UNIVERSITY OF SWAZILAND
FINAL EXAMINATION 2013

TITLE OF PAPER	:	Organic Chemistry
COURSE NUMBER	:	C303
TIME	:	Three Hours
INSTRUCTIONS	:	Answer **Any Two** Questions from **Section A** and **Any Other Two** Questions from **section B.** Each Question carries 25 Marks.

This Paper contains 9 (nine) printed pages.

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

SECTION A

MS, IR and NMR Instrumental Methods of Structure Determination

Question 1

(a) Briefly summarize the theoretical principles on which the ^{1}H and ^{13}C NMR Spectroscopy are based. (5 marks)

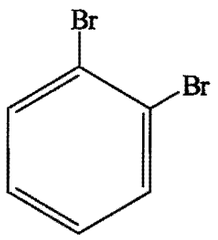
(b) Explain why:

(i) All protons in a molecule do not normally absorb radio-frequency (rf) energy at the same time? (2marks)

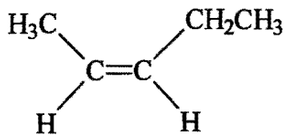
(ii) Only a few mg of sample are needed for ^{13}C NMR spectra and only a few μg of sample are needed for ^{1}H NMR spectra. (2 marks)

(iii) Coupling between the spins of two ^{13}C nuclei is hardly seen. (2 marks)

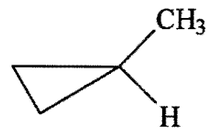
(c) For each of the following compounds below indicate on a chart the number of signals you would expect the molecule to have in the normal broadband decoupled ^{13}C spectra;



(i)
(2 marks)



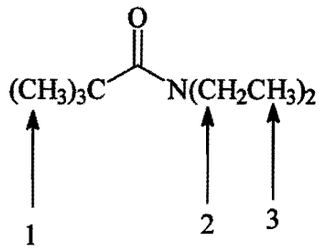
(ii)
(2 marks)



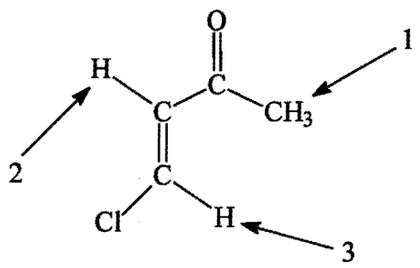
(iii)
(2marks)

(iv)
(2 marks)

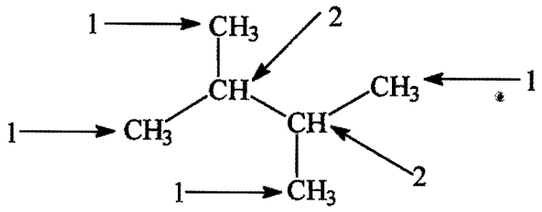
(d) Predict the splitting patterns you would expect for each proton in the molecules below:



(i)
(3 marks)

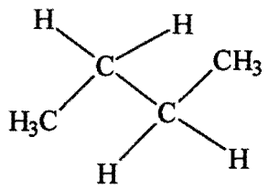


(ii)
(3 marks)



(iii)
(2 marks)

(e) Refer to the structure of n-butane shown below and answer the following questions.



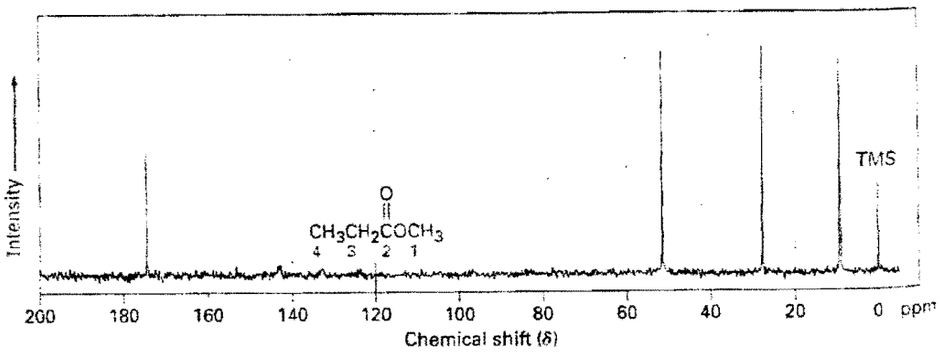
(1) Draw the structure of butane and indicate by arrow the:
- (i) Homotopic protons (1 mark)
- (ii) Enantiotopic protons and (1 mark)

