

**UNIVERSITY OF SWAZILAND
FIRST SEMESTER FINAL EXAMINATION 2010**

TITLE OF PAPER : Introductory Organic Chemistry

COURSE NUMBER : C303

TIME : Three Hours

INSTRUCTIONS : Answer any **FOUR Questions**. Each
Question carries 25 Marks.

This Examination Paper Contains 9 (Nine) Printed Pages Including This
Page

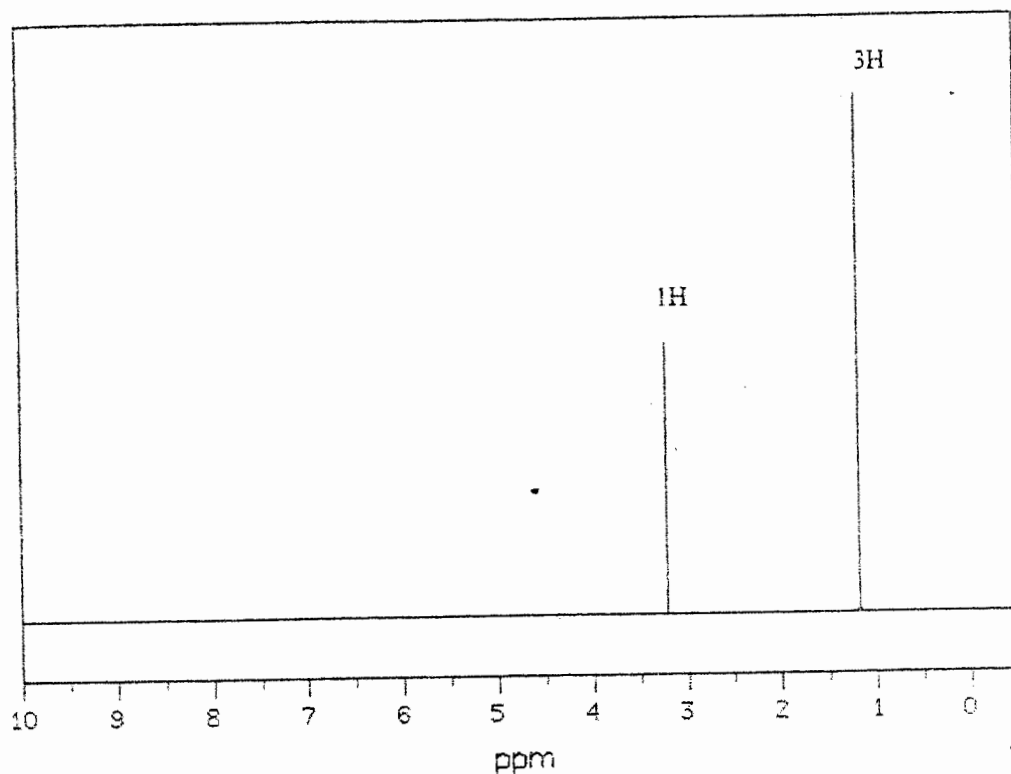
*You must not open this paper until the Chief Invigilator so has
granted permission to do.*

SECTION A
ORGANIC STRUCTURE ELUCIDATION

Question 1

- (a) Answer the following questions for compound A, molecular formula, (C₅H₁₂O) whose ¹H NMR is shown

C₅H₁₂O



- (i) Calculate the degree of unsaturation. **(2 marks)**
- (ii) Describe each signal in the ¹H NMR spectrum in terms of its integration, splitting and chemical shift. **(6 marks)**
- (iii) Draw the structure of compound A that matches the ¹H NMR data, **(4 marks)**

(b) Identify the C_3H_5Br isomers on the basis of the following information:

(i) Isomer A has the 1H NMR spectrum shown in figure 1.1. **(6 marks)**

The 200-MHz 1H NMR
Spectrum of isomer A

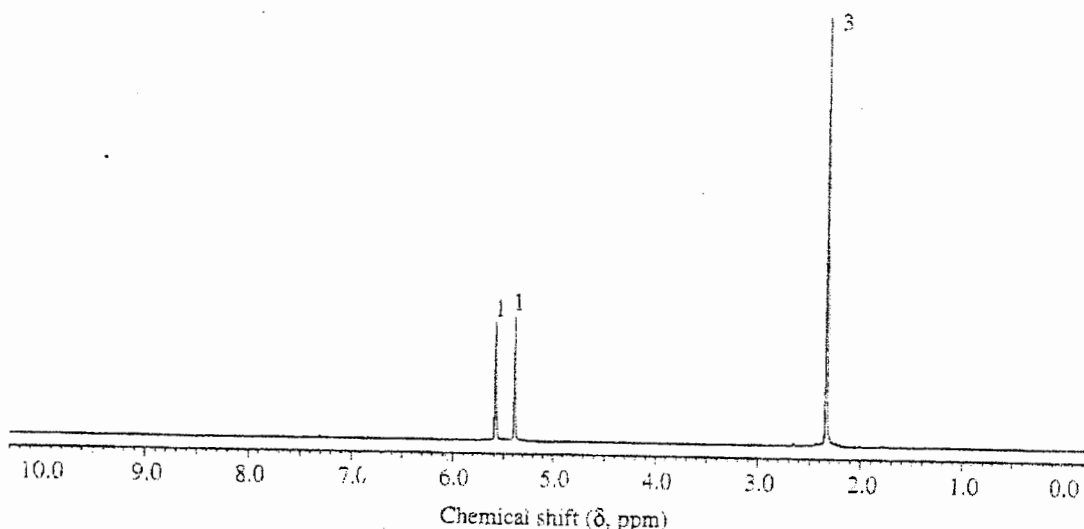


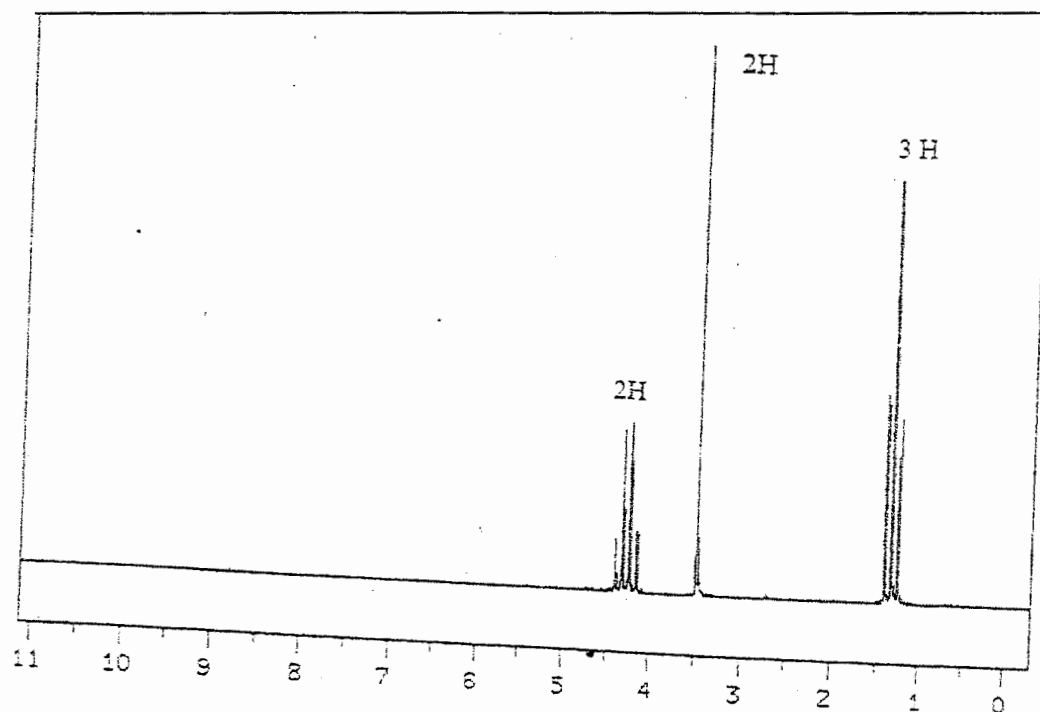
Figure 1.1 : Spectrum of C_3H_5Br

(ii) Isomer B has three peaks in its ^{13}C NMR spectrum: δ 32.6 (CH_2); 118.8 (CH_2); and 134.2 (CH). **(3 marks)**

(iii) Isomer C has two peaks in its ^{13}C NMR spectrum. δ 12.0 (CH_2); and 16.8 (CH). The peak at lower field is only half as intense as the one at higher field. **(4 marks)**

Question 2

To answer the following questions, consider the data and ^1H NMR spectrum below. The mass spectrum of this compound shows a molecular ion at $m/z = 113$, the IR spectrum has characteristic absorption at 2270 and 1735 cm^{-1} , and the ^{13}C NMR spectrum has five (5) signals.

