UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

October 30th, 2012 Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** ON ***BOTH*** **YOUR ANSWER BOOKLET** AND **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. A periodic table with atomic numbers and atomic weights and infrared data tables are located on the last two pages.

Parts 1 - 4 consist of a series of multiple choice questions numbered 1 - 31 which are to be answered on your computer answer 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***.

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**

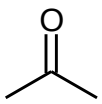
ANSWER ANY SEVEN (7) of questions 1-8 (2 marks per question)

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

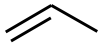
Use the following code to indicate your answers.

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

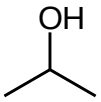
1. The relative acidities of the most acidic H in each of the following**:**



i

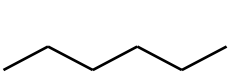


ii

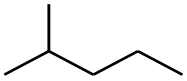


iii

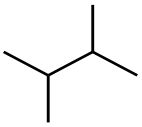
2. The heats of formation of each of the following (least exothermic to most exothermic)**:**



i

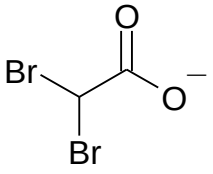


ii

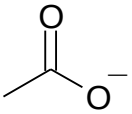


iii

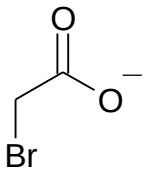
3. The relative basicity of the following:



i

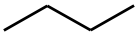


ii

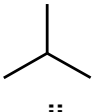


iii

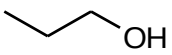
4. The boiling points of the following:



i



ii

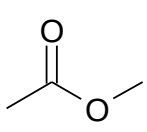


iii

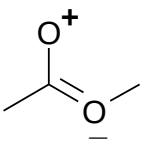
Use the following code to indicate your answers.

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

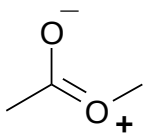
5. The relative importance of the following resonance contributors to the structure shown (all required charges are shown):



i

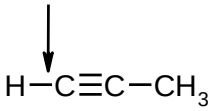


ii

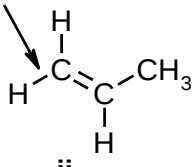


iii

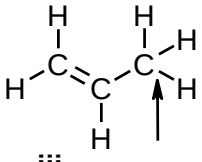
6. The relative strengths of the C-H bonds indicated in each of the following:



i

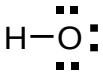


ii

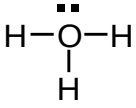


iii

7. The formal charge associated with the following molecules (most positive to most negative):



i



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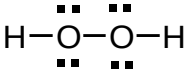
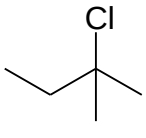
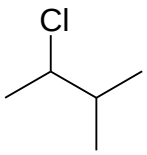


iii

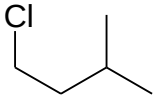
8. The relative yields of the following monochlorinated products from the u.v. light promoted reaction of Cl_2 with 2-methylbutane:



i



ii



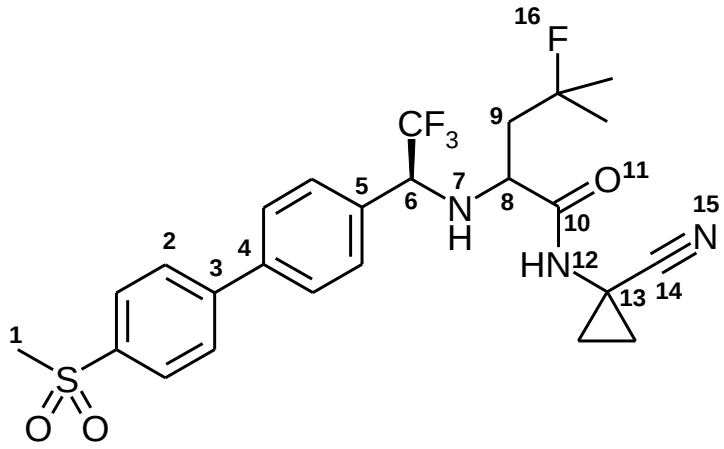
iii

Cont'd

18% **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 from the answers provided. In some cases more than one selection may be required for full credit.

Questions 9 to 17 all refer to Odanacatib (structure shown below), a potential drug (still under investigation) for osteoporosis and bone metastasis.



