified the error(s), show how you could modify the synthesis to give the desired product.



(8 marks)

END OF QUESTION PAPER.