THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

November 4th, 2009 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 spectroscopic data tables are located inside the back cover.

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.

PLEASE WRITE THE NUMBER OF YOUR LABORATORY SECTION AT THE TOP OF THE FRONT COVER ON YOUR ANSWER BOOKLET

18% PART 1: RELATIVE PROPERTIES

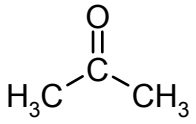
ANSWER ANY NINE (9) of questions 1-10 (2 marks per question)

Arrange the items in **questions 1-10** in **DECREASING ORDER** (*i.e*. greatest, most etc. **first**) with respect to the indicated property.

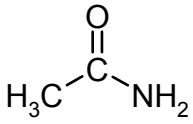
Use the following code to indicate your answers.

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

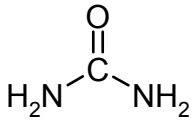
1. The relative strengths of the **C=O** bonds in each of the following molecules:



i

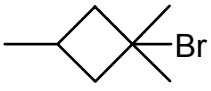


ii

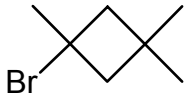


iii

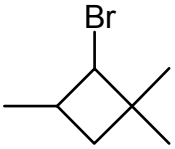
2. The relative yields of the following products from the light catalysed reaction of Br_2 with 1,1,3-trimethylcyclobutane:



i

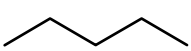


ii

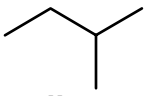


iii

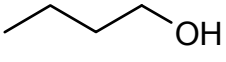
3. The boiling points of the following**:**



i



ii



iii

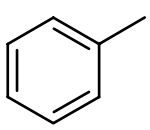
Use the following code to indicate your answers.

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

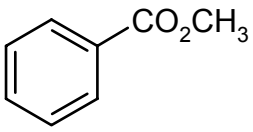
4. The number of ^{13}C-NMR peaks for the following:

Pentane	Cyclohexane	2,2-Dimethylpropane
i	**ii**	**iii**

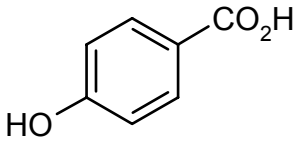
5. The relative Rf values in normal thin layer chromatography of:



i

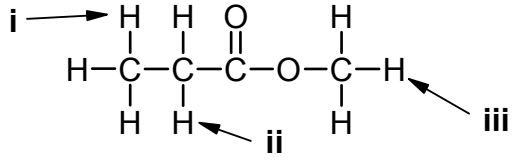


ii

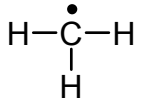


iii

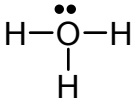
6. The ^{1}H-NMR chemical shifts (δ in ppm) of the indicated hydrogens:



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



i



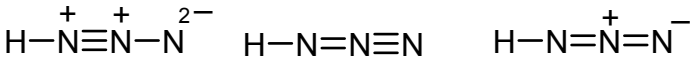
ii

iii

Use the following code to indicate your answers.

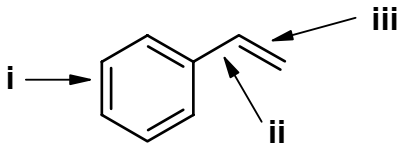
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

8. The relative importance of the following resonance contributors to HN_3 (all required charges are shown):

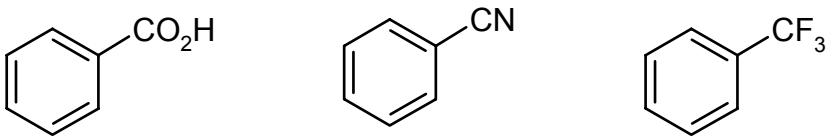


i **ii** **iii**

9. The relative length of the indicated bond:



10. The relative IHD (units of unsaturation) of the following molecules:

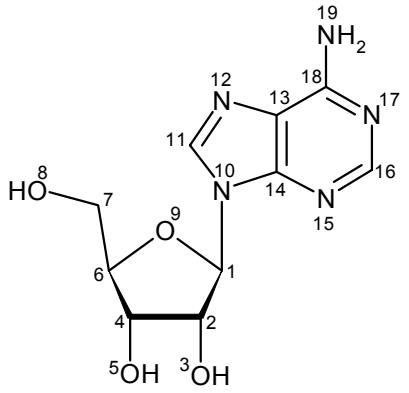


i **ii** **iii**

18% **PART 2: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 11 - 19.