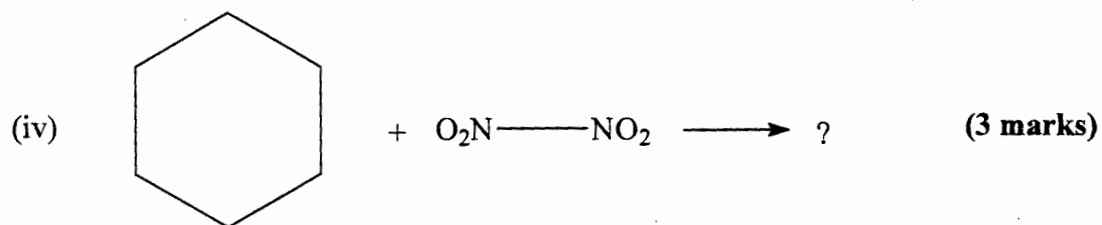
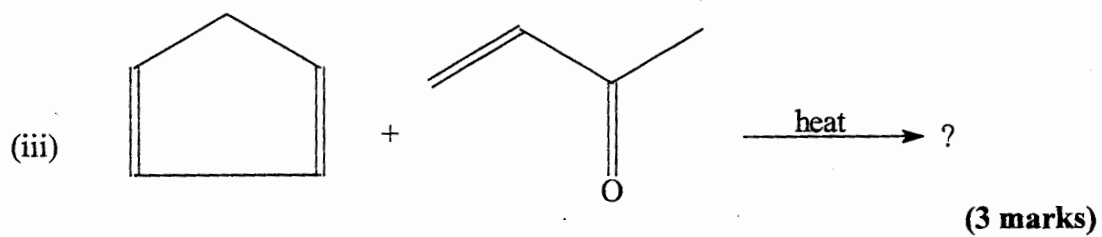
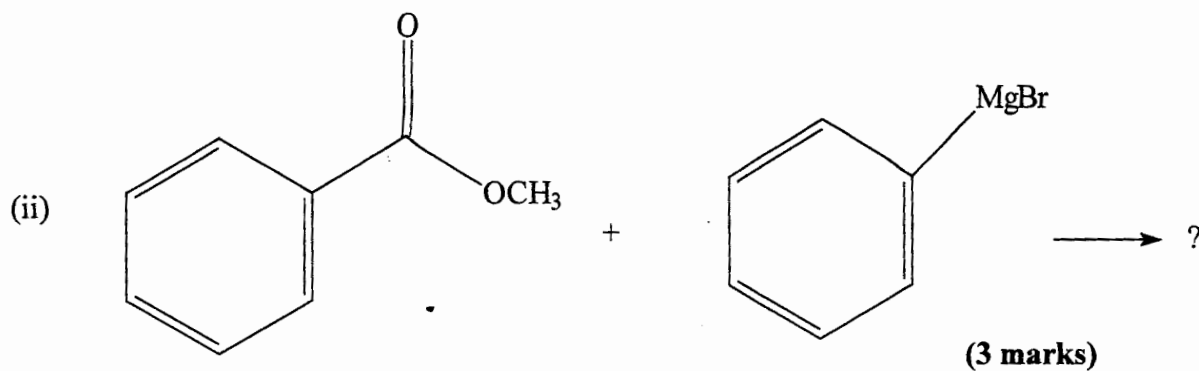
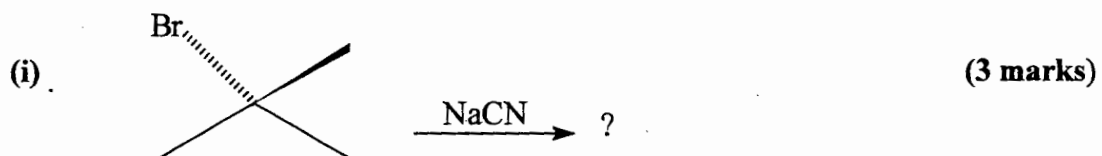


