FACULTY OF SCIENCE

MODULE CEM2B10 / CEM01B2
INTERMEDIATE ORGANIC CHEMISTRY

CAMPUS APK

NOVEMBER EXAM 2019

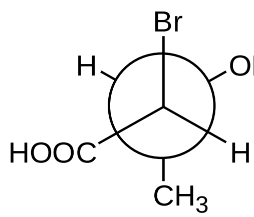
ASSESSOR	**Dr L den Drijver**	**INTERNAL MODERATOR**	**Prof HH Kinfe**
DURATION:	**3 HOURS**	**MARKS:**	**82**
DATE:	**16 November 2019**	**NUMBER OF PAGES:**	**9**

Instructions

(1) The examination is out of 82 marks and you have 3 hours to complete it. No extra time will be given.
(2) You can use a **pen** of any colour **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) 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 **[4]**

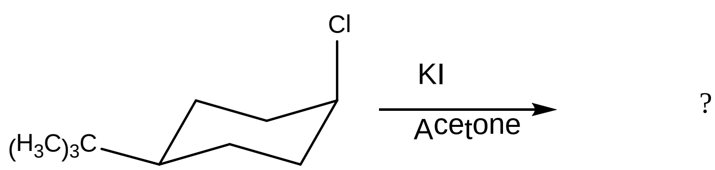
Give the Fischer projection formula of the compound below. Also give the absolute configuration (R/S) of all the stereocentres present in the molecule. (4)



QUESTION 2 **[9]**

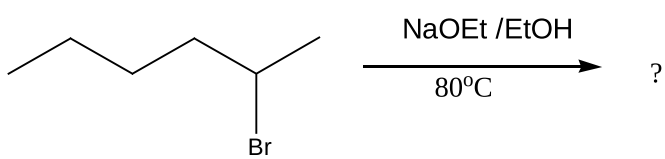
Which product(s) would you expect to obtain from each of the following reactions? For each reaction, give the mechanism (S_N1, S_N2, E1 of E2) by which the product is formed. In each case, explain your choice.

(i)



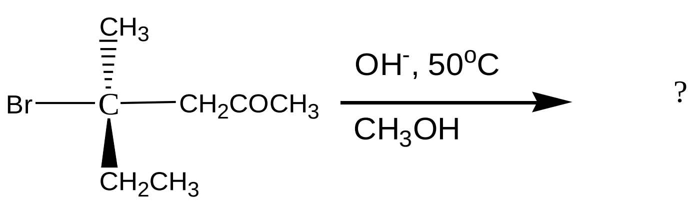
(3)

(ii)



(3)

(iii)

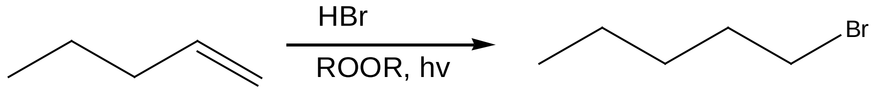


(3)

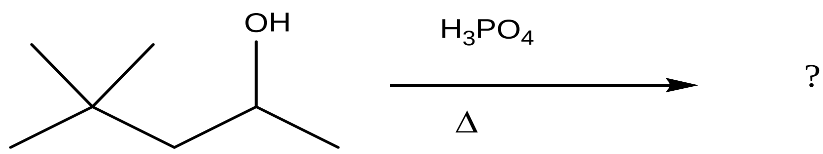
QUESTION 3 **[15]**

(a) Write full mechanisms (curved arrows) for the following reactions:

(i)

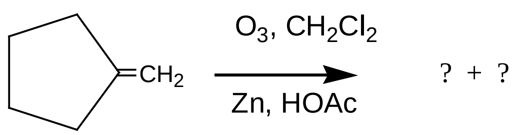


(5)

(ii)  (5)

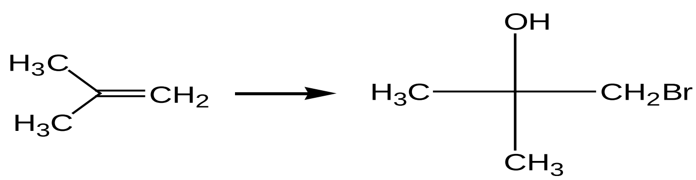
(b) Give the missing starting materials, reagents and products.