Adenosine is a key nucleoside used to form RNA. Use the structure below to answer questions **11** - **14** by select answer(s) from those provided. In some cases more than one answer may be correct; all correct answers must be selected for full marks.



Adenosine

11. What is the IHD of Adenosine ?

A. 4 B. 5 C. 6 D. 7 E. 8

12. What is the hybridizations of **O9** / **N12** respectively ?

A. sp^3,sp^3 B. sp^3,sp^2 C. sp,sp D. sp^2,sp E. sp^3,sp

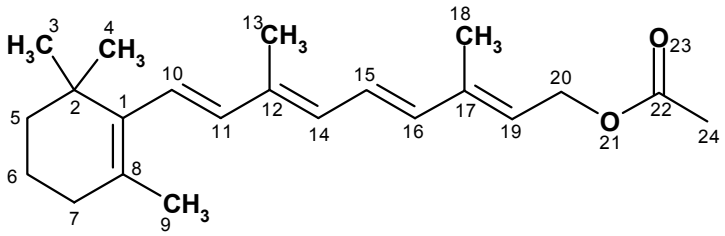
13. What is the closest value to the **O8-C7-C6** bond angle ?

A. 90° B. 180° C. 109.5° D. 120° E. 112°

14. Which one of the following bond has the highest stretching frequency (cm^{-1}) in the infrared spectrum of Adenosine ?

A. **C7-O8** B. **O8-H** C. **C6-H** D. **C11-N12** E. **C11-H**

Use the structure of Vitamin A Acetate to answer questions **15 - 19** by select answer(s) from those provided. If in some cases more than one answer may be correct, then all correct answers must be selected for full marks.



Vitamin A Acetate

15. Which C-H bond is the weakest among those listed below ?
    A. **C9-H** B. **C3-H** C. **C7-H** D. **C24-H** E. **C5-H**

16. Among the bonds listed below, which one is the longest ?
    A. **C2-C3** B. **C8-C9** C. **C22-C24** D. **C24-H** E. **C14-C15**

17. For O21, which orbitals do the two lone pairs of **O21** occupy ?
    A. sp^2 / sp^2 B. sp^3 / sp^3 C. p / p D. p / sp^2 E. p / sp^3

18. What functional groups are found in vitamin A acetate ?
    A. Ether B. aldehyde C. alkene D. ester E. ketone

19. What term(s) can be used to best describe **C20** ?
    A. primary B. secondary C. tertiary D. allylic E. benzylic

10% **PART 3: SPECTROSCOPY**

ANSWER ALL FOUR (4) OF QUESTIONS 20 - 23.

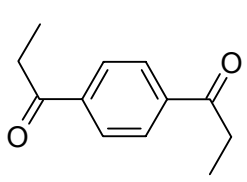
For each of questions 20-23 select the compound from the list provided that corresponds BEST with the spectroscopic data provided. The following common abbreviations have been used s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet

20. **^{1}H NMR** : δ/ppm 1.2 (t, 3H), 2.4 (q, 2H)
^{13}C-NMR: δ/ppm 8, 29, 170
IR : 1756, 1822 cm^{-1}

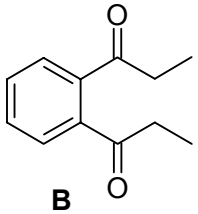
21. **^{1}H NMR** : δ/ppm 1.1 (t, 3H), 2.4 (q, 2H)
^{13}C-NMR: δ/ppm 8, 35, 212
IR : 1716 cm^{-1}

22. **^{1}H NMR** : δ/ppm 1.2 (t, 3H), 2.2 (q, 2H), 6.2 (s, 2H)
^{13}C-NMR: δ/ppm 10, 29, 178
IR : 3363, 3192, 1650 cm^{-1}

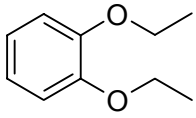
23. **^{1}H NMR** : δ/ppm 1.4 (t, 3H), 4.1 (q, 2H), 6.9 (m, 2H)
^{13}C-NMR: δ/ppm 15, 65,114, 121,149
IR : 1266 cm^{-1}



