FACULTY OF SCIENCE

MODULE	**CEM2B10 / CEM01B2**
	Intermediate Organic Chemistry
CAMPUS	**APK**
EXAM	**23 NOVEMBER 2018**

EXAMINER:	**Dr L den Drijver**
INTERNAL MODERATOR:	**Dr E Mmutlane**
DURATION: 3 HOURS	**MARKS 95**
NUMBER OF PAGES: 8	

Instructions

(1) The examination is out of 95 marks and you have 3 hours to complete it. No extra time will be given.

(2) You can use a pen of any color **except** RED AND GREEN to write your answers.

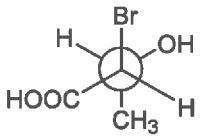
(3) Read the whole question paper carefully before you start answering. You are allowed to start with any question, just clearly number it in your answer sheet.

(4) You have been provided with Spectroscopic Correlation Tables at the end of the question paper. Make sure you use them.

(5) This is a closed book examination. You are NOT allowed to have any book, memorandum, notes, paper, photographs, document or written/printed material other than the question paper and the answer books provided by the examiner/invigilator. If you need paper for rough work, an additional exam answer sheet will be given to you, which must be clearly labelled as rough work: not for marking, and handed in together with the question paper and all your answer books.

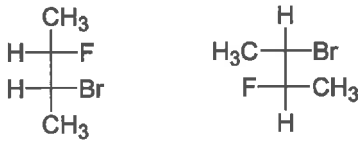
QUESTION 1

(a) Give the Fischer projection formula of the compound below. Also give the absolute configuration (R/S) of all the stereocentres present in the molecule. (4)



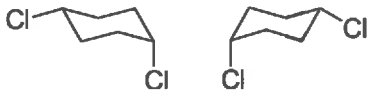
(b) Identify the relationship between the following pairs of compounds as enantiomers, diastereomers, constitutional isomers or the same compound.

(i)



(2)

(ii)

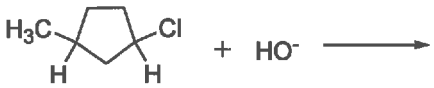


(2)

[8]

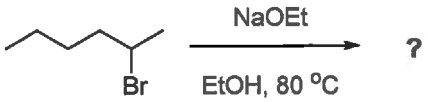
QUESTION 2

(a) Draw a complete mechanism for the following reaction and name the type of mechanism. Name both the substrate and the product using systematic IUPAC nomenclature. (6)



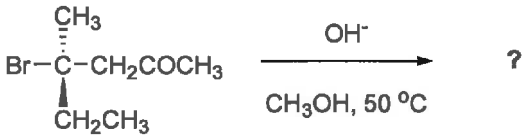
(b) Which product(s) would you expect to obtain from each of the following reactions? For each reaction, state the mechanism (S_N1, S_N2, E1 or E2) (you do not have to write the mechanism) by which the product is formed. In each case, explain your choice.

(i)



(3)

(ii)



(3)

[12]

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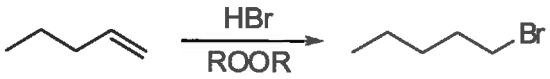
QUESTION 3

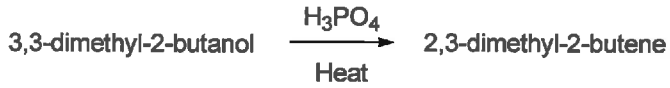
(a) Write mechanisms of the following reactions:

(i)



(5)

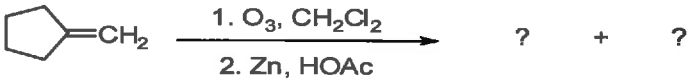
(ii)



(6)

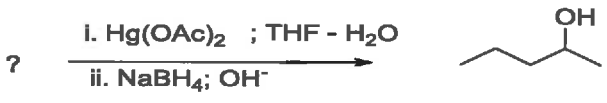
(b) Give the missing starting materials, reagents and products.

