UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

November 5th, 2014 Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** ON ***BOTH*** **YOUR ANSWER BOOKLET** AND **COMPUTER ANSWER SHEET**.
ENTER **VERSION NUMBER 1** ON THE **COMPUTER ANSWER SHEET**

The examination consists of Parts 1 - 7, each of which should be attempted. Note that some parts provide you with a choice of questions, *e.g*. answer 4 out of 5. These will be graded in numerical order until the required number have been graded, regardless of whether they are right or wrong. Parts 1 - 4 will be computer graded, and only Parts 5, 6, and 7 are to be answered in the booklet provided.

Parts 1 - 4 consist of a series of multiple choice questions numbered 1 - 31 which are to be answered on your computer answer sheet (no extra time is provided for "bubbling" in the score sheet). Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a pencil only and ***not ink***. In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

A periodic table with atomic numbers and atomic weights and infrared data tables are located on the last two pages

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***.. **Absolutely no other electronic devices are allowed.**

14% PART 1: RELATIVE PROPERTIES

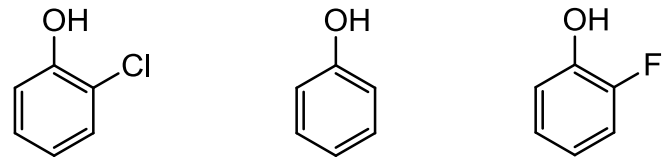
ANSWER ANY SEVEN (7) of questions 1-8 (2 marks per question)

Arrange the items in questions 1-8 in DECREASING ORDER (*i.e.* greatest, most etc. first) with respect to the indicated property.

Use the following code to indicate your answers.

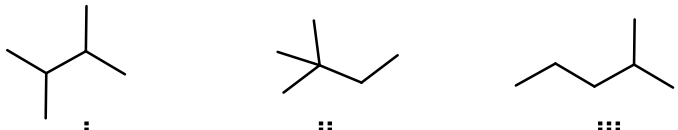
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

1. The relative acidity of each of the following compounds:



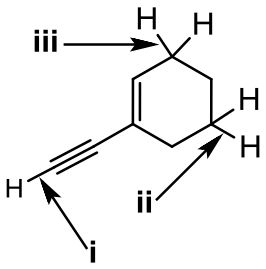
i **ii** **iii**

2. The number of types of H in each of the molecules:



i **ii** **iii**

3. The relative strengths of the **C–H** bonds indicated below:



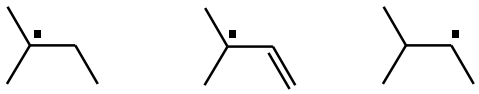
4. The relative basicity of each of the following:

i **ii** **iii**

Use the following code to indicate your answers.

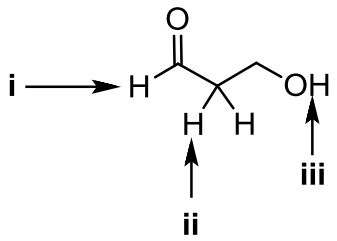
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

