

**UNIVERSITY OF SWAZILAND  
FIRST SEMESTER FINAL EXAMINATION 2011**

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**TITLE OF PAPER** : Introductory Organic Chemistry

**COURSE NUMBER** : C303

**TIME** : Three Hours

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

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This Paper contains five (5) pages.

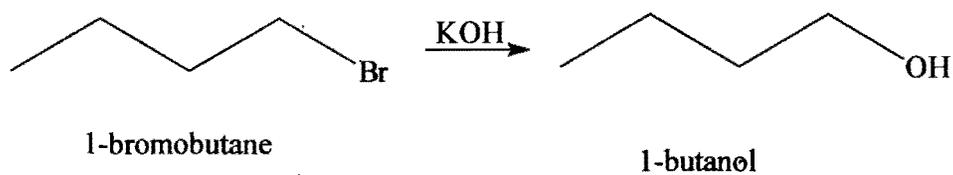
***You must not open this paper until the Chief Invigilator so has granted permission to do.***

## SECTION A

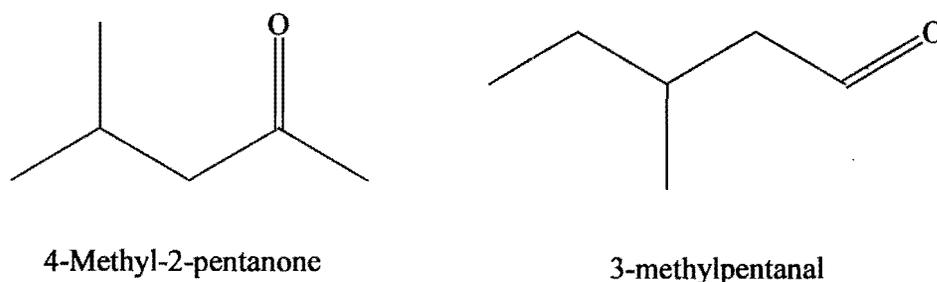
### MS, NMR AND IR METHODS FOR STRUCTURE DETERMINATION

#### Question 1

- (a) Nitriles  $R - C \equiv N$ , undergo a hydrolysis reaction when heated with aqueous acid.
- (i) Propose a structure of the compound produced by hydrolysis of propane nitrile,  $CH_3CH_2C \equiv N$ , if it has IR absorption at  $2500-3100 \text{ cm}^{-1}$  and  $1710 \text{ cm}^{-1}$ , and has  $M^+ = 74$  in the mass spectrum.
- (ii) 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)



- (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)

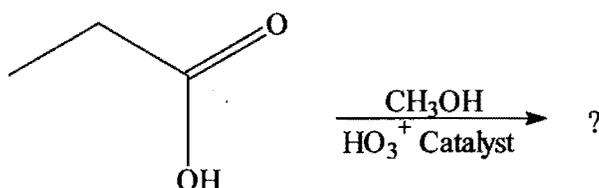


### Question 2

- (a) Explain why all protons in a molecule do not absorb radio frequency (rf) energy at the same time. (9 marks)
- (b) The carbonyl carbon resonance of 3-methyl-2-butanone occurs at 208.7 ppm downfield from TMS. How many hertz (Hz) downfield from TMS would this carbonyl absorb if the spectrometre used to measure this absorption were operating at 200 MHz? (8 marks)
- (c) An ester is suspected of being either  $(\text{CH}_3)_3\text{COOCH}_3$  or  $\text{CH}_3\text{COOC}(\text{CH}_3)$ . Its  $^1\text{H NMR}$  spectrum consists of two peaks at  $\delta$  0.9 and  $\delta$  3.6 (relative areas 3:1).
- (i) Which compound is it? Explain your answer. (4 marks)
- (ii) Describe the spectrum that would be expected if it had been the other ester. (4 marks)

### Question 3

- (a) Carboxylic acids ( $\text{RCOOH}$ ) react with alcohols ( $\text{R}'\text{OH}$ ) in the presence of an acid catalyst. The reaction products of propanoic acid with methanol has the following MS, IR, and NMR data. Propose a structure.