(i)



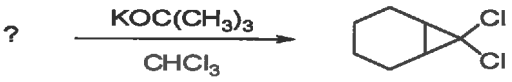
(2)

(ii)



(2)

(iii)

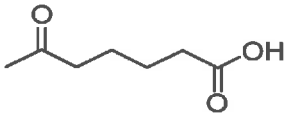


(1)

[16]

QUESTION 4

(a) An unknown alkene with formula C_7H_{12} undergoes oxidation in hot, acidic $KMnO_4$ to yield only the following product. What is the structure of the original alkene? (2)



(b) Which isomer would you expect to undergo E2 elimination faster, *trans*-1-bromo-4-*tert*-butylcyclohexane or *cis*-1-bromo-4-*tert*-butylcyclohexane? Draw each molecule in its more stable chair conformation and explain your answer. (6)

[8]

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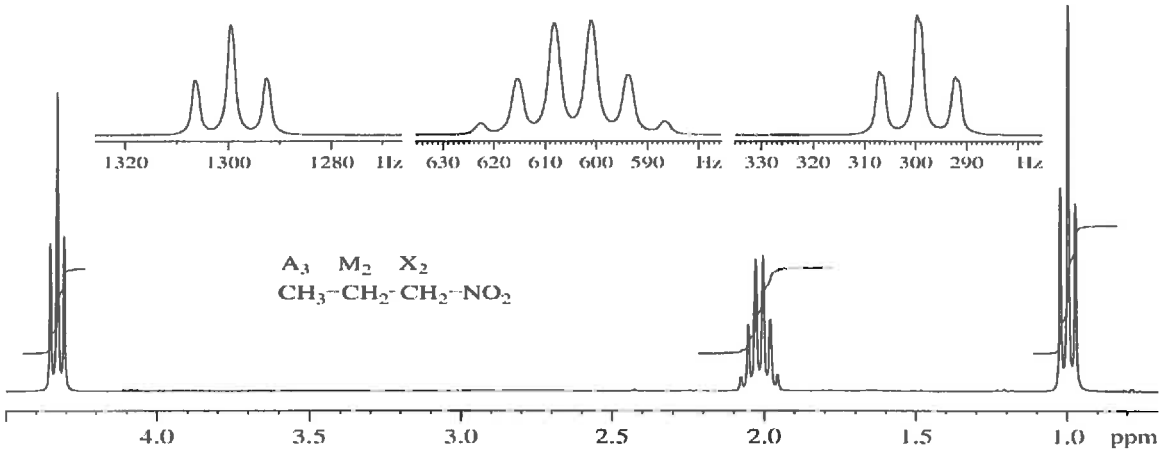
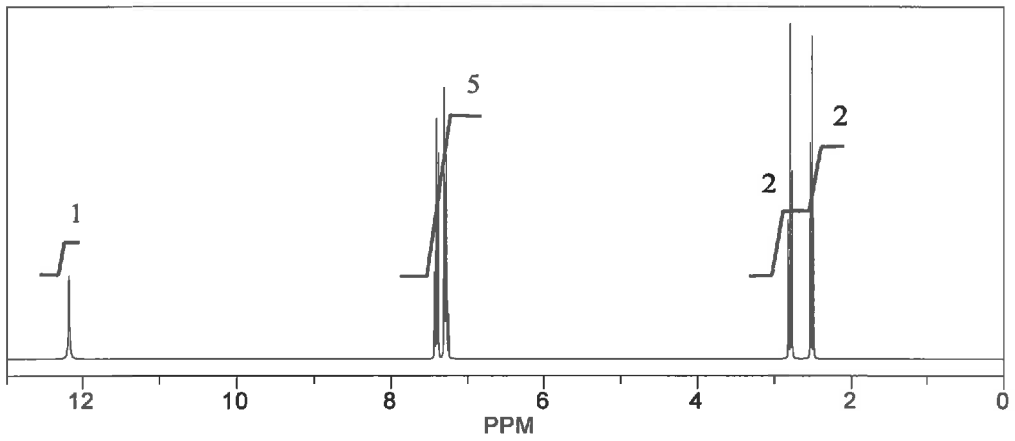
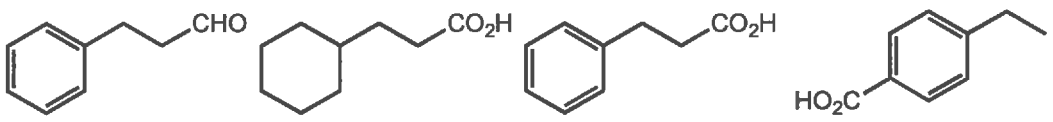
QUESTION 5

(a) Examine the ^{1}H NMR spectrum of 1-nitropropane, shown below. Assign the signals to the respective hydrogen atoms in the molecule. (3)



(b) What is the structure of the compound in the following ^{1}H-NMR spectrum (molecular formula $C_9H_{10}O_2$)? Relative integration is shown. **Explain** how you came to this conclusion. (5)





(5)

[8]

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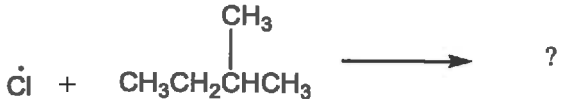
QUESTION 6

(a) What is the most stable radical that would be formed in the following reaction?