5. The relative stabilities of each of the following radicals:

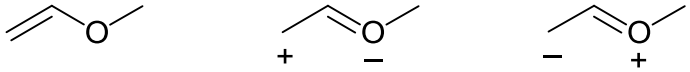


i **ii** **iii**

6. The relative acidity of each of the hydrogens indicated below:

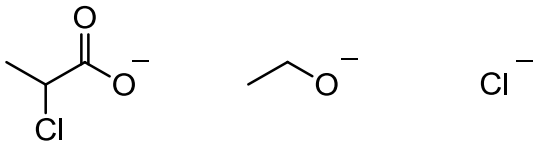


7. The relative importance of the resonance contributors shown below:



i **ii** **iii**

8. The relative basicity of the following compounds:

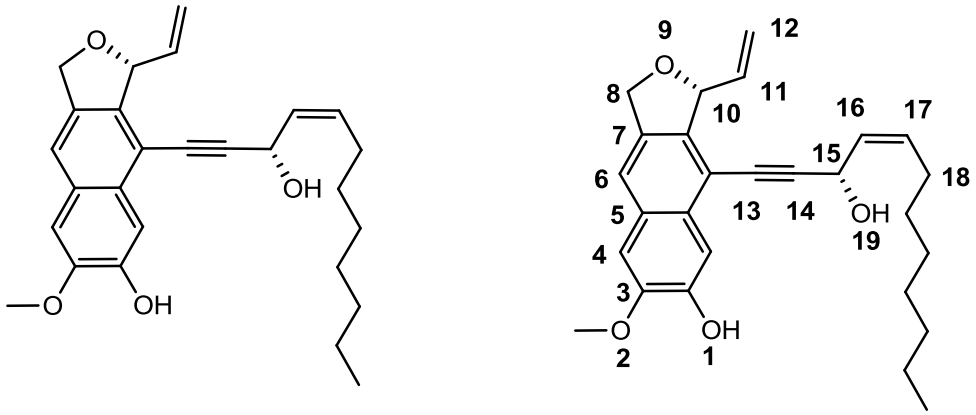


i **ii** **iii**

16% **PART 2: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 9 – 17 (2 marks per question)
For each of the questions 9 - 17 select the appropriate answer(s) from the answers provided. In some cases more than one selection may be required for full credit.

Use the structure of a natural product **Notoincitol B** as depicted below to answer the questions **9-17**.



Notoincitol B

9. What is the index of hydrogen deficiency (IHD) of Notoincitol ?

A 8 **B** 9 **C** 10 **D** 11 **E** 12

10. The most acidic H in Notoincitol is attached to which of the following atoms ?

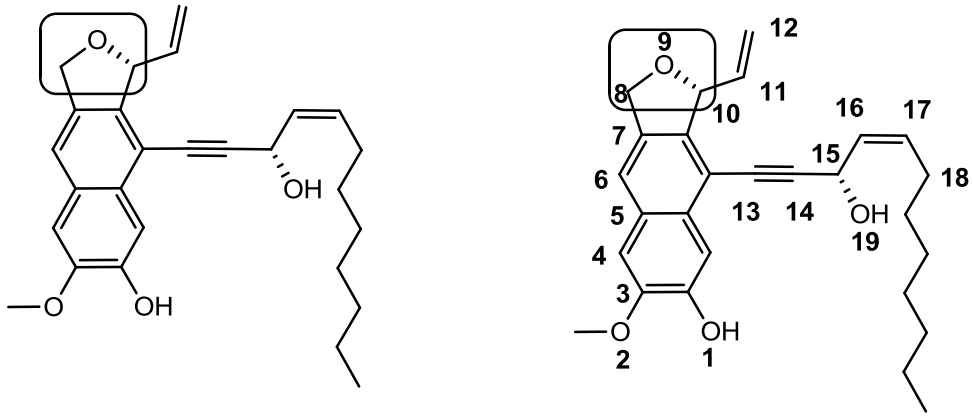
A O1 **B O2** **C O9** **D C12** **E O 19**

11. What configuration terms best describe **C10** and the alkene **C16=C17** respectively ?

A *R E* **B** *R Z* **C** *S E* **D** *S Z*

12. What is the oxidation state of **C15** ?

A +2 **B** +1 **C** 0 **D** -1 **E** -2



Notoincitol B

13. Which of the following functional groups is boxed in Notoincitol (above)?

A alcohol **B** phenol **C** ether **D** ketone **E** ester

14. Which of the following bonds is the strongest?

A C3-C4 **B C13-C14** **C C16-C17** **D C17-C18** **E O2-C3**

15. What type of orbital do the two lone pairs of electrons on **O9** occupy?

A sp^3 & sp^3 **B** sp^3 & sp^2 **C**. sp^3 & p **D**. sp^2 & p **E**. sp^2 & sp^2

16. What are the hybridizations of atoms **O2** and **C13** respectively?

A sp^3 / sp^3 **B** sp^3 / sp^2 **C** sp^2 / sp^2 **D** sp^3 / sp **E** sp^2 / sp

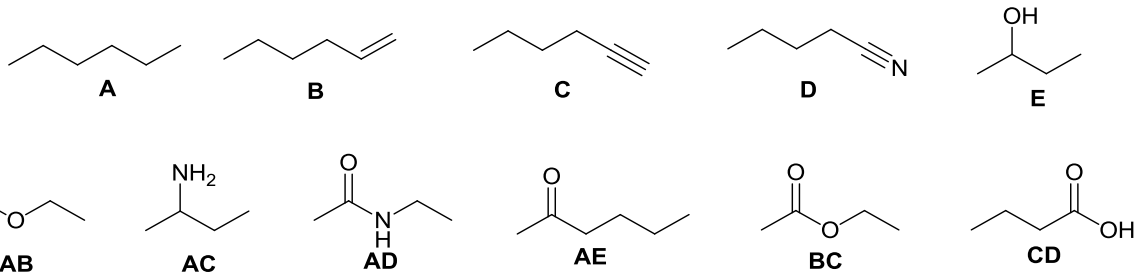
17. Which of the following terms describe position **C18**?