- Based on the mass spectral data and the IR data, what functional groups are present in this compound? **(4 marks)**
- How many types of non-equivalent protons are there in this molecule? **(4 marks)**
- Comment or describe the signal at 3.5 delta in terms of its integration, splitting pattern and chemical shift. **(4 marks)**
- Describe the signals at 4.35 delta and 1.3 delta in terms of their integration splitting and chemical shift. **(4 marks)**
- What is the significance of ^{13}C NMR data? **(4 marks)**
- Analyze all the information deduced from the data provided and then propose a structure for this compound? **(5 marks)**

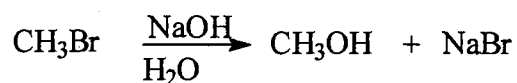
SECTION B:
ORGANIC REACTIONS AND THEIR MECHANISMS

Question 3

- (a) Draw the structure of the major product expected from each of the following reactions:



- (b) Reaction of bromomethane with sodium hydroxide in water forms methanol.



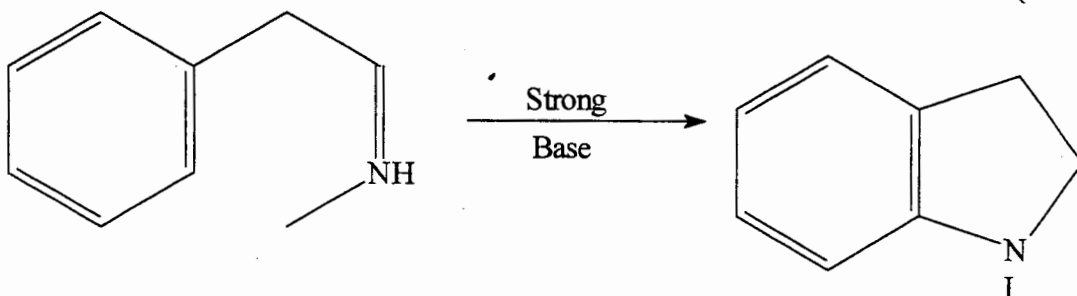
Bromomethane . methane

If sodium iodide is added to the reaction mixture the rate of methanol formation is dramatically increased (i.e. sodium iodide is catalyst).

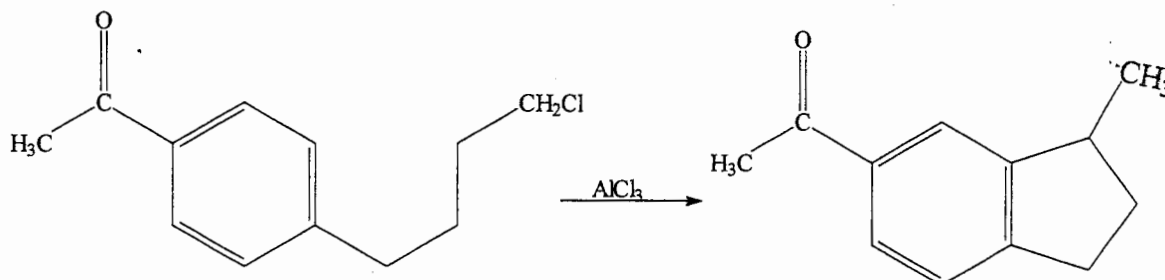
- (i) Write the complete reaction mechanism for the formation of methanol in the above reaction. **(3 marks)**
- (ii) Write a reaction pathway that accounts for the effect of added NaI. **(3 marks)**
- (iii) Draw a reaction energy diagram showing the two different reaction pathways. (i.e., catalysed and uncatalysed). Indicate structures for all energy minima in the diagram. **(4 marks)**
- (iv) Explain why adding NaI increases the reaction rate. **(3 marks)**

