UNIVERSITY OF SWAZILAND
FIRST SEMESTER FINAL EXAMINATION 2012

TITLE OF PAPER	:	Introductory Organic Chemistry
COURSE NUMBER	:	C303
TIME	:	Three Hours
INSTRUCTIONS	:	Answer any **FOUR Questions.** Each Question carries 25 Marks.

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

SECTION A

SPECTROSCOPY AND STRUCTURE DETERMINATION

Question 1

(a) Explain why all protons in a molecule do not absorb radio frequency (rf) energy at the same time. (8 marks)

(b) 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)

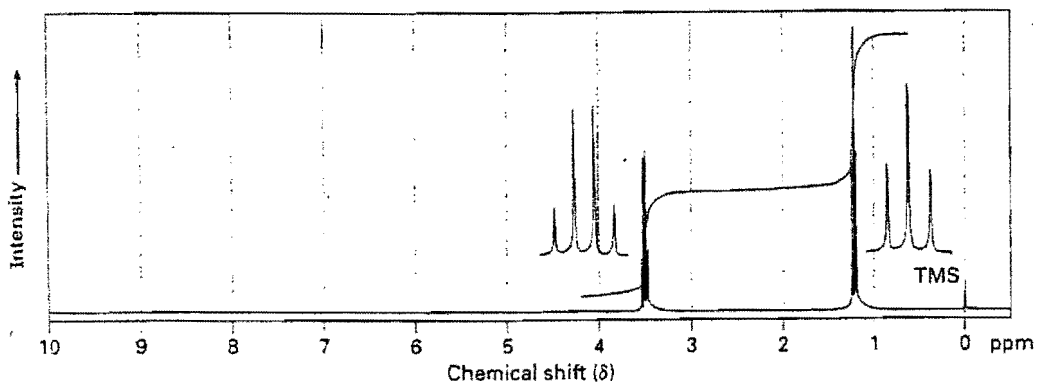


Figure 1. An integrated ^1H NMR spectrum for $C_4H_{10}O$

(c) Propose a structure for an aromatic hydrocarbon C11H16, that has the following ^{13}C NMR data. (6 marks)

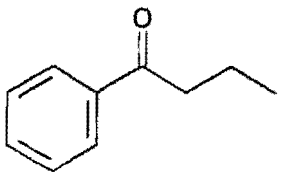
Broadband decoupled ^{13}C NMR: 29.5, 31.8, 50.2, 125.5, 127.5, 130.3, 139.8 δ

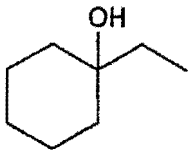
DEPT - 90 : 125.5, 127.5, 130.3 δ
DEPT - 135 : Positive Peaks at 29.5, 125.5, 127.5, 130.3 δ Negative Peak at 50 δ

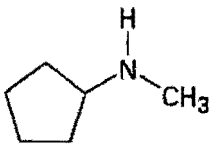
(d) It is known that addition of HBr to a terminal alkyne leads to the Markovnikov addition product with the Br bonding to the more highly substituted carbon. How would you use ^{13}C NMR to **identify** the product of the addition of 1 equivalent of HBr to hex-1-yne. (5 marks)

Question 2

(a) What fragments might you expect in the mass spectra of the following compounds? Explain how the fragments and their m/z values arise. (18 marks)

(a) 