A primary **B** secondary **C** tertiary **D** allylic **E** benzylic

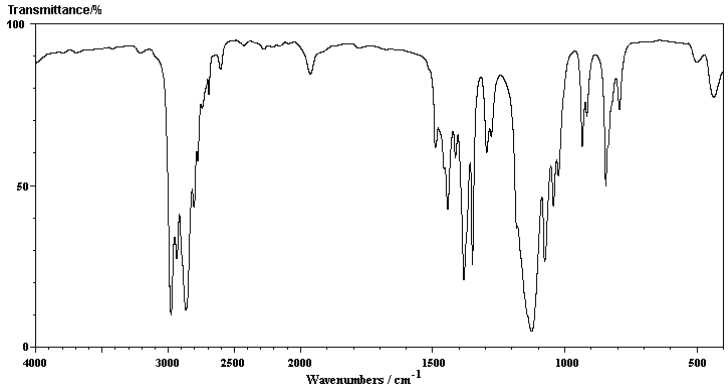
15% **PART 3: SPECTROSCOPY**

ANSWER ALL SIX (6) OF QUESTIONS 18 – 23 (2.5 marks per question).

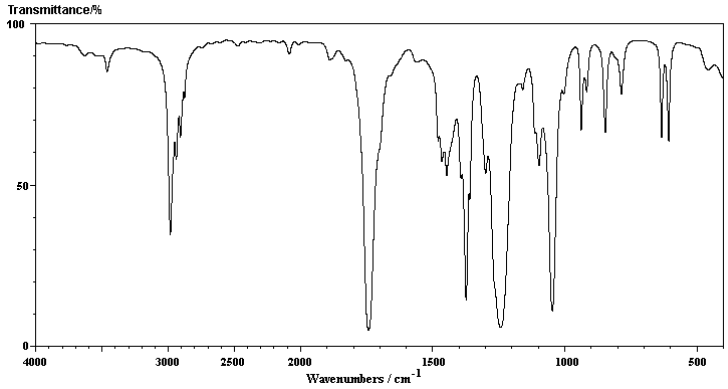
For each of the questions 18-23, match the IR spectra to a structure in the list below:



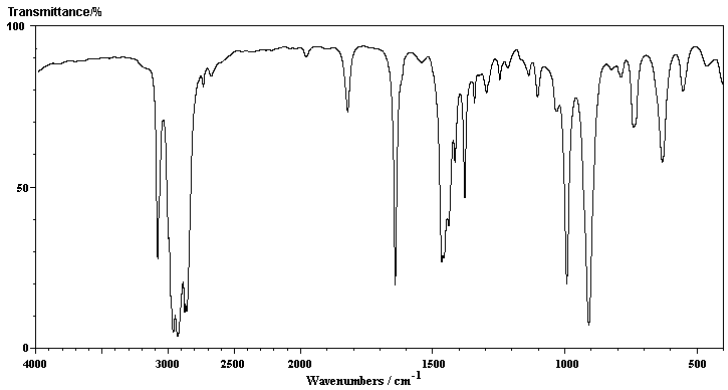
18.

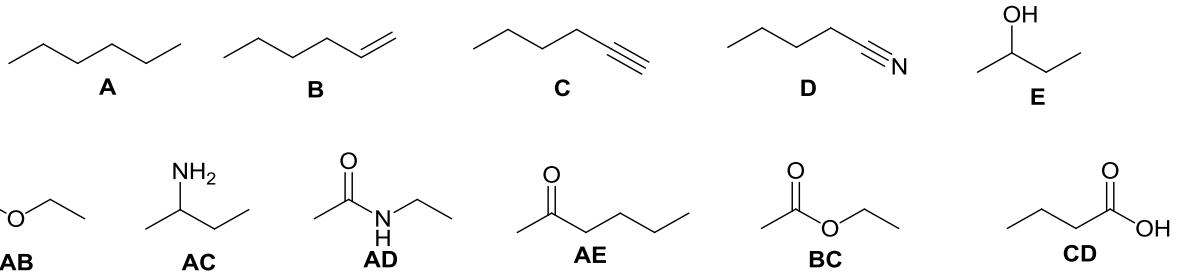


19.

