FACULTY OF SCIENCE

DEPARTMENT OF CHEMISTRY

MODULE **CEM2B10**
INTERMEDIATE ORGANIC CHEMISTRY

CAMPUS **APK**

SUPPLEMENTARY EXAM - JANUARY 2019

ASSESSOR: Dr L den Drijver **INTERNAL MODERATOR: Dr E Mmutlane**

DURATION 3 HOURS **MARKS 94**

NUMBER OF PAGES: 8

Instructions

(1) The examination is out of 94 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

1.1 Of the three molecules below, one contains a stereocentre. Identify the molecule and draw Fischer projections of enantiomers.

(a) 2-fluoropropane

(b) 2-methylbutane

(c) 2-bromopentane (3)

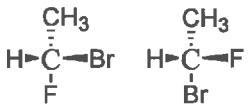
1.2 Identify the following as:

(a) diastereomers

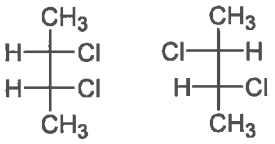
(b) constitutional isomers

(c) 2 molecules of the same compound or

(d) enantiomers

A. 

B. 

C. 

(3)

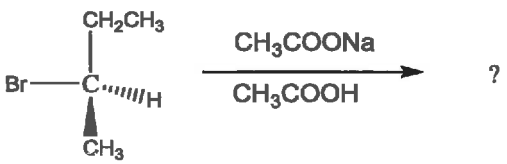
[6]

QUESTION 2

2.1 Write a mechanism for the following reaction. Name the substrate and product and draw a free-energy diagram for the reaction. (8)

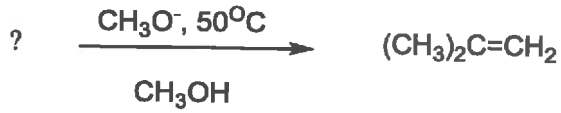
2.2 Give the missing reactants, substrates and products. Also give the mechanism. (Eg. E_1, S_N2)

(a)



(2)

(b)

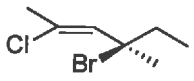


(2)

[12]

QUESTION 3

3.1 Name the following compound using (E) / (Z) as well as (R)/(S) designations:

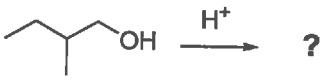


(2)

3.2 Which of the following alkenes is more stable? Explain.
trans-2-hexene or 2-methyl-2-pentene (2)

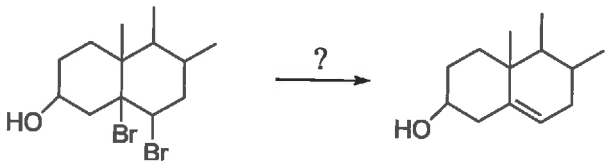
3.3 When *cis*-1-bromo-4-tert-butyl-cyclohexane is treated with sodium ethoxide in ethanol, it reacts rapidly to yield 4-tert-butylcyclohexene. Under the same conditions *trans*-1-bromo-4-tert-butylcyclohexane reacts very slowly. Write conformational structures and explain the difference in reactivity. (4)

3.4 Fill in the missing reagents, products or starting materials:
(a)



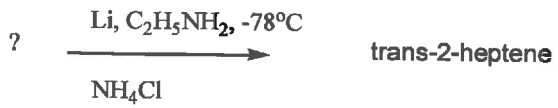
(1)

(b)



(1)

(c)



(1)

3.5 Start with ethyne and describe a synthesis for *cis*-2-butene. Use any other reagents that may be needed. (5)

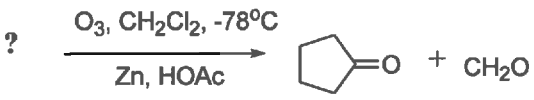
[16]

QUESTION 4

4.1 Write a mechanism for the addition of IC*l* to 2-methyl-2-butene. (5)

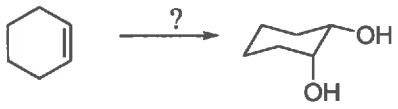
4.2 Fill in the missing starting material, reagents and products:

(a)



(1)

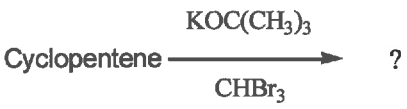
(b)



(2)

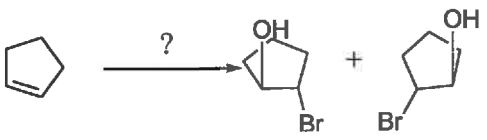
(c) *cis*-2-pentene $\xrightarrow{Br_2}$? (2)

(d)