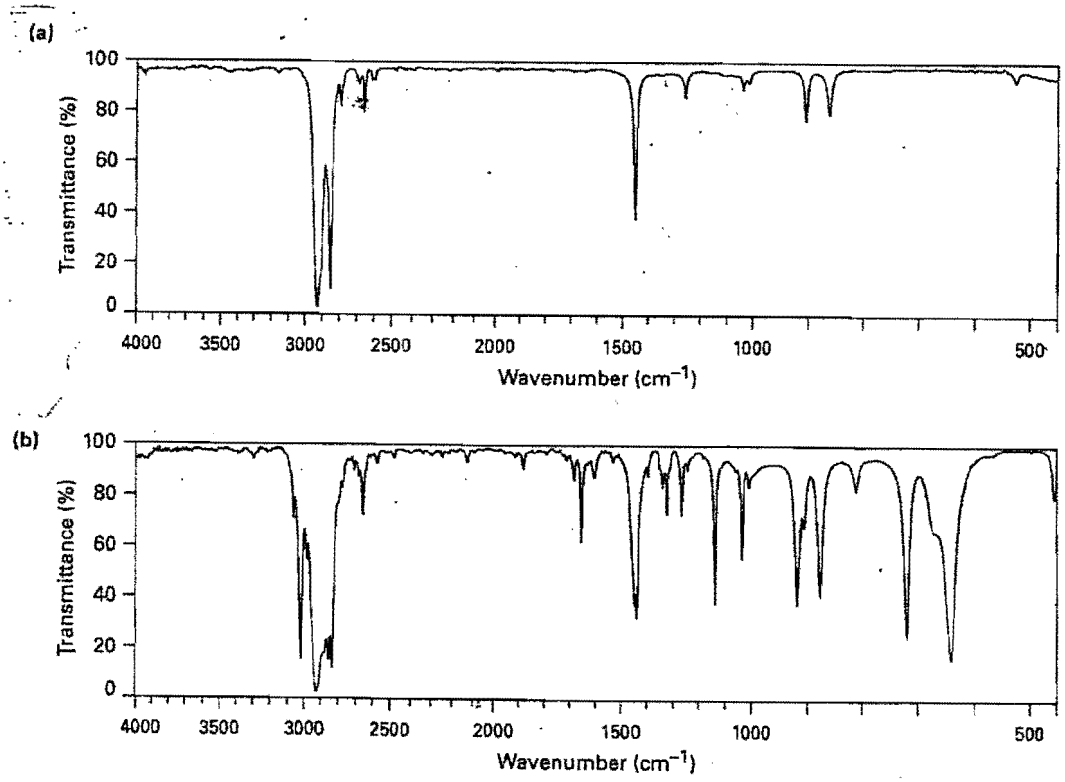
(b) 

(c) 

(b) Assume that you are in the laboratory carrying out the catalytic hydrogenation of cyclohexene to cyclohexane. Explain how you would use a mass spectrometer to determine when the reaction is finished. (7 marks)

Question 3

(a) Two infrared spectra are shown. One is the spectrum of cyclohexane, and the other is the spectrum of cyclohexene. Identify them and explain your answer. (12 marks)



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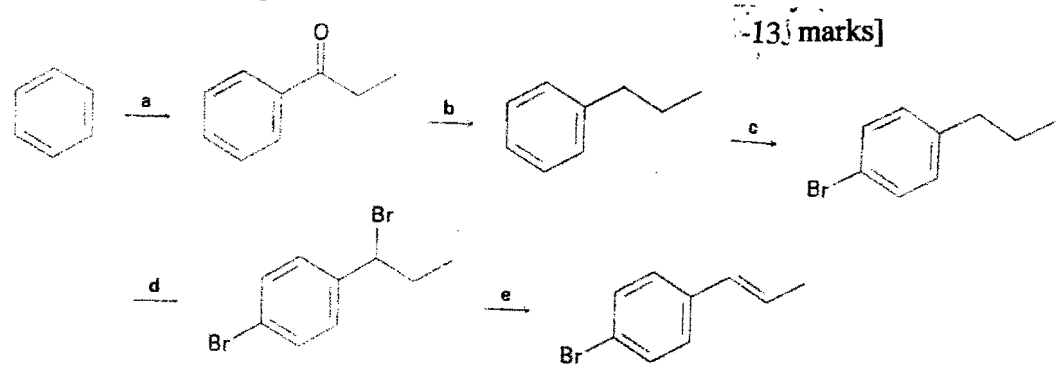
(b) Assume that you are carrying out the base-induced dehydrodrobromination of 3-bromo-3-methylpentane to yield an alkene. How could you use IR spectroscopy to tell which of the two possible elimination products is formed. (13 marks)