Question 4

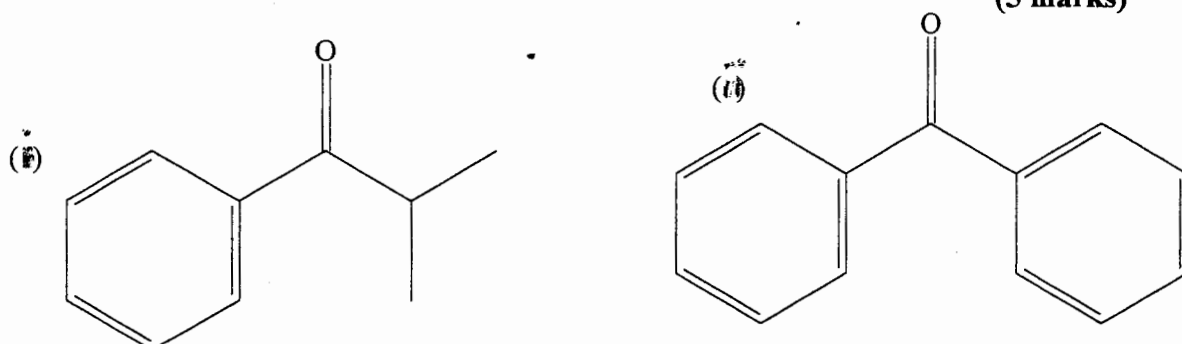
- (a) Write the complete stepwise mechanism for the following reaction showing all intermediate structures and all electron flow with arrows. **(5 marks)**



- (b) Propose a mechanism to account for the following reaction. **(5 marks)**

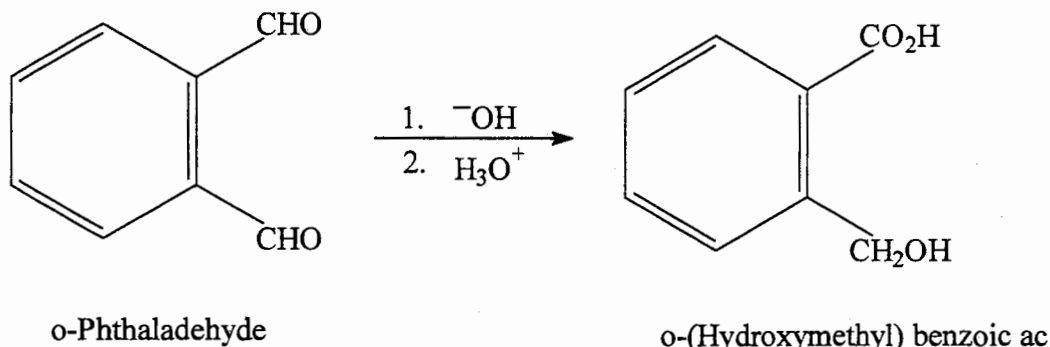


- (c) Identify and draw the structure of the carboxylic acid chloride that might be used in a Friedel-Craft acylation reaction to prepare each of the following acylbenzenes. **(5 marks)**



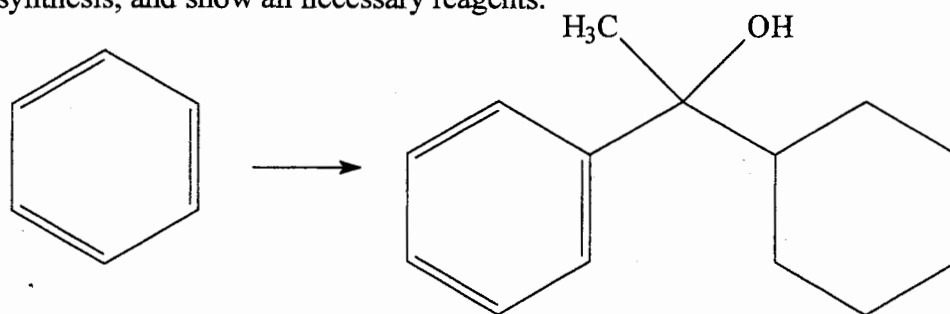
- (d) (i) Reaction of 3-dimethylbut-1-ene with HBr leads to an alkylbromide $\text{C}_6\text{H}_{13}\text{Br}$. On treatment of this bromide with KOH in methanol, elimination of HBr to give an alkene occurs and a hydrocarbon that is isomeric with the starting alkene is formed. What is the structure of this hydrocarbon, and how do you think it is formed from the alkylbromide? **(5 marks)**