(1)

(e)



(1)
[12]

QUESTION 5

5.1 How many monochloro products would be formed from the reaction of 2-methylbutane with chlorine? Show the structures. (4)

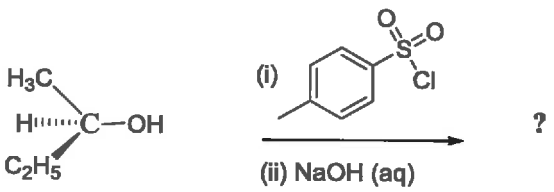
5.2 Write a mechanism for the monochlorination of methane. (3)

5.3 Write a mechanism for the addition of HBr on propene in the presence of peroxide. (5)
[12]

QUESTION 6

6.1 Start with 2-methyl-2-butene and show the steps by which the compound is converted to an alcohol during oxymercuration-demercuration. Name the product. (8)

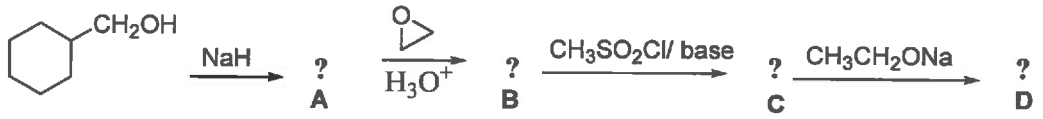
6.2 Show the configuration of the products when the following compound is treated with tosyl chloride, followed by hydroxide ion. Name the final product.



(3)

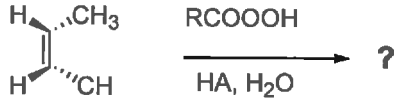
6.3 Give the structures of the products and starting materials (A-C):

(a)



(4)

(b)



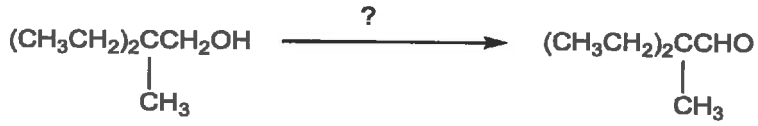
(2)
[17]

QUESTION 7

7.1 Draw a mechanism for the reduction of propanone with sodium borohydride. (5)

7.2 Fill in the missing reagents, starting materials and products:

(a)



(1)

(b)

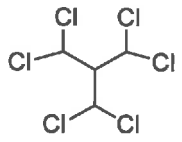
(1)

(c)

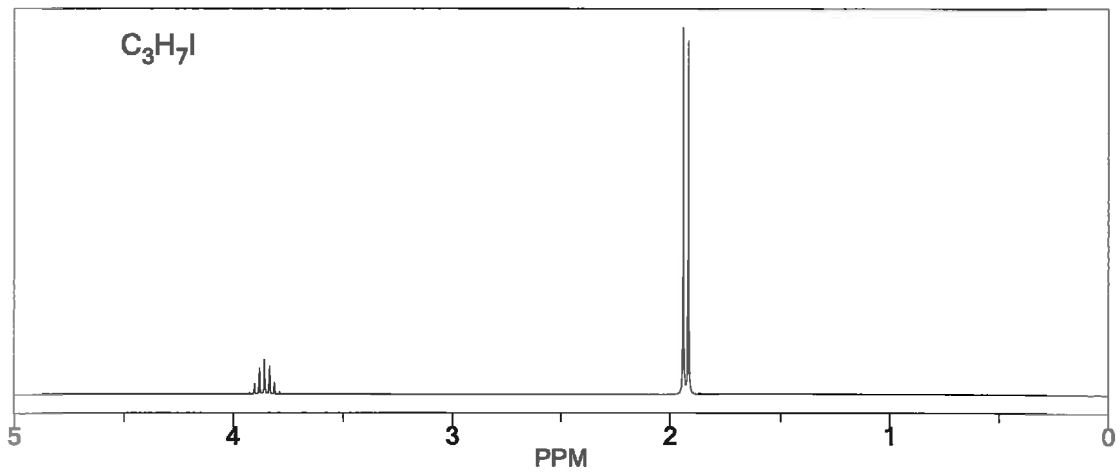
(2)
[9]

QUESTION 8

8.1 Sketch the ^{1}H-NMR spectrum you would expect for the following compound, showing the splitting patterns and relative position of each signal: (7)



8.2 Propose a structure for the compound with the following ^{1}H-NMR and assign the peaks to the relevant hydrogens: (3)



[10]

