# UNIVERSITY OF SWAZILAND
# FIRST SEMESTER FINAL EXAMINATION 2014/2015

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

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This Paper contains seven (7) pages.

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

## SECTION A : NMR SPECTROSCOPY

### Question 1

(a) The integrated $^1H$ NMR spectrum of a compound of formula $C_4H_{10}O$ is shown in Figure 1. Examine the spectrum, interpret all the signals and propose a structure for the compound that fits the spectral data. (6 marks)

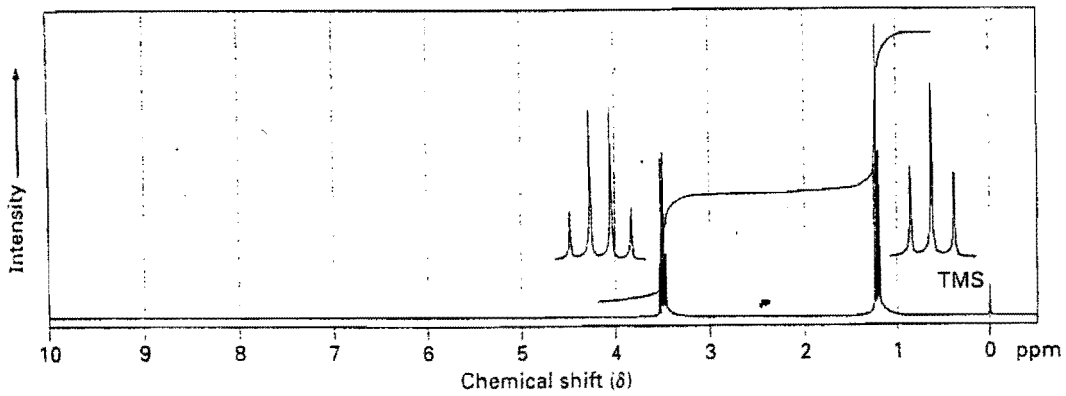



Figure 1. An integrated $^1H$ NMR spectrum for $C_4H_{10}O$

(b) Predict and write down the splitting patterns you would expect for each proton in the following molecules: (8 marks)

(a) $CHBr_2CH_3$

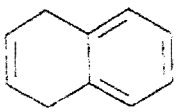
(b) $CH_3OCH_2CH_2Br$

(c) $ClCH_2CH_2CH_2Cl$

(d) $CH_3CH(CH_3)COCH_2CH_3$

(e) $CH_3CH_2COCH(CH_3)CH_3$

(f)



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

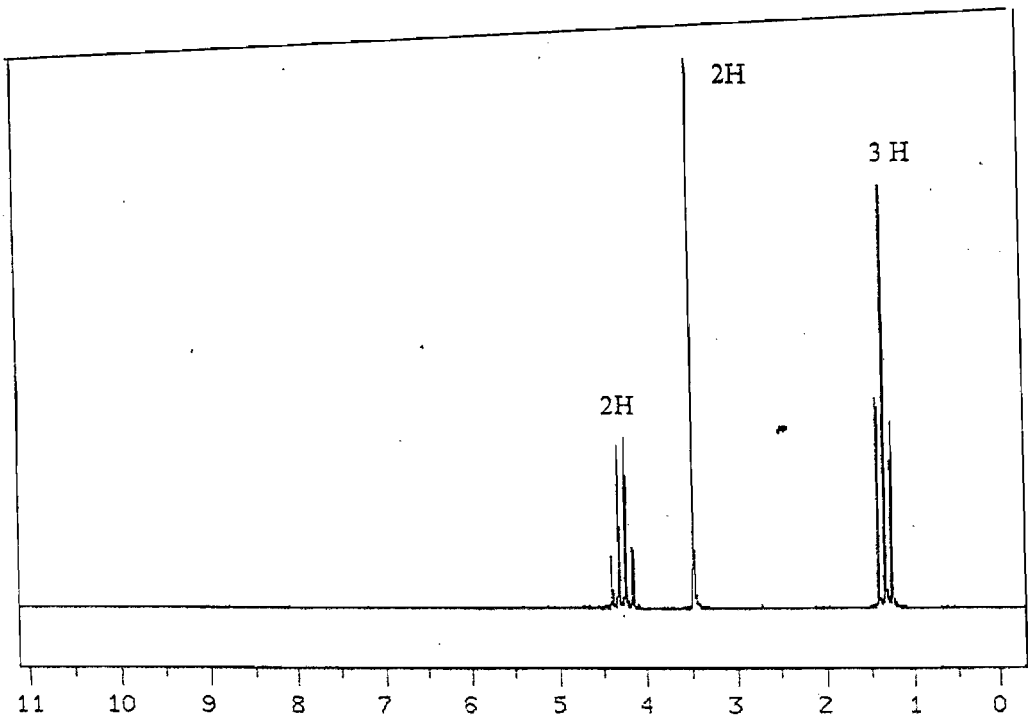
Broadband decoupled $^{13}C$ NMR: 29.5, 31.8, 50.2, 125.5, 127.5, 130.3, 139.8 δ