- (ii) When o-phthalaldehyde is treated with base, o-hydroxymethylbenzoic acid is formed. Show the mechanism for this reaction. **(5 marks)**



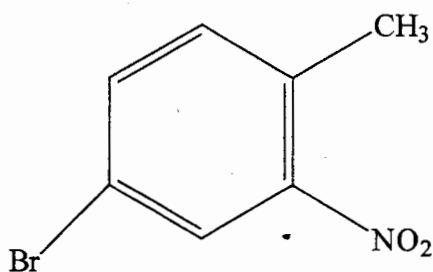
Question 5

- (a) Outline the synthetic steps necessary to carry out the conversion below. You may use any organic or inorganic reagents you need. Show the structures of all intermediate compounds that would probably be isolated during the course of your synthesis, and show all necessary reagents.



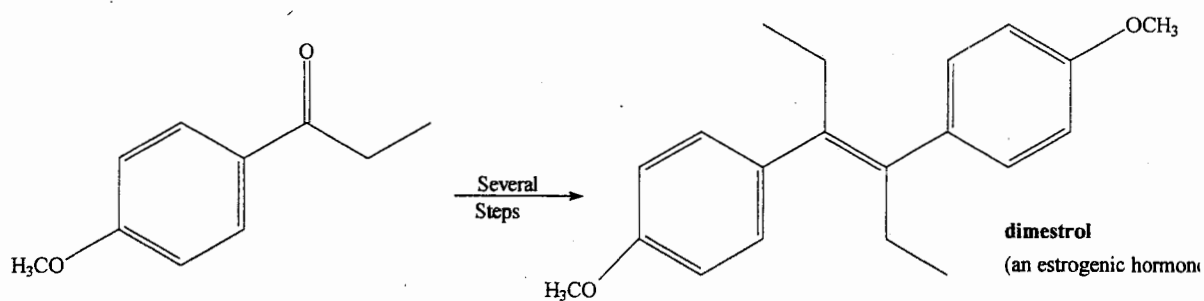
(8 marks)

- (b) Outline a synthetic route from benzene to 4-bromo-2-nitrotoluene. Show the major reagents for each step. **(8 marks)**



4-Bromo-2-nitrotoluene

- (c) Propose a synthesis of Dimestrol starting from *p*-methoxypropiophenone as the only source of carbon.

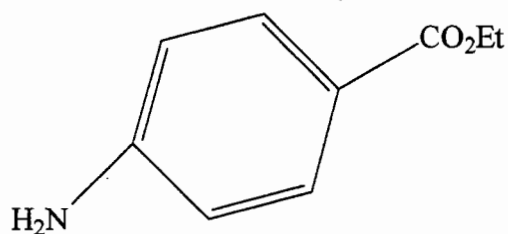


dimestrol
(an estrogenic hormone)

(9 marks)

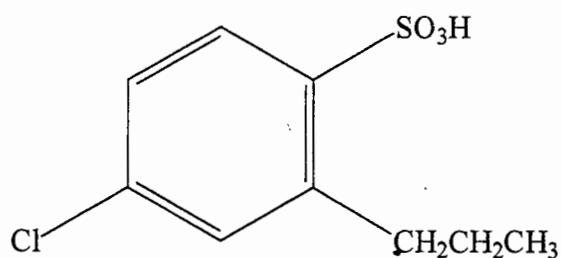
Question 6

- (a) Ethyl-4-aminobenzoate (Benzocaine) is a local anaesthetic with a range of applications. Outline a laboratory synthesis route to benzocaine from benzene. **(8 marks)**



Benzocaine

- (b) Describe an efficient synthesis of 4-chloro-2-propylbenzenesulphonic acid. Show all the reagents for each step of the route. **(8 marks)**



4-chloro-2-propylbenzenesulphonic acid

- (c) Show how you would accomplish the following transformation. More than one step may be required. Show all reagents and all intermediate structures. **(9 marks)**