(i)



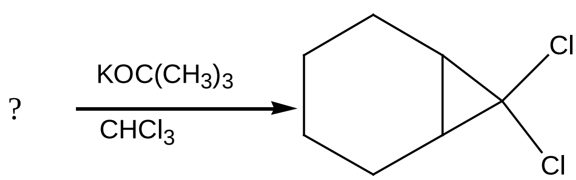
(2)

(ii)



(2)

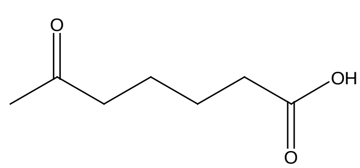
(iii)



(1)

QUESTION 4 [8]

(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) Dehydrohalogenation of meso-1,2-dibromo-1,2-diphenylethene by the action of sodium ethoxide in ethanol yields (E)-1-bromo-1,2-diphenylethene. Similar dehydrohalogenation of either of the enantiomeric forms of 1,2-dibromo-1,2-diphenylethane yields (Z)-1-bromo-1,2-diphenylethene. Provide an explanation for the results. (6)

QUESTION 5 [11]

TABLE 9.1 Approximate Proton Chemical Shifts

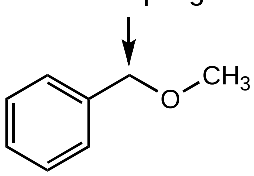
Type of Proton	Chemical Shift (δ, ppm)	Type of Proton	Chemical Shift (δ, ppm)
1° Alkyl, RCH_3	0.8–1.2	Alkyl bromide, RCH_2Br	3.4–3.6
2° Alkyl, RCH_2R	1.2–1.5	Alkyl chloride, RCH_2Cl	3.6–3.8
3° Alkyl, R_3CH	1.4–1.8	Vinylic, $R_2C{=}CH_2$	4.6–5.0
Allylic, $R_2C{=}C(R){-}CH_3$	1.6–1.9	Vinylic, $R_2C{=}CH(R)$	5.2–5.7
Ketone, $RC(=O)CH_3$	2.1–2.6	Aromatic, ArH	6.0–8.5
		Aldehyde, $RC(=O)H$	9.5–10.5
Benzylic, $ArCH_3$	2.2–2.5		
Acetylenic, $RC{\equiv}CH$	2.5–3.1	Alcohol hydroxyl, ROH	0.5–6.0[a]
Alkyl iodide, RCH_2I	3.1–3.3	Amino, $R{-}NH_2$	1.0–5.0[a]
Ether, $ROCH_2R$	3.3–3.9	Phenolic, ArOH	4.5–7.7[a]
Alcohol, $HOCH_2R$	3.3–4.0	Carboxylic, $RC(=O)OH$	10–13[a]

[a]The chemical shifts of these protons vary in different solvents and with temperature and concentration.

(a) Briefly explain how you might distinguish between 1-butyne and 2-butyne by comparing their ^{1}H-NMR spectra. (2)

(b) Draw the structure for the compound that has the chemical formula C_4H_8O and shows one singlet, one triplet and one quartet in the proton NMR. (3)

(c) Which one of the following best represents the predicted approximate chemical shift and coupling for the hydrogen(s) indicated with the arrow? (2)



A) 1.10 ppm, singlet
B) 2.10 ppm, triplet
C) 3.40 ppm, triplet
D) 4.5 ppm, singlet
E) 5.3 ppm, doublet

(d) How many chemically distinct ^{1}H NMR signals are there in the following compound?