9. What is the oxidation state of **C10** ?

A. -4 **B.** -3 **C.** -2 **D.** -1 **E.** 0 **AB**. +1 **AC**. +2 **AD** +3 **BC**. +4

10. Which of the following atoms are sp^3 hybridized?

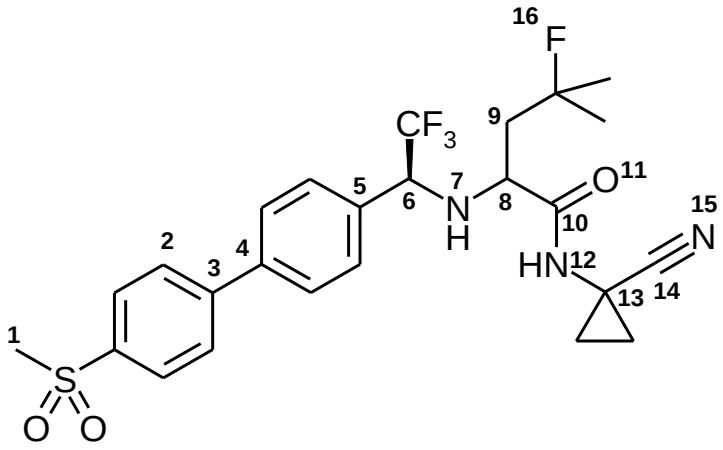
A. C-1 **B.** C-3 **C.** C-6 **D.** C-9 **E.** C-13

11. Which of the following atoms is the most basic ?

A. C-5 **B.** N-7 **C.** C-8 **D.** N-12 **E.** F-16

12. Which of the following bonds listed is the strongest?

A. C2-C3 **B.** C3-C4 **C.** C8-C9 **D.** C10-O11 **E.** C14-N15



13. What are the hybridizations for **N-7** and **N-12** respectively?

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

14. Which orbitals do the lone pairs on **O-11** occupy?

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

15. What type of functional groups is **N-7** a part of ?

A. 1^o amine **B.** 2^o amine **C.** 3^o amine **D.** 1^o amide **E.** 2^o amide **AB**. 3^o amide

16. What term(s) can be used to best describe **C-6**?

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

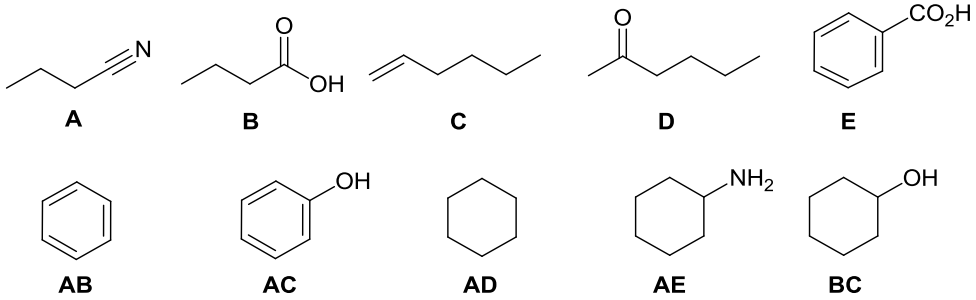
17. What is the approximate bond angle at **N12-C13-C14**?

A. 60^0 **B.** 90^0 **C.** 109.5^0 **D.** 120^0 **E.** 180^0

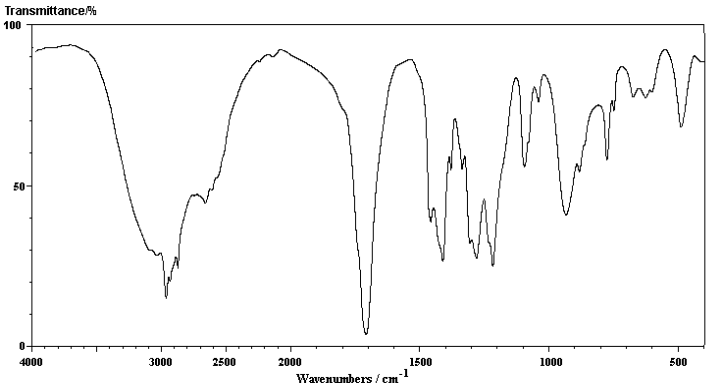
15% **PART 3: SPECTROSCOPY**

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

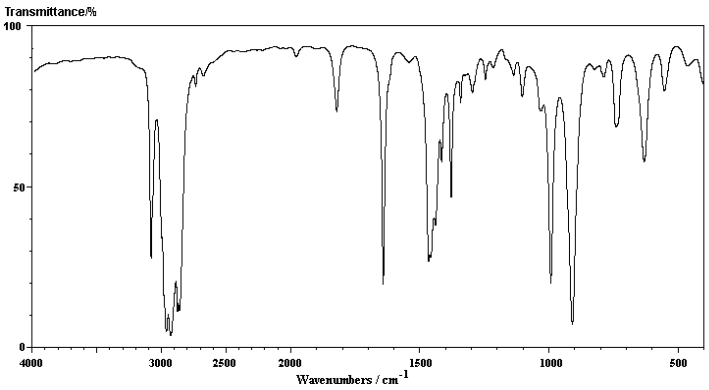
For each of the questions 18-23, match the IR spectra to a structure in the list below:



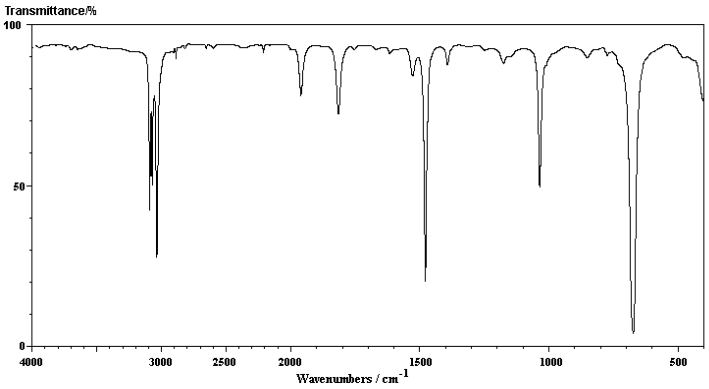
18.

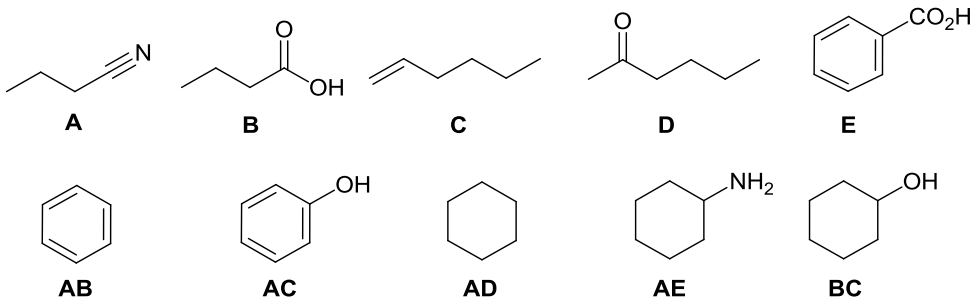


19.

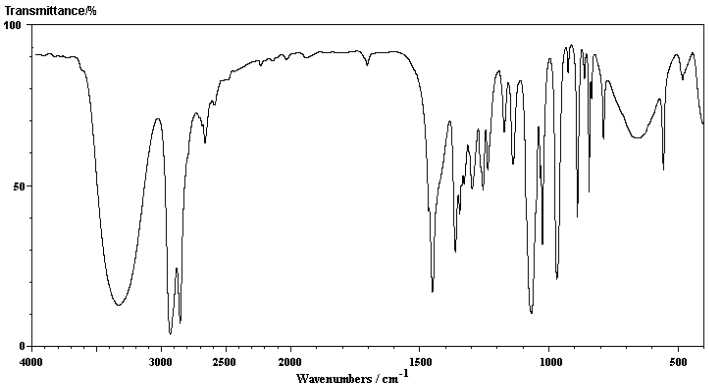


20.