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

(d) It is known that addition of HBr to a terminal alkyne leads to the Markovnikov addition product with the Br bonding to the more highly substituted carbon. Explain how would you use $^{13}C$ NMR to **identify** the major product of the addition of one equivalent of HBr to hex-1-yne. (5 marks)

## Question 2

To answer the following questions, consider the data and $^{1}$HNMR spectrum below. The mass spectrum of this compound shows a molecular ion at m/z = 113, the IR spectrum has characteristic absorptions 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? (4 marks)

(b) How many types of non-equivalent protons are there in this molecule? (4 marks)

(c) Comment or describe the signal at 3.5 delta in terms of its integration, splitting pattern and chemical shift. (4 marks)

(d) Describe the signals at 4.35 delta and 1.3 delta in terms of their integration splitting and chemical shift. (4 marks)

(e) What is the significance of $^{13}$C NMR data? (4 marks)

(f) Analyze all the information deduced from the data provided and then propose a structure for this compound? (5 marks)

**Question 3**

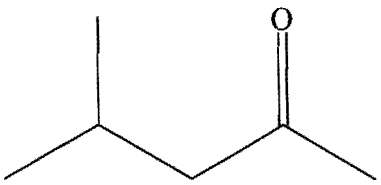
(a) Nitriles R – C ≡ N, undergo a hydrolysis reaction when heated with aqueous acid.

Propose a structure of the compound produced by hydrolysis of propane nitrile, $CH_3CH_2C{\equiv}N$, if it has IR absorption at 2500-3100 $cm^{-1}$ and 1710 $cm^{-1}$, and has $M^+$ = 74 in the mass spectrum. Explain your answer. (8 marks)

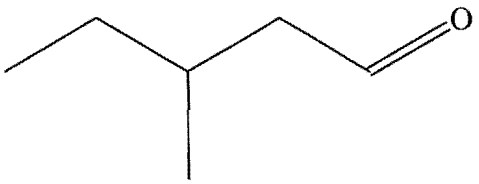
(b) Assume you are carrying out the conversion of 1-bromobutane to 1-butanol. Explain how you could use IR spectroscopy to determine when the reaction is complete. (8 marks)


1-bromobutane 1-butanol

(c) 4-Methyl-2-pentanone and 3-methyl pentanal are isomers. Explain how you could tell them apart, both by mass spectrometry and by infrared spectroscopy. (9 marks)