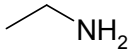
A



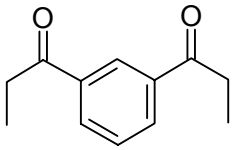
B



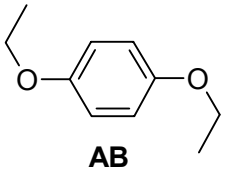
C



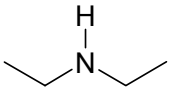
D



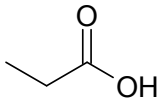
E



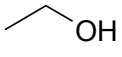
AB



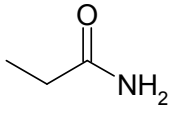
AC



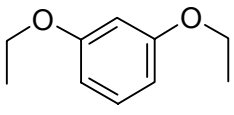
AD



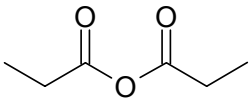
AE



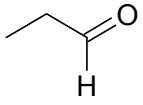
BC



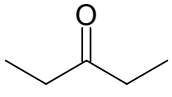
BD



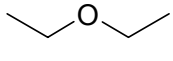
BE



CD



CE



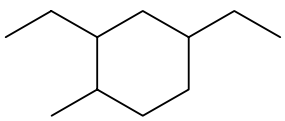
DE

14% **PART 4: NOMENCLATURE**

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

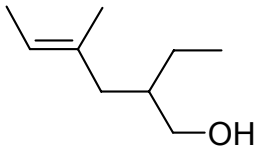
For each of questions 24 to 27, select the correct name for the compound shown:

24



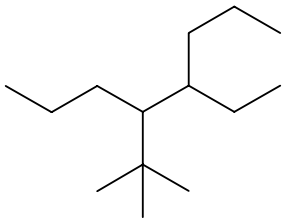
A. 2,4-diethyl-1-methylcyclohexane
B. 1,3-diethyl-4-methylcyclohexane
C. 1-methyl-2,4-diethylcyclohexane
D. 4-methyl-1,3-diethylcyclohexane
E. 1-methyl-2,4-diethylbenzene

25



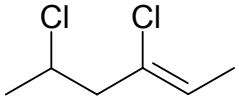
A. (Z)-2-ethyl-4-methylhex-4-enol
B. (Z)-5-ethyl-3-methylhex-2-en-6-ol
C. (E)-5-ethyl-3-methylhex-2-en-6-ol
D. (E)-3-methanol-5-methylhept-5-ene
E. (E)-2-ethyl-4-methylhex-4-en-1-ol

26



A. 4-ethyl-5-isopropyloctane
B. 4-(1,1-dimethylethyl)-5-ethyloctane
C. 4-(1,1-dimethylethyl)-5-propylheptane
D. 5-(1,1-dimethylethyl)-4-propylheptane
E. 4-isobutyl-5-propylheptane

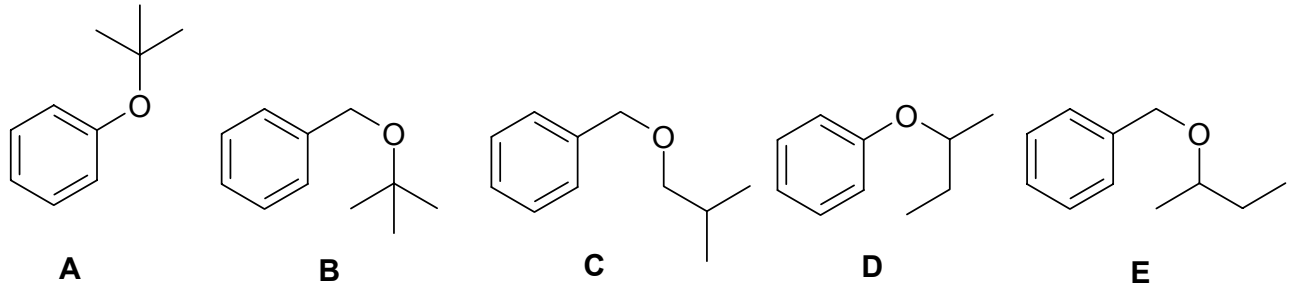
27



A. (Z)-3,5-dichlorohex-2-ene
B. (E)-3,5-dichlorohex-2-ene
C. (Z)-2,4-dichlorohex-4-ene
D. (E)-2,4-dichlorohex-4-ene
E. (E)-3,5-dichlorohex-2-yne

