UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

November 6th, 2013 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

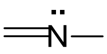
ANSWER ANY SEVEN (7) of questions 1-8 (2 marks per question)

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

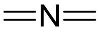
Use the following code to indicate your answers.

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

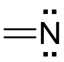
1. The relative formal charge on the nitrogen atom in each of the following molecules:



i

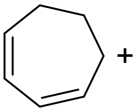


ii

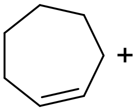


iii

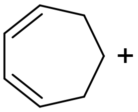
2. The relative stabilities of the following carbocations**:**



i

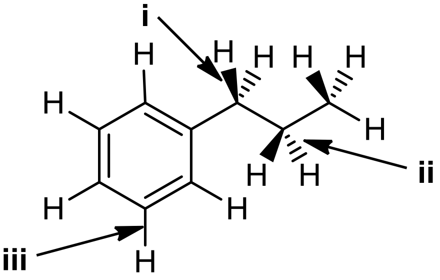


ii



iii

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



4. The relative basicity of each of the following:

CH_4 **i**

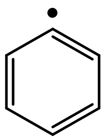
NH_3 **ii**

CH_3O^- **iii**

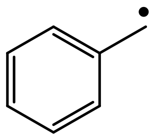
Use the following code to indicate your answers.

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

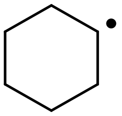
5. The relative stabilities of each of the following radicals:



i

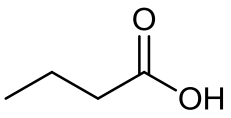


ii

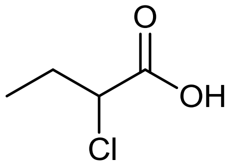


iii

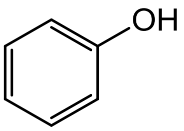
6. The relative acidity of each of the following :



i

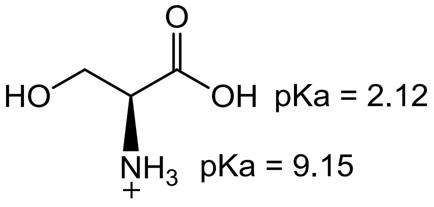


ii

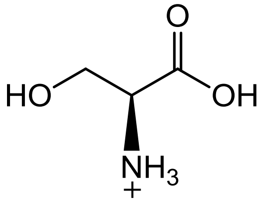


iii

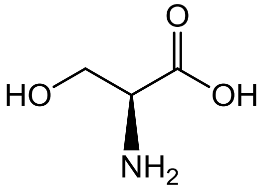
7. The amino acid serine is shown below along with the pKa values:



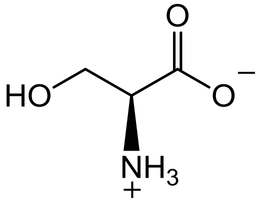
Rank the relative amounts of each of the following species in a solution of pH = 2.5:



i

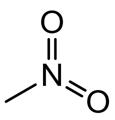


ii

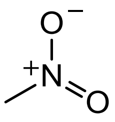


iii

8. The relative importance of the following resonance contributors of nitromethane:



i



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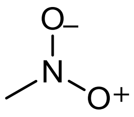


iii

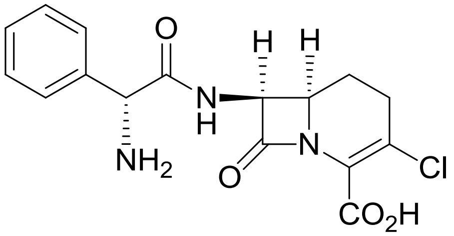
16% PART 2: MOLECULAR PROPERTIES

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.

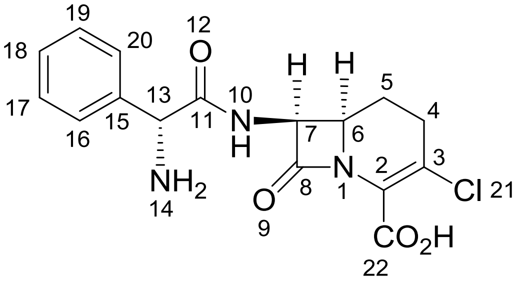
Loracarbef is an antibacterial compound. Use its structure as depicted below to answer the questions **9-17**.