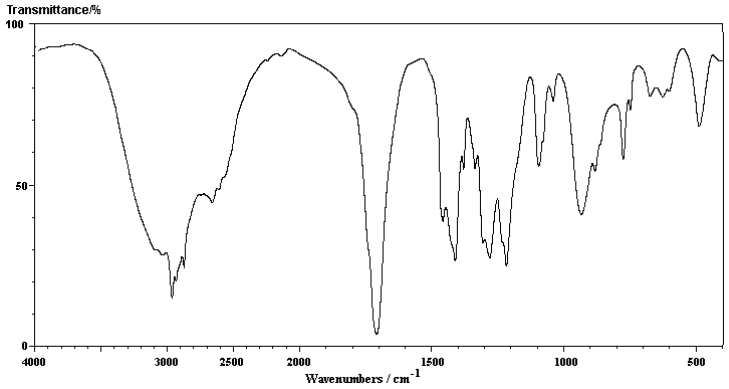


20.

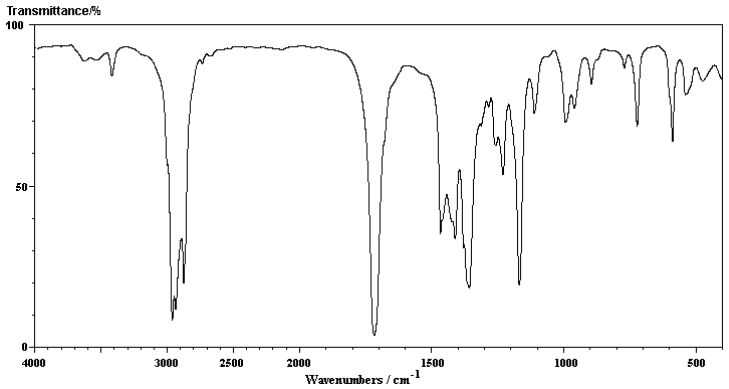



A
B
C
D
N
OH
E
O
AB
NH2
AC
O
N
H
AD
O
AE
O
O
BC
O
OH
CD

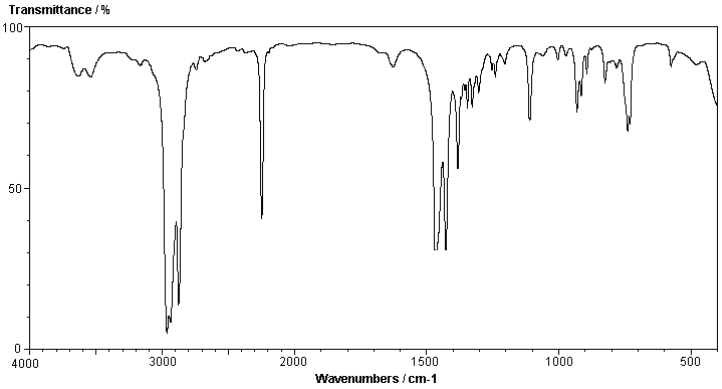
21.


Transmittance/%
100
50
0
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

22.


Transmittance/%
100
50
0
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

23.

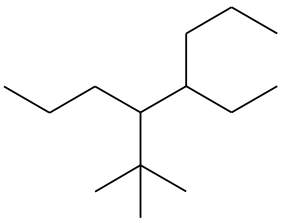

Transmittance / %
100
50
0
4000
3000
2000
1500
1000
500
Wavenumbers / cm-1

14% **PART 4: NOMENCLATURE**

ANSWER ANY SEVEN (7) of the questions 24-31 (2 marks per question).

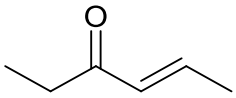
For each of questions 24 to 27, select the correct IUPAC name for the compound shown:

24.