(2) Which of the protons named in (i), (ii) and (iii) would show:
- (iii) Different NMR absorption (1 mark)
- (iv) The same NMR absorption. Explain your answer (1 mark)

(3) (v) How many signals would you expect to find in the 1HNMR spectrum of 1-bromobutane. (1 mark)

Question 2

(a) (i) Assign the resonances in the ^{13}C NMR spectrum of methyl propanoate, $CH_3CH_2CO_2CH_3$



^{13}C NMR Spectrum of Methyl Propanoate

(ii) Propose a structure for an aromatic hydrocarbon $C_{11}H_{16}$, that has the following ^{13}C NMR data. (6 marks)

Broadband decoupled ^{13}C NMR: 29.5, 31.8, 50.2, 125.5, 127.5, 130.3, 139.8 δ

DEPT - 90 : 125.5, 127.5, 130.3 δ
DEP - 135 : Positive Peaks at 29.5, 125.5, 127.5, 130.3
* Negative Peak at 50 δ.

(iii) It is well known that addition of hydrogen bromide (HBr) to a terminal alkyne leads to the Markovnikov addition product with the bromine atom bonding to the more highly substituted carbon. Explain how ^{13}C NMR can be used to **identify** the product of the addition of 1 equivalent of HBr to hex-1-yne.? (5 marks)

(b) (i) Propose a structure for a compound $C_5H_{12}O$, that fits the following:

^{1}HNMR data : 0.92 δ (3H, triplet, J = 7 Hz)
1.2 δ (6H, singlet), 1.50 δ (2 H, quartet, J = 7 Hz)
1.64 δ (1H broad singlet) (6 marks)

(ii) The carbon resonance of 3-methyl-2-butanone occurs at 208.7 ppm down field from TMS. How many hertz downfield from TMS would this carbonyl carbon absorb if the spectrometer used to measure this absorption were operating at 200 HMz? (5 marks)

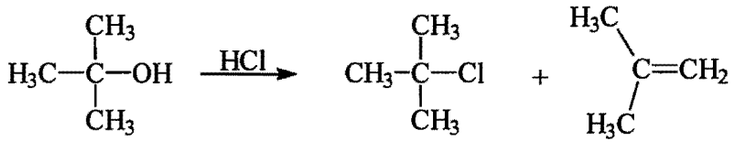
(iii) When measured on a spectro meter operating at 200 MHz chloroform ($CHCl_3$) shows a single sharp absorption at 7.3 δ.

i. How many parts per million down field from TMS does chloroform absorb? (2 marks)

(c) How many hertz down field from TMS would chloroform absorb if the measurement were carried out on a spectrometer operating at 360 MHz? (2 marks)

(d) What would be the position of the chloroform absorption in δ units when measured on a 360 MHz spectrometer? (2 marks)

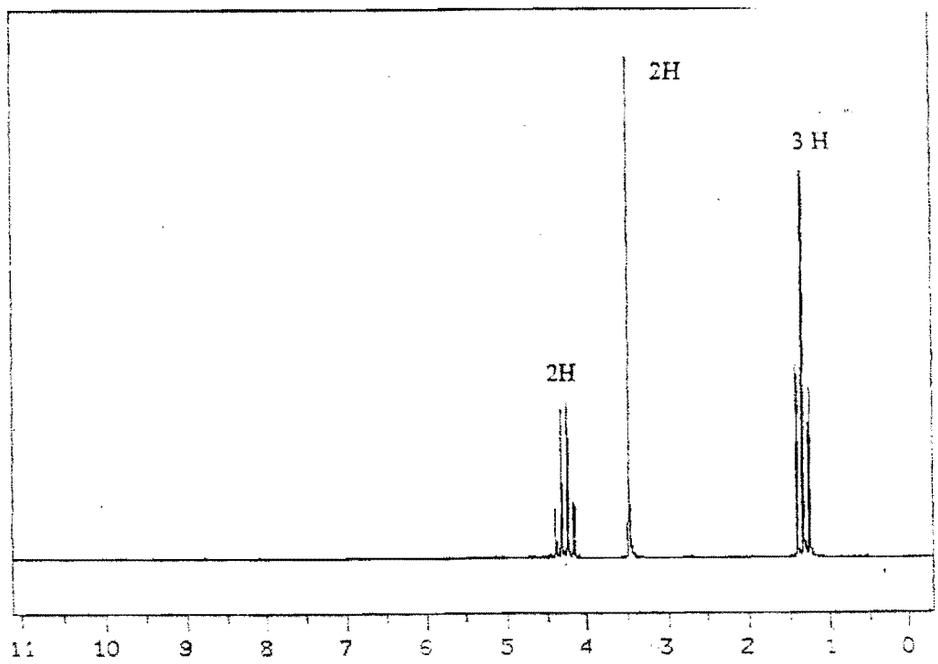
(e) Treatment of tert-butyl alcohol with hydrogen chloride yields a mixture of tert-butyl chloride (S_N1) product and 2-methyl propene (E1 product). After chromatographic separation. How would you use ^{1}HNMR to help you decide which was which. (2 marks)