Loracarbef



Loracarbef

(with atoms numbered)



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

A 6 **B** 7 **C** 8 **D** 9 **E** 10

10. Of the atoms listed below, which is the most basic ?

A O9 **B C2** **C N10** **D N14** **E Cl 21**

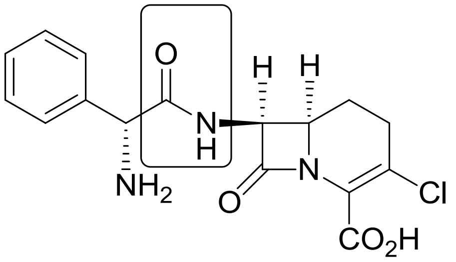
11. What configuration terms best describe **C6** and the alkene **C2=C3** respectively ?

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

12. What is the oxidation state of **C13**?

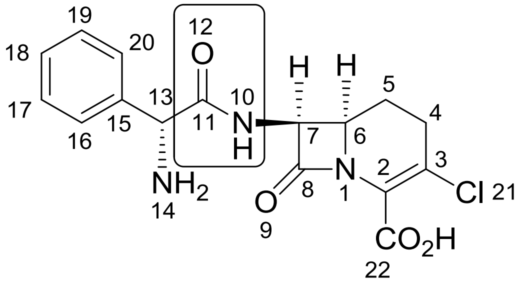
A +2 **B** +1 **C** 0 **D** -1 **E** -2

Loracarbef



Loracarbef

(with atoms numbered)



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

A. alcohol **B**. amide **C**. ether **D**. ketone **E**. amine

14. Which of the following bonds is the longest ?

A C15-C20 B C13-C15 C N10-C11 D C4-C5 E C2-C3

15. What type of orbital does the lone pair of electrons on **N10** occupy ?

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

16. What are the hybridizations of atoms **C4** and **N14** respectively ?

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

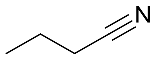
17. Which of the following terms describe position **C13** ?

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

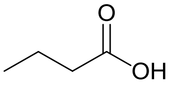
15% **PART 3: SPECTROSCOPY**

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

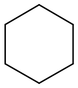
For each of the questions 18-23, match the IR spectra to a structure in the list below:



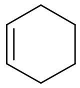
A



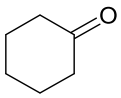
B



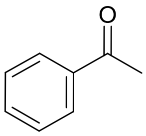
C



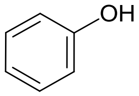
D



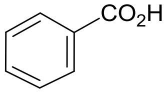
E



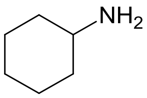
AB



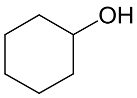
AC



AD

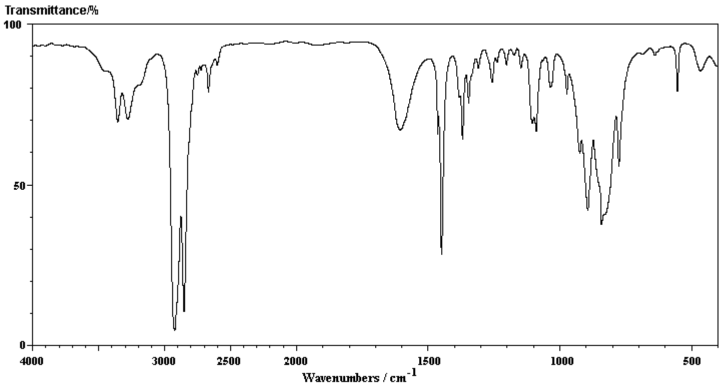


AE

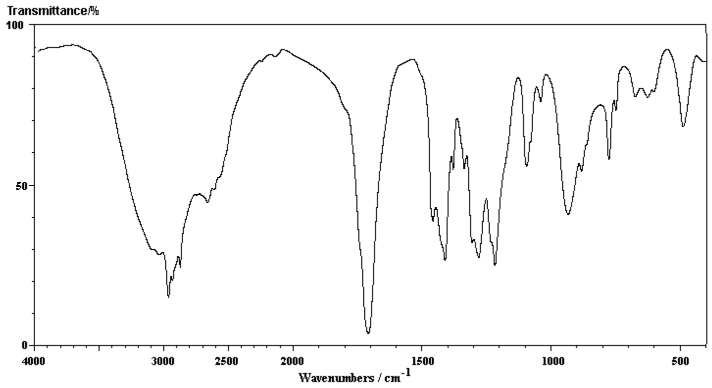


BC

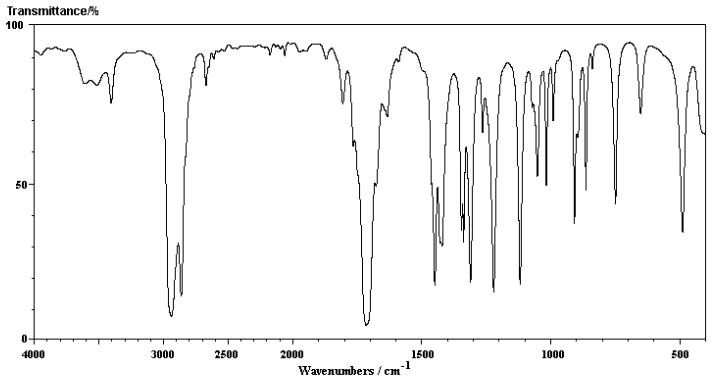
18.

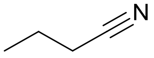


19.

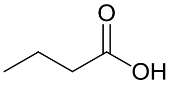


20.

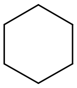




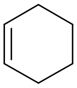
A



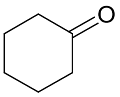
B



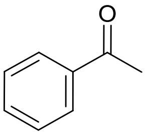
C



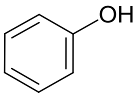
D



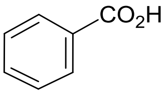
E



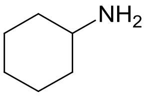
AB



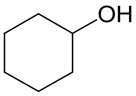
AC



AD

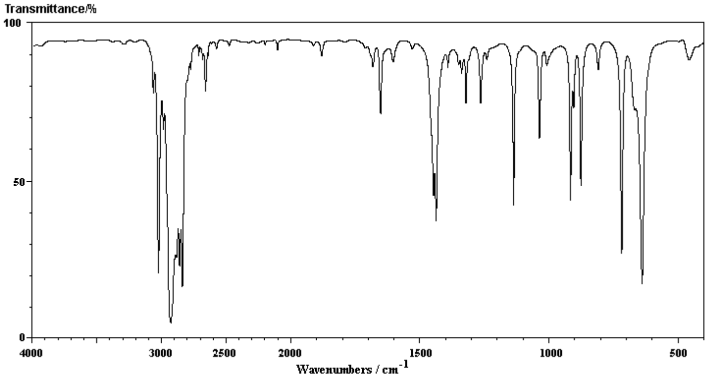


AE



BC

21.



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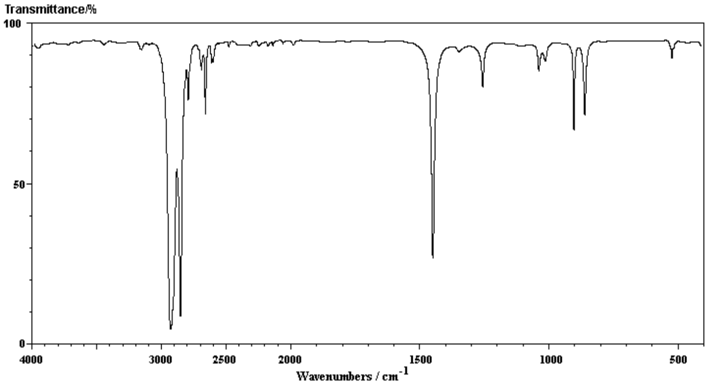
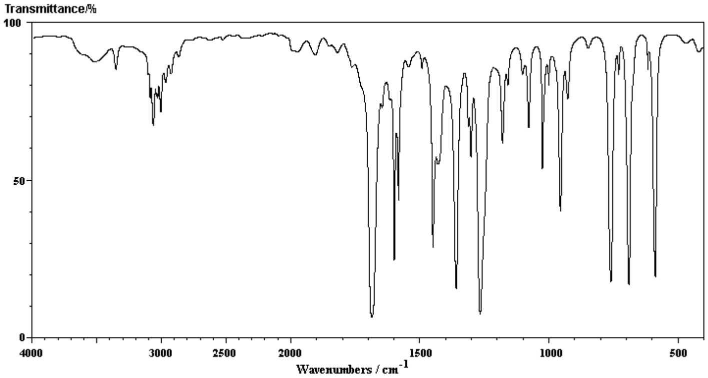


23.