(1)

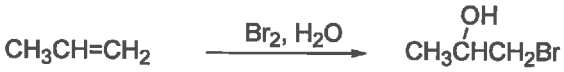
(b) Name the three steps that are involved in the chlorination of methane and give an example of each. (3)

(c) Radical chlorination of pentane will lead to 4 products. Draw their structures and assign (*R*) or (*S*) where applicable. (5)

[9]

QUESTION 7

(a) Consider the following reaction:



Explain how the product is formed by showing a complete mechanism (draw it with arrows). Is this a Markovnikov or Anti-Markovnikov product? Explain your answer. (7)

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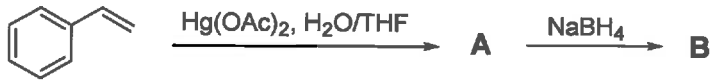
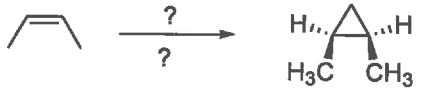
(b) Fill in the missing product, reagent or substrate:

(i)



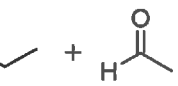
(2)

(ii)



(2)

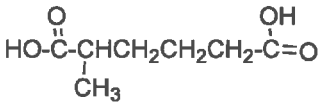
(iii)



(2)

(c) Compound A is a flammable liquid with molecular formula C_7H_{12}. It reacts with 1 mol equivalent of H_2. On treatment of A with hot basic $KMnO_4$ it gives the dicarboxylic acid C. Compound B is the isomer of A and also reacts with 1 mol equiv of H_2, but yields cyclohexanone after treatment with acidic $KMnO_4$. Suggest structures for A and B.

Compound C:

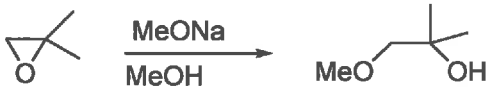


(4)

[17]

QUESTION 8

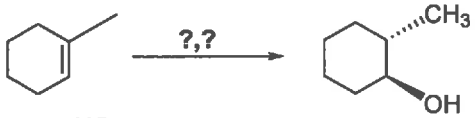
(a) Provide a mechanistic explanation for the following observation:



(4)

(b) Fill in the missing reagents, products and starting materials:

(i)



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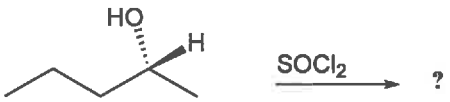
(ii)



(1)

(iii)

(1)

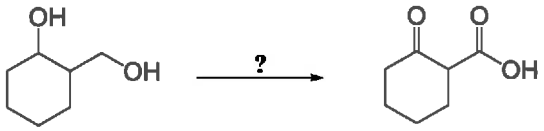
[8]

QUESTION 9

(a) What restrictions are there on the use of Grignard reagents? Explain. (6)

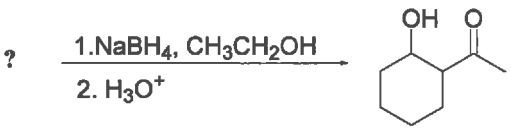
(b) Fill in the missing reagents, starting materials and products:

(i)



(2)

(ii)



(1)