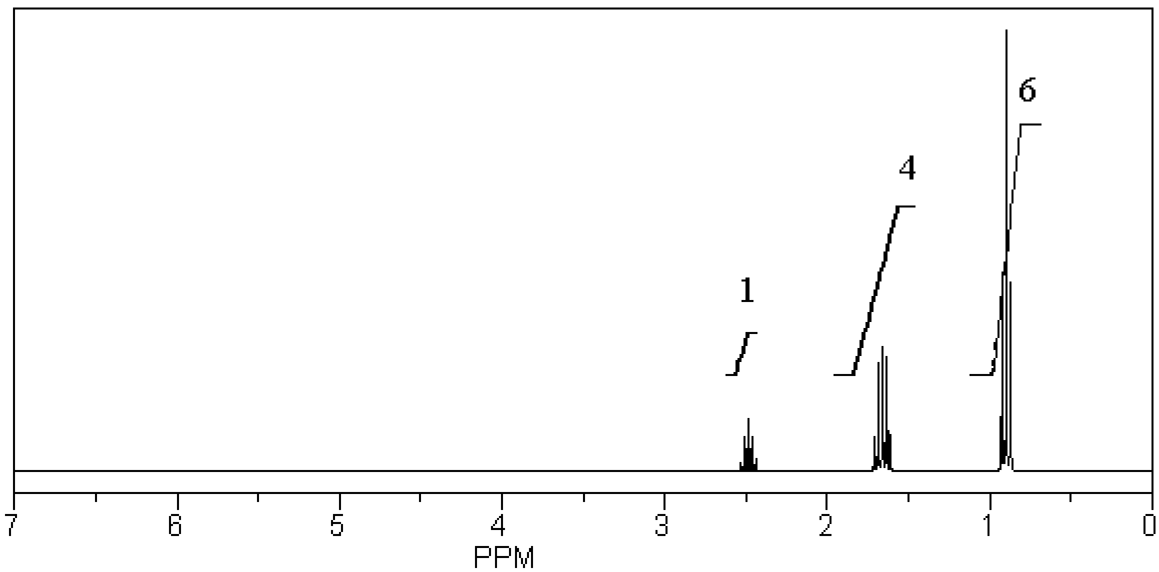
$ClCH_2CH(Br)CH_3$ (Br on the central carbon)

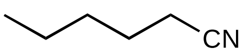
(2)

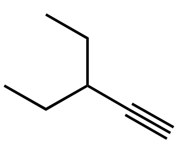
A) 1

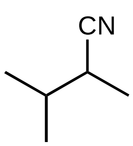
B) 2
C) 3
D) 4
E) 5

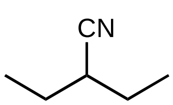
(e) What is the structure of the compound in the following ^{1}H-NMR spectrum with the molecular formula $C_6H_{11}N$? In the IR spectrum you notice a stretch at about 2250 cm^{-1}. Relative integration is shown. (2)

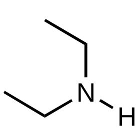


A) 

B) 

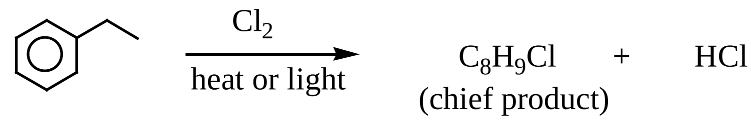
C) 

D) 

E) 

QUESTION 6 **[10]**

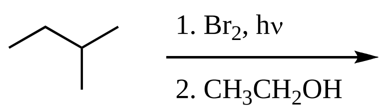
(a) What feature would you expect to see in the ^{1}H NMR spectrum of B after subjecting A to the following reaction? (2)

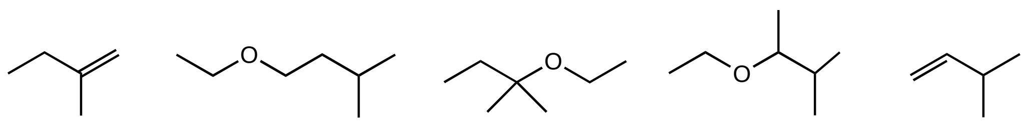


A B

1. There would be only 4 aromatic protons at low field.
2. The signal for the protons on the benzylic carbon would be a doublet.
3.The signal for the methyl protons would be a triplet.
4. The signal for the methyl protons would be a doublet.
5.The signal for the methyl protons would integrate for only 2 hydrogens.