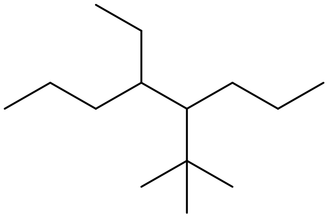


14% PART 4: NOMENCLATURE

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

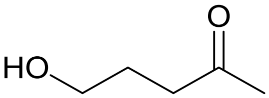
For each of questions 24 to 27, select the correct IUPAC name for the compound shown:

24.



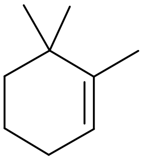
A. 4-(1,1-dimethylethyl)-5-ethyloctane
B. 5-(1,1-dimethylethyl)-4-ethyloctane
C. 4-ethyl-5-(1,1-dimethylethyl)octane
D. 5-ethyl-4-(1,1-dimethylethyl)octane
E. 4,5-diethyl-2,2-dimethyloctane

25.



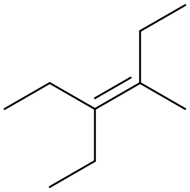
A. 5-hydroxypentan-2-one
B. 1-hydroxypentan-4-one
C. 2-oxapentan-1-ol
D. 5-hydroxypentan-2-al
E. 1-oxypentan-4-one

26.



A. 1,1,2-trimethylcyclohexene
B. 1,2,2-trimethylcyclohexene
C. 1,1,6-trimethylcyclohexene
D. 1,6,6-trimethylcyclohexene
E. 2,2,3-trimethylcyclohexene

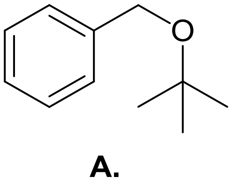
27.



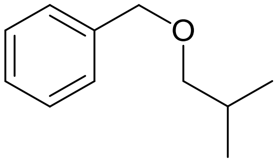
A. *cis*-3-methyl-4-ethylhex-3-ene
B. *trans*-3-methyl-4-ethylhex-3-ene
C. *cis*-3-ethyl-4-methylhex-3-ene
D. *trans*-3-ethyl-4-ethylhex-3-ene
E. 3-ethyl-4-methylhex-3-ene

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

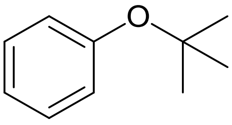
28. isobutyl phenyl ether



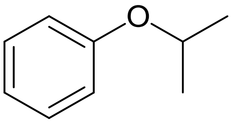
A.



B.



C.



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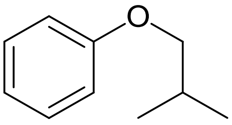
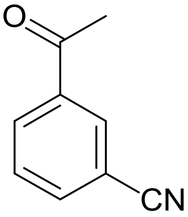


E.

29. o-nitrobenzaldehyde



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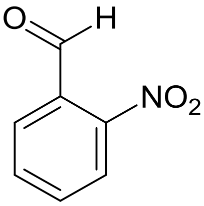

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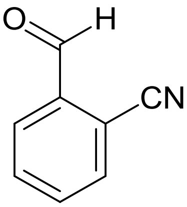

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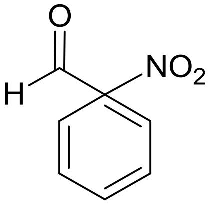

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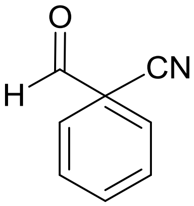
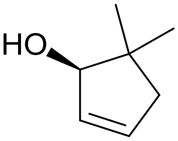
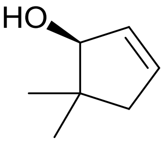


E

30. (R)-5,5-dimethylcyclopent-2-en-1-ol :



A.