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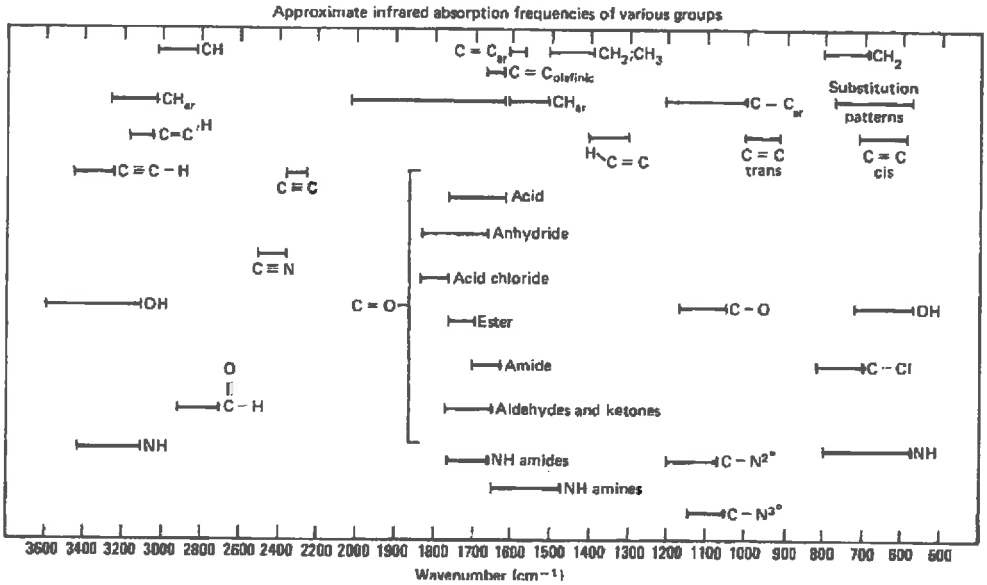
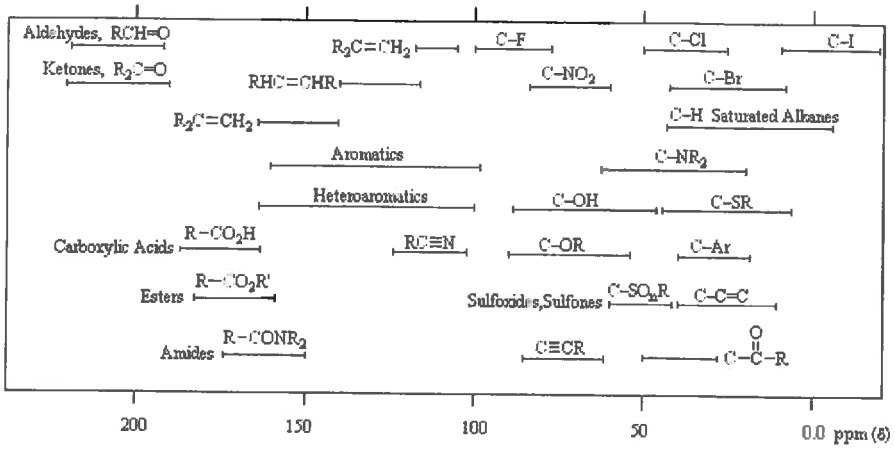
REFERENCE TABLES





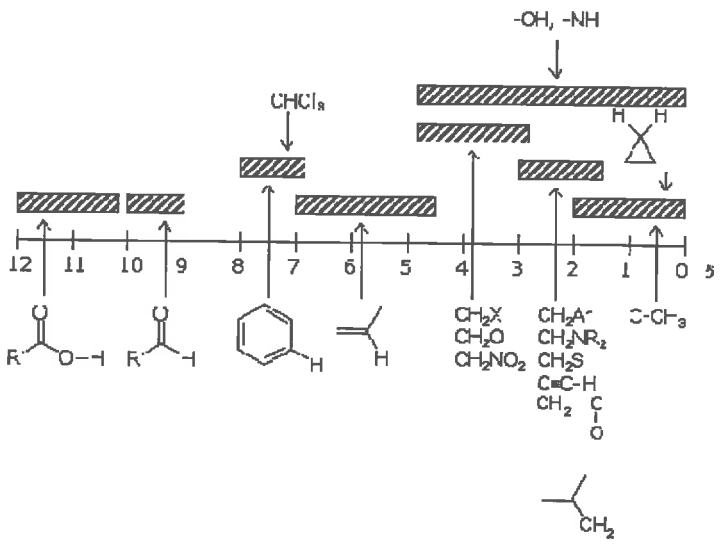


Table of Characteristic IR Absorptions

frequency, cm^{-1}	*bond*	*functional group*
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H-bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in-ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in-ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m = medium, w = weak, s = strong, n = narrow, b = broad, sh = sharp