(SN1 product) (E1 product)

Question 3

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



(a) Based on the mass spectral data and the IR data, what functional groups are present in this compound? (6 marks)

(b) How many types of non-equivalent protons are there in this molecule? (6 marks)

(c) Comment or describe the signal at 3.5 delta in terms of its integration, splitting pattern and chemical shift. (6 marks)

(d) Describe the signals at 4.35 delta and 1.3 delta in terms of their integration splitting and chemical shift. (6 marks)

(e) What is the significance of ^{13}C NMR data? (6 marks)

(f) Analyse all the information deduced from the data provided and then propose a structure for this compound? (3 marks)

SECTION B

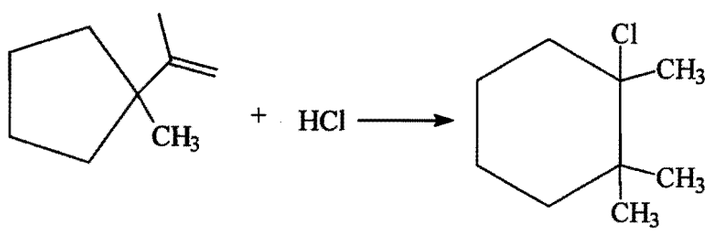
Reactions and Synthesis of Organic Compounds

Question 4

(a) There are four particularly broad types of organic reactions. Name and explain how each type of reaction occurs (8 marks)

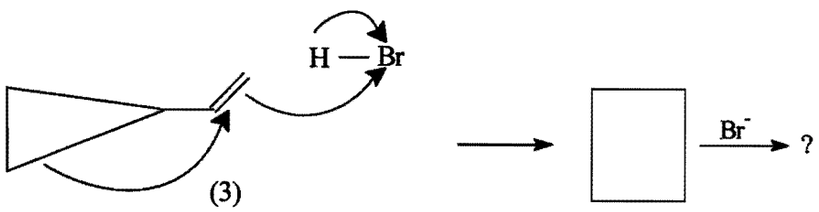
(b) What is a mechanism of a reaction? Name and explain the two general kinds of mechanism by which organic reactions take place. (6 marks)

(c) Addition of HCl to 1-isopropenyl-1-methyl cyclopentane (1) yields 1-chloro-1,2,2-trimethylcyclohexane (2). Propose a mechanism, showing the structures of the intermediates and using curved arrows to indicate electron flow in each case. (10 marks)



(1) (2)

(d) Vinylcyclopropane (3) reacts with HBr to yield a rearranged alkyl bromide. Follow the flow of electrons as represented by the curved arrows, show the structure of the carbocation intermediate in the box and show the structure of the final product. (9 marks)



(3)

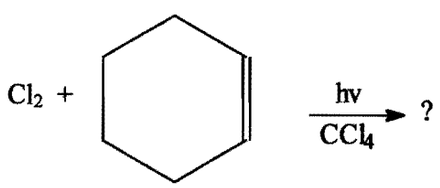
Question 5

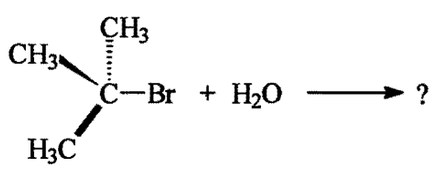
(a) The energy changes that occur during the progress of a reaction can be depicted graphically using an energy diagram. Draw such diagram for each of the following:

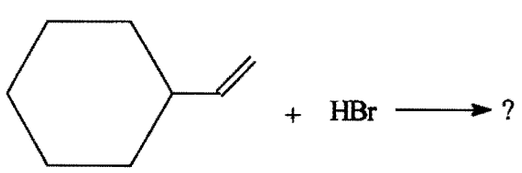
(i) A one – step reaction that is fast and highly exergonic. (3 marks)

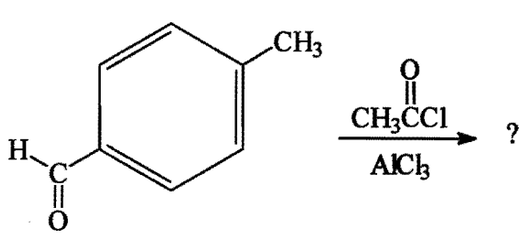
(ii) The overall reaction of ethylene with HBr. (5 marks)

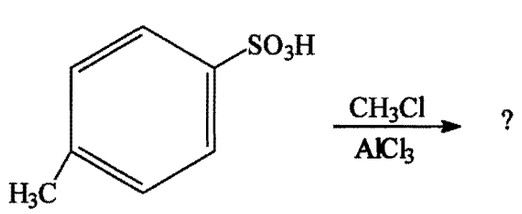
(b) Write the structure of the major product expected from the following reactions. (5 marks each)

(i) 

(ii) 

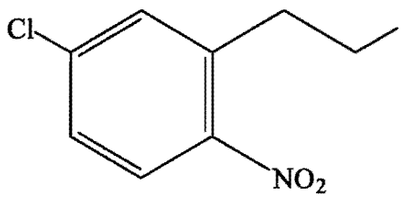
(iii) 

(iv) 

(v) 

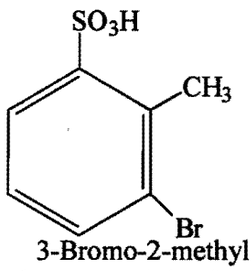
Question 6

(a) Outline a synthetic route from benzene to the following compounds:

(i) 

4-Chloro-1-nitro-2-propyl benzene

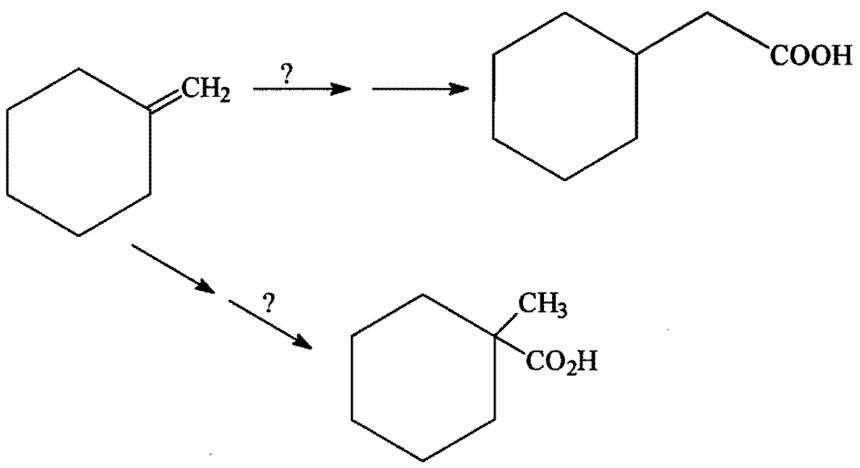
(8 marks)

(ii) 

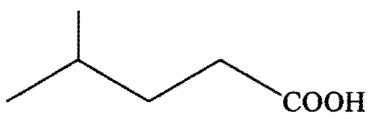
3-Bromo-2-methyl benzene sulphonic acid

(6 marks)

(b) Describe a plan showing how you would carry out the following transformations in the laboratory. (5 marks)



(c) Show how the malonic ester synthesis method is used to prepare the following carboxylic acids. (6 marks each)

(i) 

(ii)