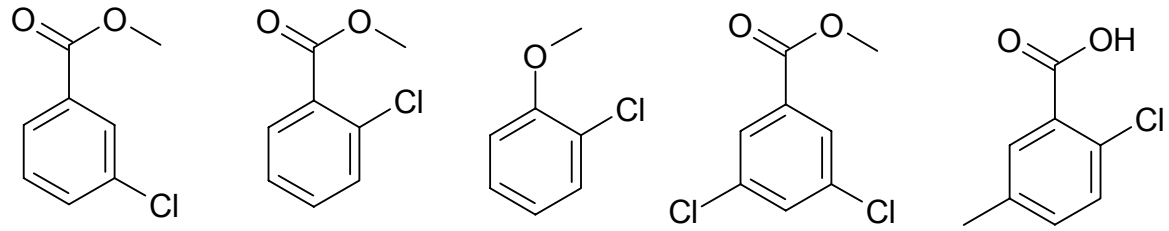
For each of questions 28 to 31, select the correct structure for the name provided:

28. benzyl t-butyl ether



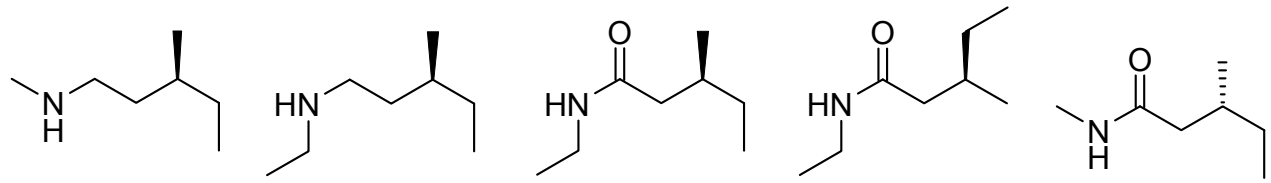
A **B** **C** **D** **E**

29. methyl *meta*-chlorobenzoate :



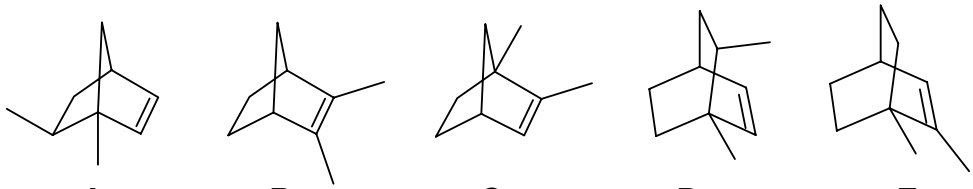
A **B** **C** **D** **E**

30. (S)-(N)-ethyl-3-methylpentanamide :



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

31. 1,2-dimethylbicyclo[2.2.1]hept-2-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.

Two unknown samples (**A** and **B**) were sent to a laboratory for analyses. Both samples were found to have a molecular ion peak at *m/z* 70 by electron impact ionization mass spectrometry. Combustion analyses revealed that both samples had similar elemental contents: C: 85.63%, H: 14.37%. The ^{1}H and ^{13}C NMR spectra indicated that each sample consisted of an acyclic compound: Compound **A** had 5 sets of ^{1}H signals and 4 carbon signals, while compound **B** had 4 sets of ^{1}H signals and 5 carbon signals.

(a) What are the molecular formulas of **A** and **B** ?

(b) What is the IHD of **A** and **B** ?

(c) Propose structures for **A** and **B** that fit with the information given above.

(d) Further analyses determined that compound **A** had heats of formation $\Delta H_f°$, **A** (liquid) = -15.5 kcal mol^{-1}, and compound **B** had heats of combustion $\Delta H_c°$, **B** (liquid) = -792 kcal mol^{-1}. Given the heats of combustion data:

$\Delta H_C°$, C (graphite) = -93.9 kcal mol^{-1}

$\Delta H_C°$, H_2 (gas) = -68.4 kcal mol^{-1}

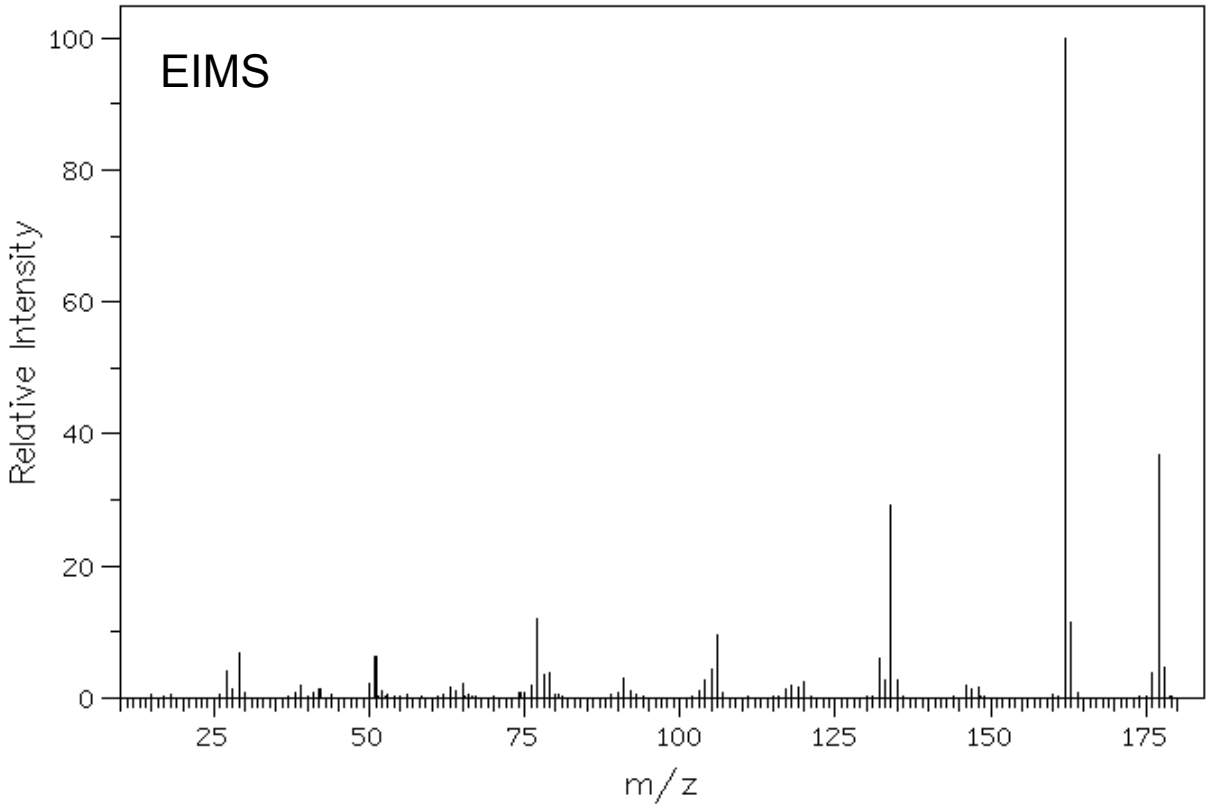
Calculate $\Delta H_C°$ for compound **A**, and $\Delta H_f°$ for compound **B**.

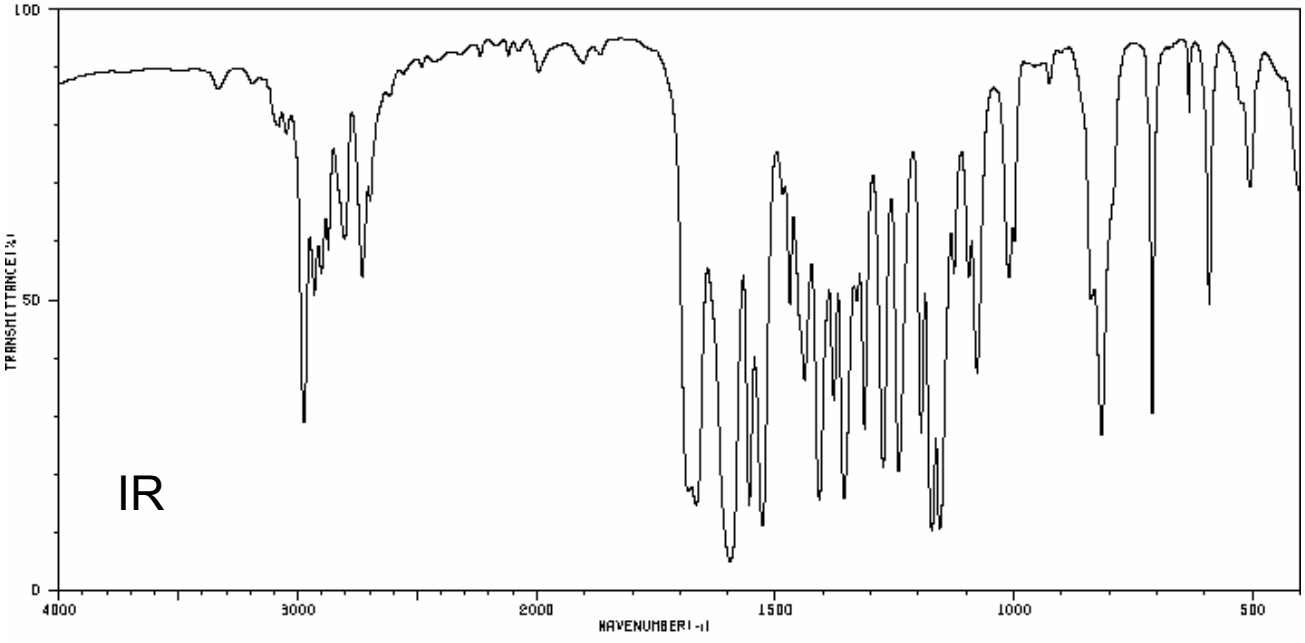
(e) Using your answer from part (d), state which molecule is more stable, **A** or **B** ? Briefly explain your choice.