(b) What would be the major product of the following reaction sequence? (2)





I II III IV V

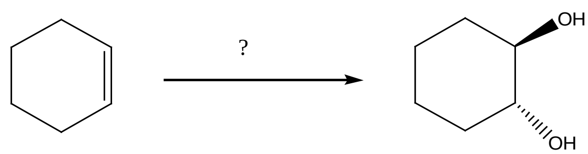
A) I
B) II
C) III
D) IV
E) V

(c) Give a mechanism for the radical polymerisation of ethylene. (6)

QUESTION 7 **[9]**

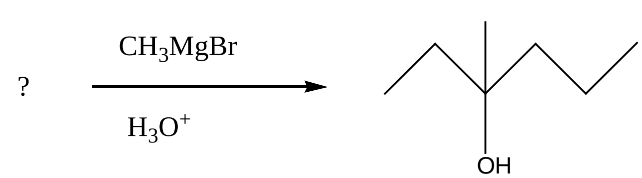
(a) Give the missing starting material, reagent or product for the following reactions:

(i)



(2)

(ii)



(2)

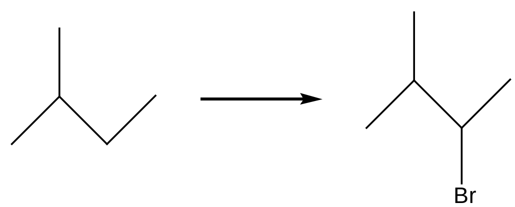
(b) Ethyl 2-methylpropylether can be prepared via 2 routes in a Williamson synthesis. Give the 2 routes, explain which one will be better **and** why. (5)

QUESTION 8 **[16]**

Show how you would prepare **any four** of the following compounds from the given starting materials. You are allowed to use any reagents.

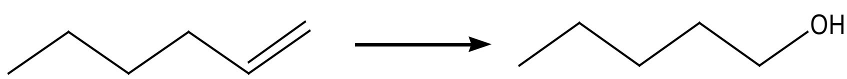
(a) 1- butene from 2-butene.

(b)

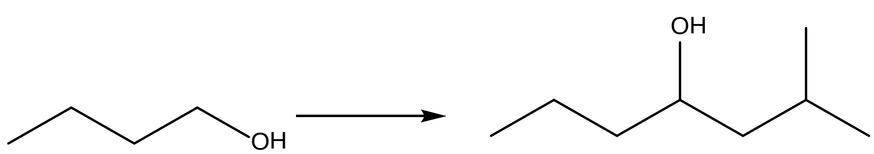


(c) (±)-2,3-butanediol from 2-butyne.