MS  $M^+ = 88$

IR  $1735 \text{ cm}^{-1}$

$^1\text{H NMR}$   $1.11\delta$  (3 H, triplet,  $J = 7 \text{ Hz}$ );  $2.32\delta$  (2 H, quartet,  $J = 7 \text{ Hz}$ );  $3.65\delta$  (3 H, singlet)

Broadband – decoupled  $^{13}\text{C NMR}$ : 9.3, 27.6, 51.4, 174.  $\delta$  (8 marks)

- (b) Propose a structure for a compound  $\text{C}_5\text{H}_{12}\text{O}$  that fits the following:  $^1\text{H NMR}$  data:  $0.9\delta$  (3 H, triplet  $J = 7 \text{ Hz}$ );  $1.2\delta$  (6 H, singlet);  $1.50\delta$  (2 H, quartet  $J = 7 \text{ Hz}$ );  $1.64\delta$  (1 H, broad singlet) (9 marks)

- (c) Propose a structure for the alcohol  $\text{C}_4\text{H}_{10}\text{O}$  that has the following

$^{13}\text{C NMR}$  spectral data:

Broadband – decoupled  $^{13}\text{C NMR}$

19.0, 31.7, 69.5  $\delta$

Dept – 90: 31.7  $\delta$

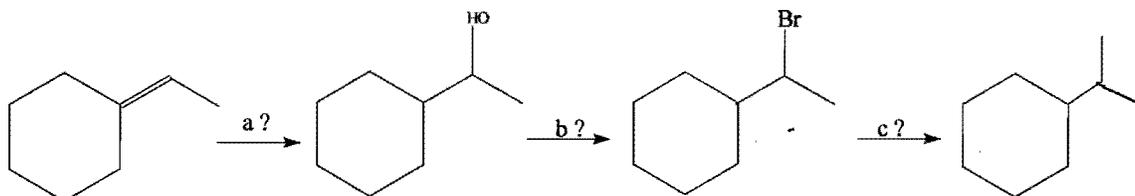
Dept – 135 positive peak at 19.0  $\delta$ , negative peak at 69.5  $\delta$  (8 marks)

SECTION B:

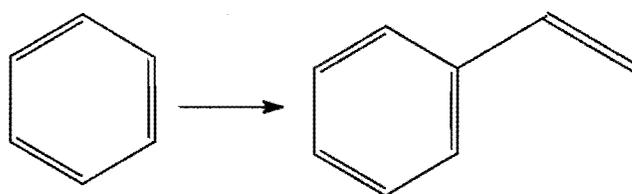
REACTIONS AND SYNTHESIS OF ORGANIC COMPOUNDS

**Question 4**

- (a) Identify reagents a – c in the following scheme. (12 marks)

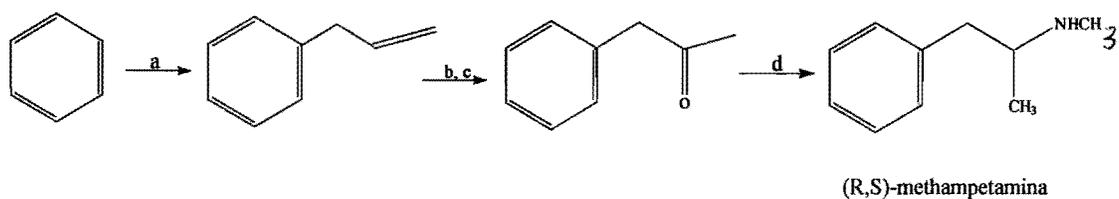


- (b) Outline a sequence of reactions to carry out the following conversion. (13 marks)

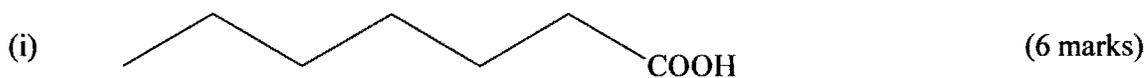


**Question 5**

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



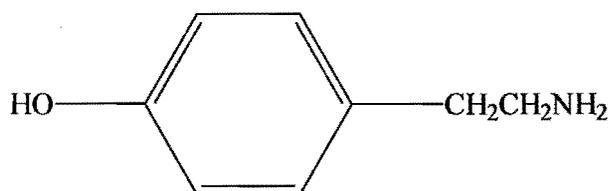
- (b) Using a malonic ester synthesis method, write a sequence of reactions for the synthesis of the following carboxylic acids (13 marks)



**Question 6.**

Tyramine is an alkaloid found, among other places, in ripe cheese. Outline a scheme, with all the necessary reagents and conditions, for the synthesis of tyramine from benzene.

(25 marks)



Tyramine