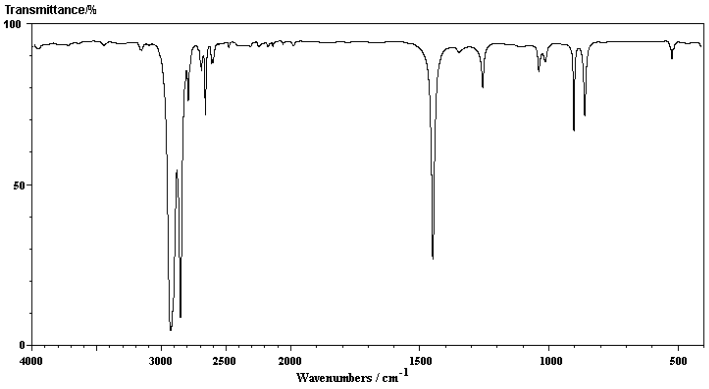



N
O
OH
O
CO2H
A
B
C
D
E
OH
NH2
OH
AB
AC
AD
AE
BC

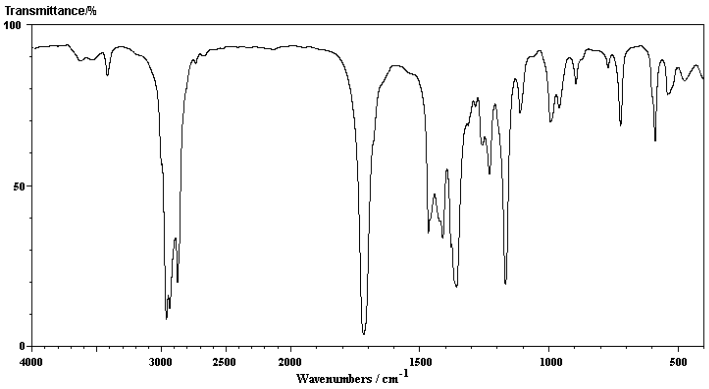
21.


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.

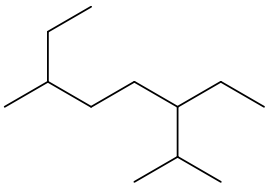

Transmittance/%
100
50
0
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm-1

14% **PART 4: NOMENCLATURE**

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

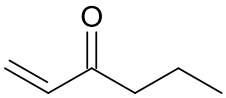
For each of questions 24 to 27, select the correct IUPAC name for the compound shown:

24.



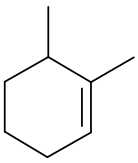
A. 3-isopropyl-6-ethylheptane
B. 2,6-dimethyl-3-ethyloctane
C. 3,7-dimethyl-6-ethyloctane
D. 2-ethyl-5-isopropylheptane
E. 3-ethyl-2,6-dimethyloctane

25.



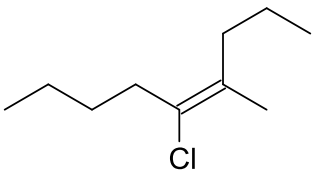
A. hex-3-on-3-ene
B. hex-1-en-3-one
C. hex-1-en-3-al
D. hex-3-al-3-ene
E. 3- hydroxy-1-hexene

26.



A. 1,6-dimethylcyclohexene
B. 2,3-dimethylcyclohexene
C. 1,2-dimethylcyclohexene
D. 2,3-dimethylcyclohex-1-ene
E. 5,6-dimethylcyclohex-1-ene

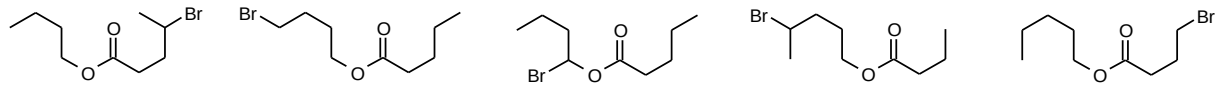
27.



A. (Z)-5-chloro-4-methylnon-4-ene
B. (E)-5-chloro-4-methylnon-4-ene
C. (Z)-5-chloro-6-methylnon-5-ene
D. (E)-5-chloro-6-methylnon-5-ene
E. 1-sec-pentylene-1-chloropentane

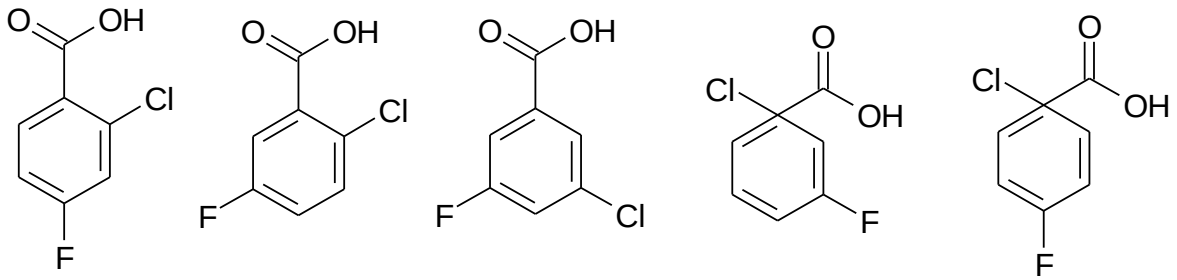
For each of questions 28 to 31, select the correct structure for the IUPAC name provided:

28. 4-bromobutyl pentanoate



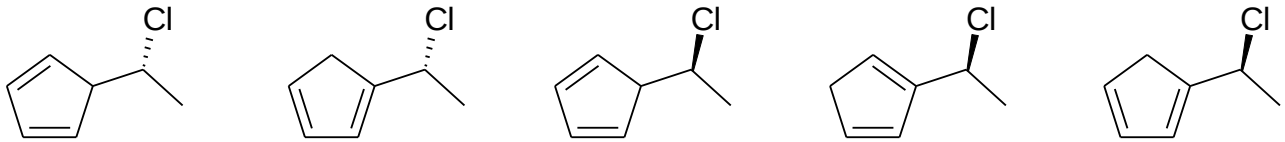
A **B** **C** **D** **E**

29. 2-chloro-4-fluorobenzoic acid



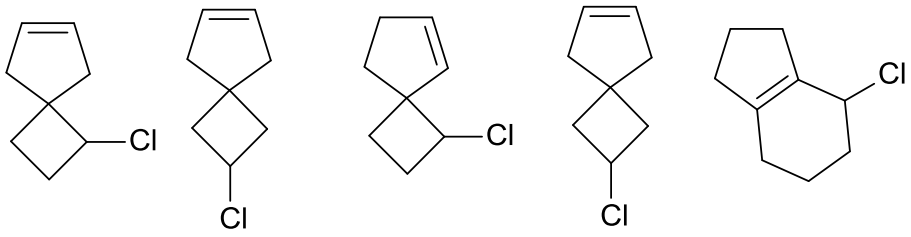
A **B** **C** **D** **E**

30. (R)-1-(1-chloroethyl)cyclopenta-1,3-diene :



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

31. 2-Chlorospiro[3.4]oct-6-ene:



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

Cont'd

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.

Elemental analysis (CHN) of an unknown organic molecule **X** determined that it contained 69.8% carbon, 11.6% hydrogen and 0% nitrogen by weight.

a) What is the empirical formula of this molecule ?

b) The molecular weight of this molecule was determined to be 86 g/mol. What is its molecular formula ?

c) What is the index of hydrogen deficiency for this molecule?

d) Draw an isomer of **X** that would have a characteristic IR peak at 1715 cm^{-1}, and that contains five types of carbon, and four types of hydrogen.

e) Draw a resonance structure of the isomer you proposed in part **d** above.

f) Draw another isomer of **X** that would fit the molecular formula and would have a characteristic IR peak at 1715 cm^{-1}, and that contains four types of carbon, and three types of hydrogen.

g) Draw another isomer of **X** that contains a stereocentre.

h) Draw an isomer of **X** that has no sp^2 or sp-hybridized atoms, no significant IR signals in either the 1715 or 3500 cm^{-1} region, and that has three types of carbon and three types of hydrogen.

Cont'd

13% **PART 6: THERMODYNAMICS**

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

a) What type of isomers are cyclohexane and *trans*-hex-3-ene ?

b) Write a balanced equation for the combustion of cyclohexane.

c) Draw a line diagram structure of *trans*-hex-3-ene.

d) One of these isomers has a heat of combustion (ΔH_C^o) = -938 kcal mol^{-1}.

Calculate ΔH_f^o, for this isomer using the following heats of combustion:

ΔH_C^o, C (graphite) = -93.9 kcal mol^{-1}

ΔH_C^o, H_2 (gas) = -68.4 kcal mol^{-1}

e) The other isomer has a heat of formation (ΔH_f^o) = -19.3 kcal mol^{-1}.

Match each of the above named isomers to their corresponding heat of formation

STATE which isomer is more stable and ***briefly*** justify your choice.

Cont'd

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 points, in which an aldehyde, ethanal, undergoes alkylation to give a new aldehyde, propanal, when reacted with a base, lithium diisopropylamide (LDA) and then an alkylating agent, methyl bromide.

Step 1. An acid / base reaction in which a proton is removed from ethanal by the amide ion coming from lithium diisopropylamide (LDA) to create a resonance stabilized carbanion (an enolate) and diisopropyl amine.

Step 2. Attack of the enolate (the nucleophile) on to the electrophilic carbon of methyl bromide leading to the formation of a new C-C bond and loss of a bromide anion.

b) While the pK_a of the most acidic proton in ethanal is 20 the pK_a of ethane is 50. **Explain the difference (if applicable use curly arrows).**

c) Based on the information provided in the question what alkylating agent should you use, if you wanted to prepare hexanal?

**** THE END ****

ASC / IRH / VI Oct 2012

Cont'd

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)