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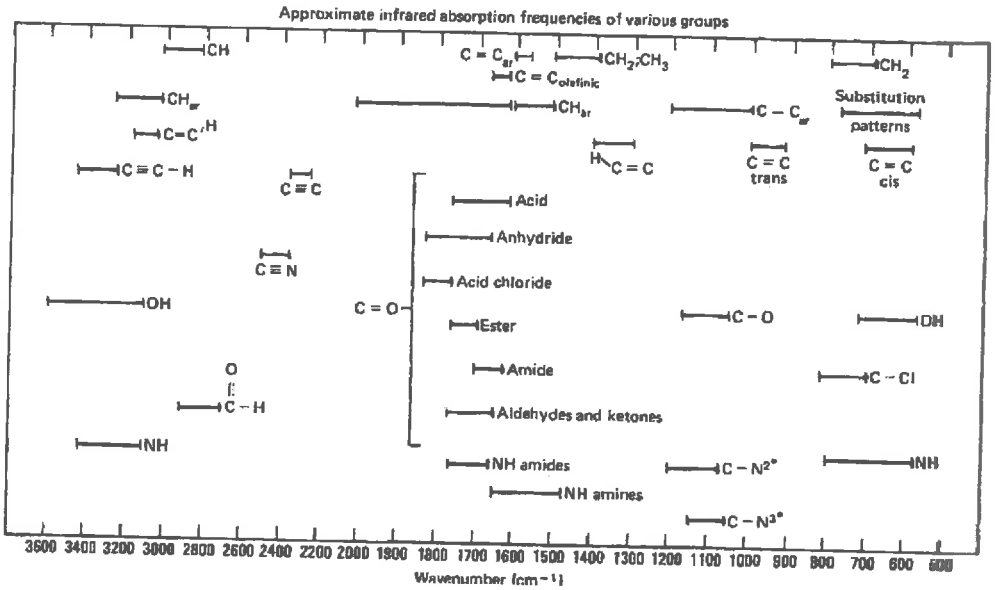
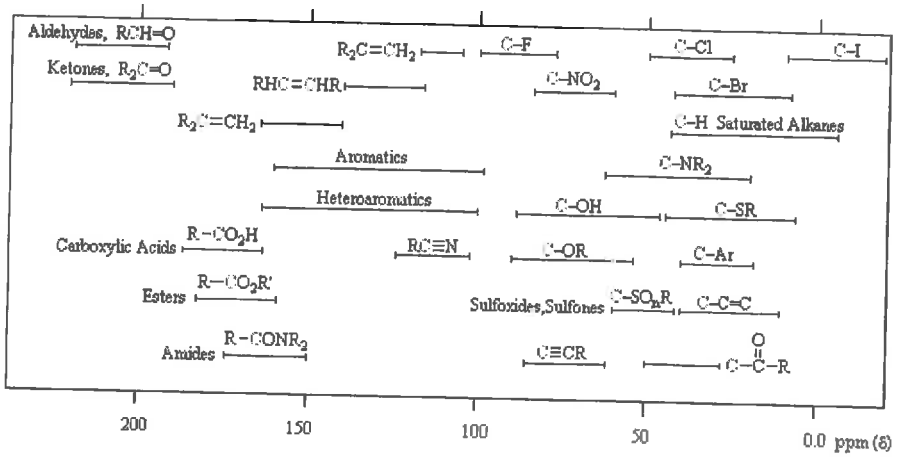
REFERENCE TABLES





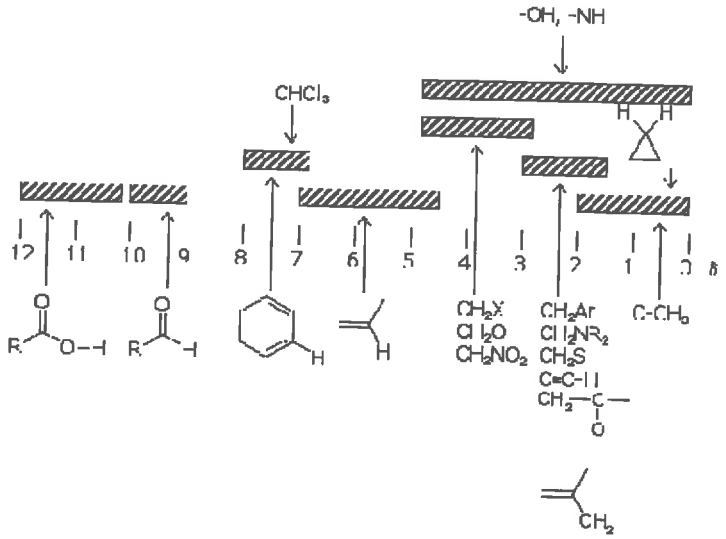


Table of Characteristic IR Absorptions

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