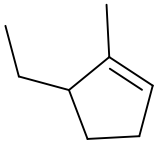
A. 4-ethyl-5-isopropyloctane
B. 4-(1,1-dimethylethyl)-5-ethyloctane
C. 4-(1,1-dimethylethyl)-3-propylheptane
D. 5-(1,1-dimethylethyl)-4-propylheptane
E. 5-ethyl-4-(1,1-dimethylethyl)-octane
AB. 3-propyl-4-(1,1-dimethylethyl)-heptane

25.



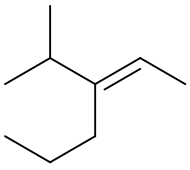
A. *trans*-hex-4-on-2-ene
B. *trans*-hex-4-en-3-one
C. *trans*-hex-2-en-4-one
D. *cis*-hex-4-on-2-one
E. *cis*-hex-4-en-3-one
AB.*cis* -hex-2-en-4-one

26.



A. 1-methyl-5-ethylcyclopentene
B. 5-ethyl-1-methylcyclopentene
C. 1-methyl-2-ethylcyclopentene
D. 2-ethyl-1-methylcyclopentene
E. 2-methyl-3-ethylcyclopentene
AB 3-ethyl-2-methylcyclopentene

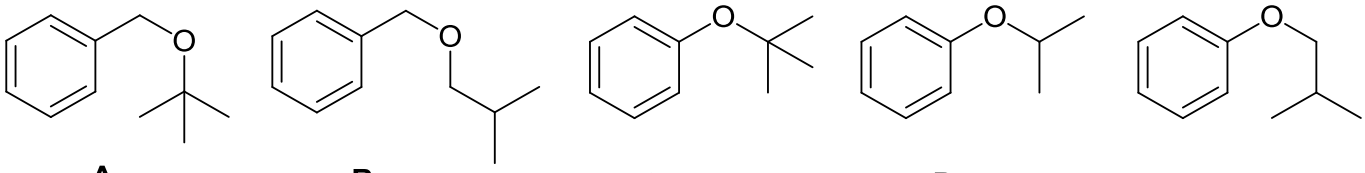
27.



A. *E*-3-isopropylhex-2-ene
B. *Z*-3-isopropylhex-2-ene
C. *E*-4-isopropylhex-4-ene
D. *Z*-4-isopropylhex-4-ene
E. *Z*-4-propylhex-4-ene
AB. *E*-4-methyl-3-propylpent-2-ene

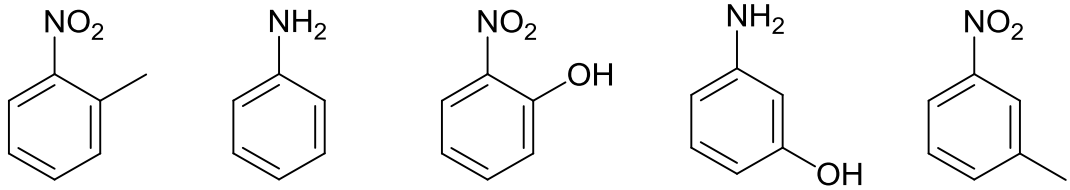
For each of questions 28 to 31, select the correct structure for the IUPAC name provided:

28. benzyl isobutyl ether



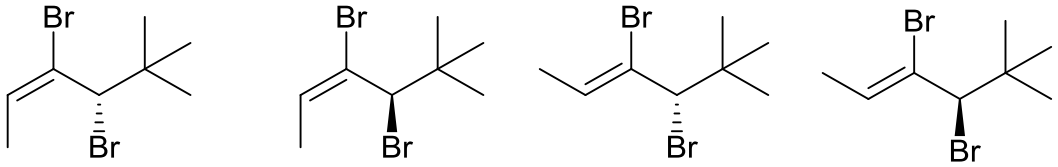
A. **B.** **C.** **D.** **E.**

29. o-nitrophenol



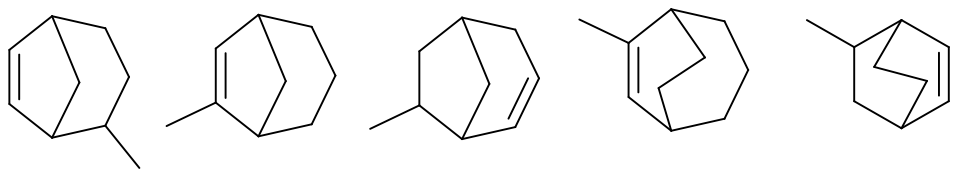
A **B** **C** **D** **E**

30. (2Z,4S)-3,4-dibromo-5,5-dimethylhex-2-ene :



A. **B.** **C.** **D.**

31. 6-methylbicyclo[3.2.1]oct-6-ene:



A **B** **C** **D** **E**

13% **PART 5: STRUCTURE DETERMINATION**

Write your answer in the booklet provided. For FULL marks you MUST show your work. PARTIAL marks will be awarded.