SECTION B

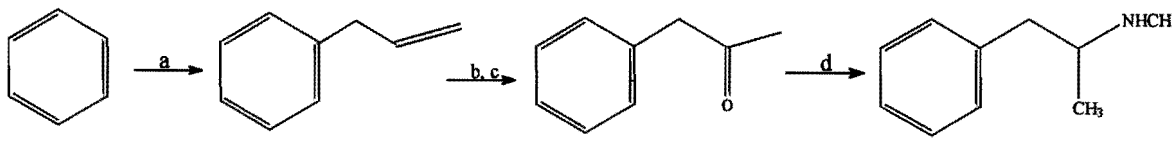
REACTIONS AND SYNTHESIS OF ORGANIC COMPOUNDS

Question 4

(a) Identify the reagents represented by the letters a-e in the following scheme: [13 marks]



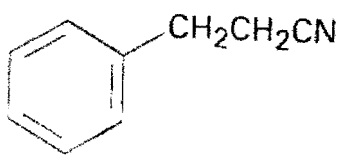
(b) Fill in the reagents a – d in the following synthesis of racemic methamphetamine from benzene. (12 marks)



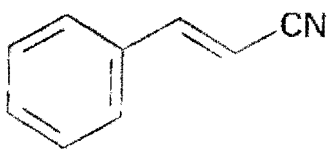
(R,S)-methampetamina

Question 5

(a) Electrophilic substitution on 3-phenylpropanenitrile occurs at the ortho and para positions, but reaction with 3-phenylpropenenitrile occurs at the meta position. Explain, using resonance structures of the intermediates. (15 marks)

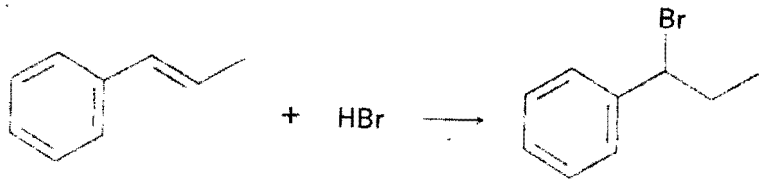


3-Phenylpropanenitrile



3-Phenylpropenenitrile

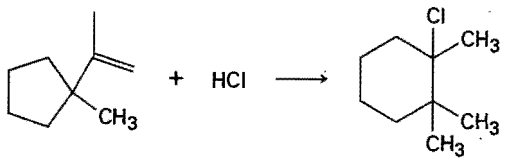
(b) Addition of HBr to 1-phenylpropene yields only (1-bromopropyl) benzene. Propose a mechanism for the reaction, and explain why none of the other regioisomer is produced.



10 marks]

Question 6

(a) (i) Addition of HCl to 1-isopropenyl-1-methylcyclopentane yields 1-chloro-1,2,2-trimethylcyclohexane. Suggest a mechanism, showing the structures of the intermediate and using curved arrows to indicate electron flow. (6 marks)



(ii) Draw an energy diagram for the reaction, labeling all points of interest and making sure that the relative energy levels on the diagram are consistent with the information given. (6 marks)

(b) (i) The reaction of hydroxide ion with chloromethane to yield methanol and chloride ion is an example of a general reaction type called nucleophilic substitution reaction:

$$HO^- + CH_3Cl \quad CH_3OH + Cl^-$$

The value of ΔH° for the reaction is -75 kJ/mol, and the value of ΔS° is +54 J/(K.mol). What is the value of ΔG° (in kJ/mol) at 298 K? Is the reaction exothermic or endothermic? Is it exergonic or endergonic?

(6 marks)

(ii) The addition of water to entylene to yield ethanol has the following thermodynamic parameters:

$H_2C=CH_2 + H_2O$ $\quad$ $CH3CH_2OH$ $\quad$ $\Delta H^\circ = -44$ kJ/mol
$S^\circ = -0.12$ kJ/(K.mol)
$K_{eq} = 24$

(a) Is the reaction exothermic or endothermic?
(b) Is the reaction favorable (spontaneous) or unfavorable (nonspontaneous) at room temperature (298 K)?

(7 marks)