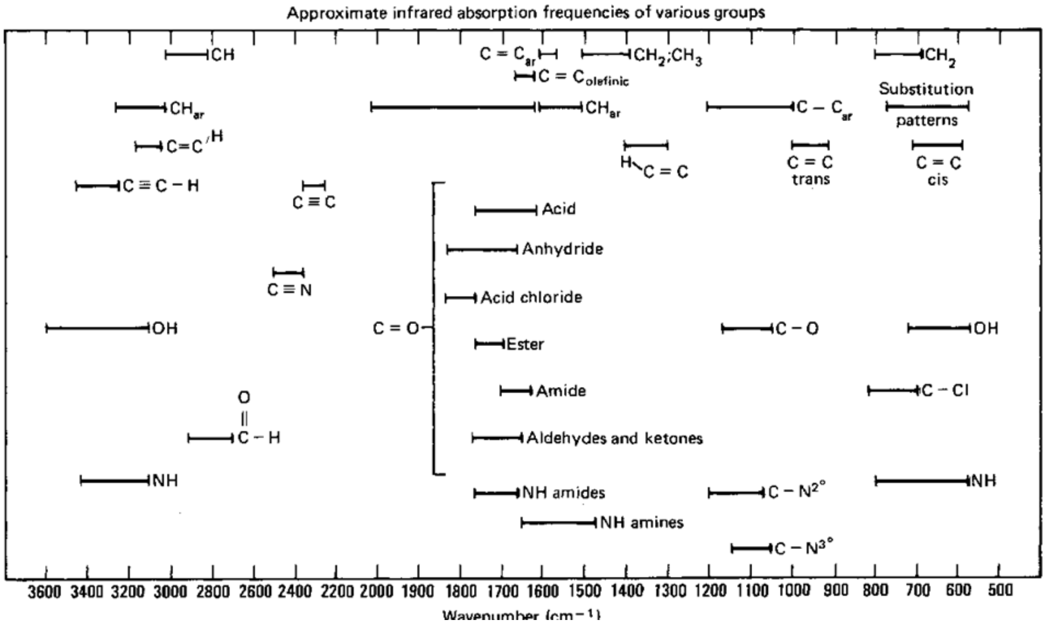
(d)

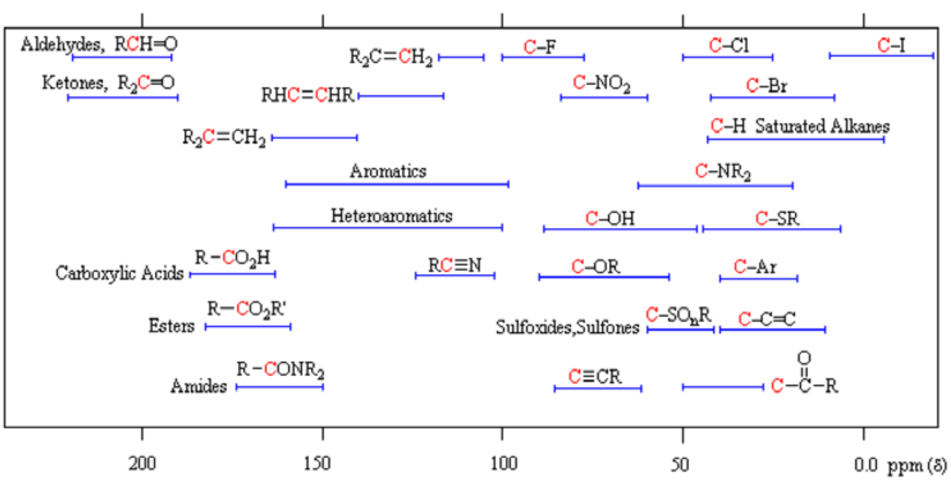


(e)



REFERENCE TABLES





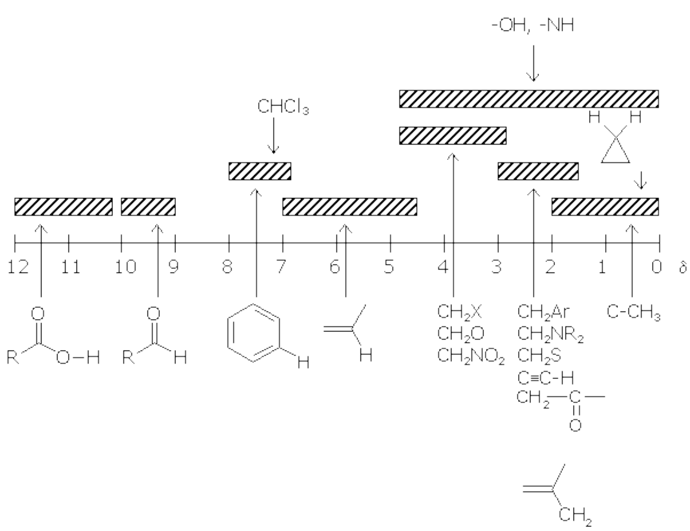


Table of Characteristic IR Absorptions

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

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