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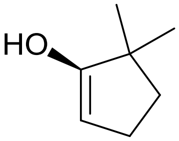

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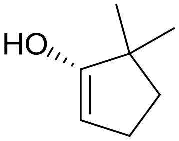
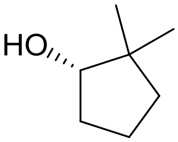
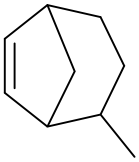


D.

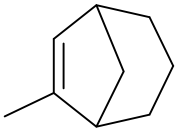


E.

31. 2-methylbicyclo[3.2.1]oct-6-ene:



A



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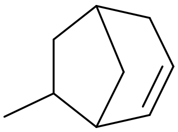
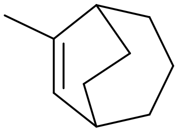


C



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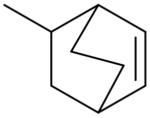

E

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.

Unknown organic molecule **X** has a molecular formula of C_8H_{14}. Answer the following questions about molecule **X** and its isomers.

a) What is the Index of Hydrogen Deficiency (IHD) of this molecule?

b) Draw an isomer of **X** that has 3 types of H atoms

c) Draw an isomer of **X** that has a double bond in the *E* configuration

d) Draw an isomer of **X** that displays distinct stretching frequencies at 2150 cm^{-1} and at 3300 cm^{-1}

e) **i.** Which of the isomers you drew for **b**, **c** and **d** is the most acidic ?

ii. Use structural arguments to briefly explain why this site is the most acidic.

iii. Show a balanced reaction equation for deprotonation of this isomer at its most acidic site. Be sure to use a base that would be strong enough to do this deprotonation.

f) Use the isomer of **X** you drew in part **c** to answer the following questions:

i. Draw a reaction equation to show the major product(s) of reacting this isomer of **X** with Br_2 in the presence of light. Explain why this(these) is(are) the expected product(s).

ii. After performing the reaction described in **f i** above, a chemist tested the product mixture and found a product with molecular formula $C_8H_{14}Br_2$. Explain what this tells you.

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 student was working in the laboratory and labeled three vials for isomeric compounds **X**, **Y**, and **Z**. The student remembered that **Z** was definitely pent-1-yne, however (s)he forgot which was 1,3-pentadiene and which was 1,4-pentadiene…

Compound	ΔH_C^o	ΔH_f^o
X	-768.93 kcal mol^{-1}	**?**
Y	?	18.12 kcal mol^{-1}
Z= pent-1-yne	?	34.49 kcal mol^{-1}

a) Draw line diagrams of the three compounds:
pent-1-yne, 1,3-pentadiene, and 1,4-pentadiene.

b) Since the student had the heats of combustions for graphite and H_2 (s)he determined that it was possible to determine the heat of formation (ΔH_f^o) of compound **X**.

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}

c) Match 1,3-pentadiene and 1,4-pentadiene to the above heat of formation values, ΔH_f^o. Use structural arguments to justify your answer of which of the two isomers is more stable and ***briefly*** justify your choice.

d) Show how the stability of pent-1-yne relates to the other two by drawing an energy diagram to illustrate the relative energy differences.

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 an alcohol, 3-methylbut-2-en-1-ol, undergoes nucleophilic substitution when reacted with HBr to give a mixture of two alkyl bromides.

Step 1. An acid / base reaction where 3-methylbut-2-en-1-ol is protonated by HBr to give an oxonium ion and a bromide ion.

Step 2. Loss of a water molecule from this species creating a resonance stabilized primary carbocation.

Step 3. Attack of the bromide ion as a nucleophile on the carbocation to give the product, 1-bromo-3-methylbut-2-ene, a primary alkyl bromide..

b) The carbocation formed in **step 2** has resonance stablisation. Use curly arrows to derive the other major contributor**.**

c) Draw the structure of the other alkyl bromide that is produced by the reaction.

d) Is the carbocation produced in **part b** primary, secondary or tertiary ? Briefly explain your choice.

**** THE END ****

WLB / IRH / ERS Nov 2013

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

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(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

PERIODIC TABLE

1 1A	**2** 2A	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	**18** 8A
1 **H** 1.008																	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											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)