ANSWER ALL OF THE QUESTIONS

A. Compound **X** has molecular formula C_6H_{12},:

i. What is the Index of Hydrogen Deficiency (IHD) of **X** ?

ii. Draw a structure of **X** that has 1 type of H and 1 type of C

iii. Draw a structure of **X** with 3 types of H and 3 types of C that displays IR stretching frequencies at 1650 cm^{-1} and at 3100 cm^{-1}

B. Compound **Y** has molecular formula $C_4H_8O_2$,:

i. Identify four functional groups that are possible in **Y** ?

ii. Draw a structure of **Y** that has an approximate pKa = 5

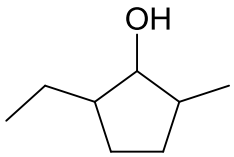
iii. Draw a structure of **Y** that has acidic protons with pKa = 15 and 20

iv. Identify a base that would deprotonate the structure for **Y** that you drew in part **ii** but not the structure you drew in part **iii**.

C.

i. Draw the structure of Z-5-(1,2-dimethylpropyl)dec-5-ene

ii. Give the IUPAC name for the structure shown below:



13% **PART 6: THERMODYNAMICS**

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

Thermodynamic Data		
compound	ΔH_{comb}^{o}	ΔH_{comb}^{o}
butan-1-ol	-2670 kJ mol^{-1}	-638.14 kcal mol^{-1}
***tert*-butanol**	-2644 kJ mol^{-1}	-631.51 kcal mol^{-1}
diethyl ether	-2732 kJ mol^{-1}	-652.53 kcal mol^{-1}

Using thermodynamic data to examine the relative energy differences between isomers:

a) Write a balanced chemical equation that corresponds to the heat of combustion values for these isomers.

b) Draw an energy diagram (with clearly labeled reactants, products, and ΔH values) to illustrate the relative energy difference between these three isomers. Circle the most stable isomer on your diagram.

c) Briefly compare the relative stabilities of the two alcohols (butan-1-ol and *tert*-butanol):

i. state which of these two alcohols is more stable

ii. provide a molecular level explanation for the difference in stability between these two structures

Relating physical property data to interactions on the molecular level:

d) Provide a molecular level explanation to explain *why* the boiling point of diethyl ether is significantly lower than the boiling points of the two alcohols

Contrasting the molecular level phenomena that correlate to these different trends:

e) Briefly state how the *structural features that explain trends in stability* **are different than** *those that explain trends in boiling points*

13% **PART 7: MECHANISM**

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

a) Draw a mechanistic sequence using double headed (*i.e.* electron pair) curly arrows that represents the ***single reaction sequence*** described verbally by the following description, in which 3-bromocyclohexanone, undergoes elimination when reacted with sodium hydride to form cyclohex-2-enone.

Step 1. An acid / base reaction where 3-bromocyclohexanone is deprotonated by sodium hydride to give a resonance stabilized carbanion and a hydrogen molecule.

Step 2. The lone pair of the carbanion forms a pi bond and a bromide ion acts as a leaving group to give cyclohex-2-enone and sodium bromide.

b) The intermediate formed in **step 1** is a resonance-stabilized carbanion. Use curly arrows to derive other resonance contributors of the carbanion.

c) What is the approximate pKa of the proton removed in **step 1**?
Suggest a different base that could be used instead of sodium hydride.

**** THE END ****

INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY (1)
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
$-CH_3$		(bend)	1450 and 1375	6.90 and 7.27	m
$-CH_2-$		(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride		1800	5.55	s
C–O	Alcohols, Ethers, Esters,				
	Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids (2)		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		ca. 3500	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro ($R–NO_2$)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C–X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad

Cont'd

PERIODIC TABLE

1 1A																	18 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)