4-Methyl-2-pentanone

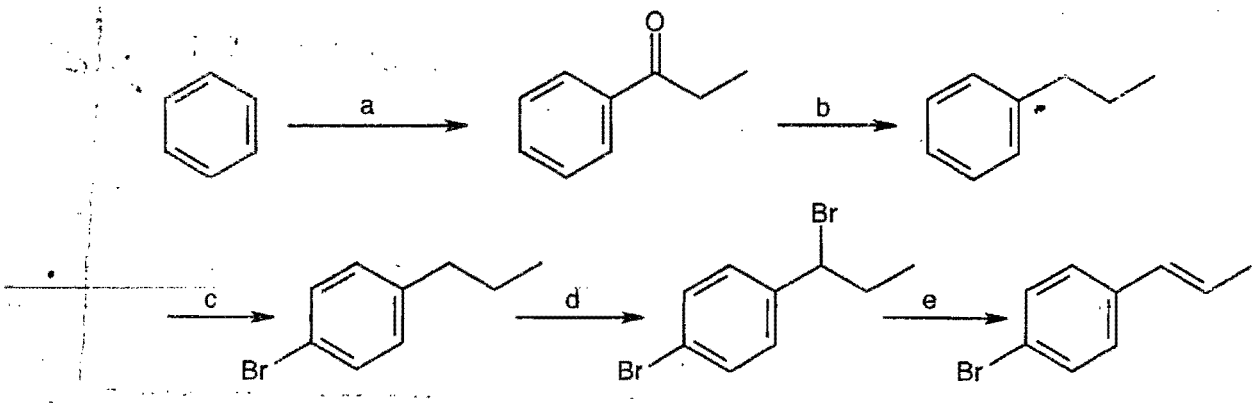



3-methylpentanal

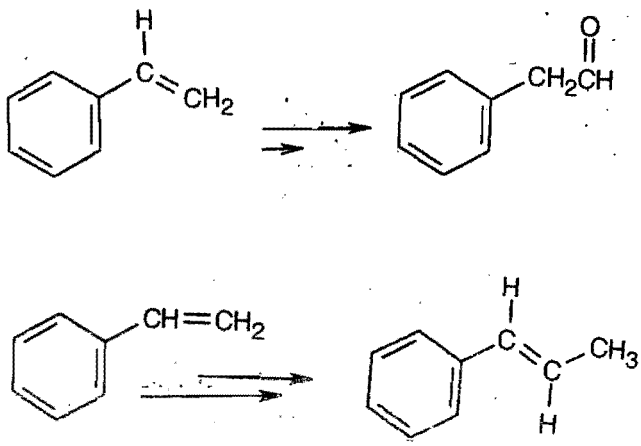
## SECTION B : REACTIONS AND SYNTEHSIS OF ORGANIC COMPOUNDS

**Question 4**

(a) Identify and write down the reagents represented by the letters a- e in the following scheme. (10 marks)

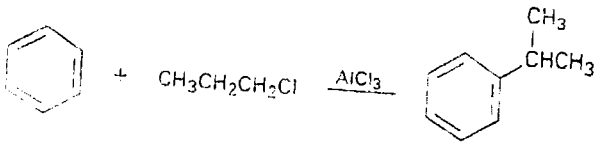



(b) Write down a reaction scheme showing how you would carry out the following conversions. More than one step is needed in each case. (15 Marks).

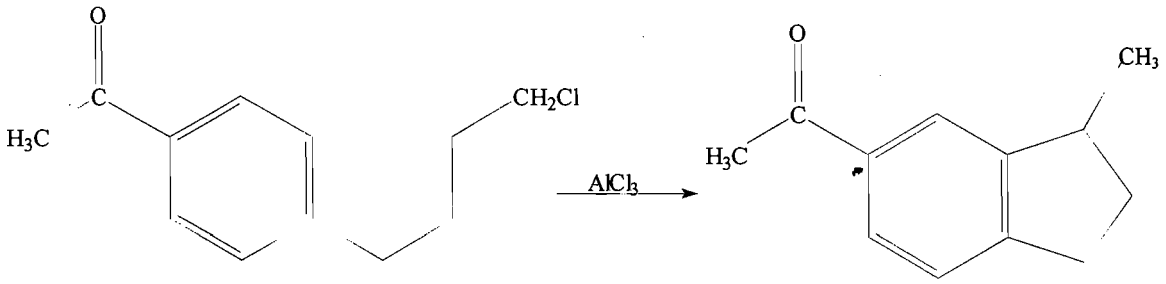


## Question 5

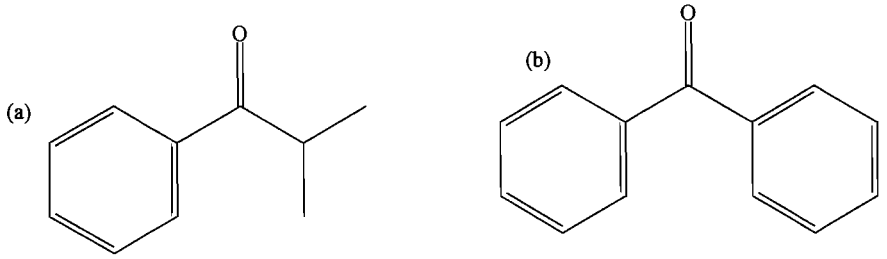
(a) Explain the observation that the reaction of benzene with 1-chloropropane yields isopropylbenzene as the major product. (5 marks)




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

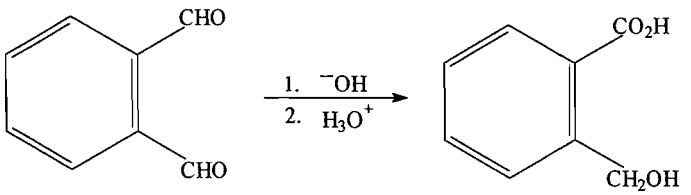



(c) Identify and draw the structure of the carboxylic acid chloride that might be used in a Friedel-Craft acylation reaction to prepare each of the following acylbenzenes. (5 marks)




(d) (i) Reaction of 3-dimethylbut-1-ene with HBr leads to an alkylbromide $C_6H_{13}Br$. 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)

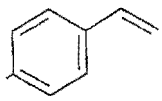



o-Phthaladehyde

o-(Hydroxymethyl) benzoic ac

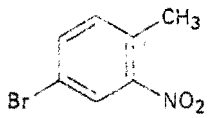
## Question 6

(a) Styrene is an important industrial chemical, used for the manufacture of polystyrene plastics and films. Show how styrene might be prepared from benzene using the reactions you have studies. (8 marks)



**Styrene**

(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) Synthesize 2-methylpentanoic acid from diethylmalonate. Show all the steps and reagents. (9 Marks)