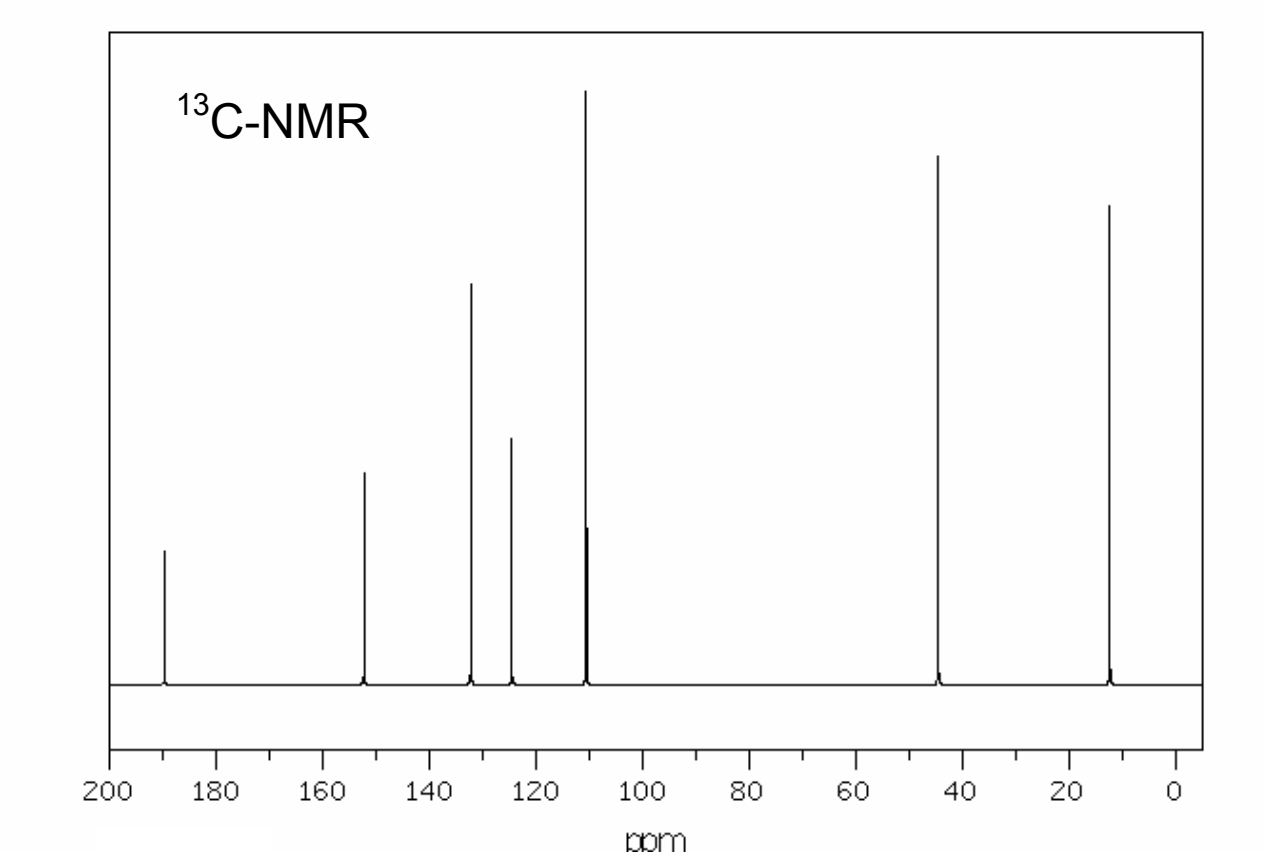
14% **PART 6: SPECTROSCOPY**

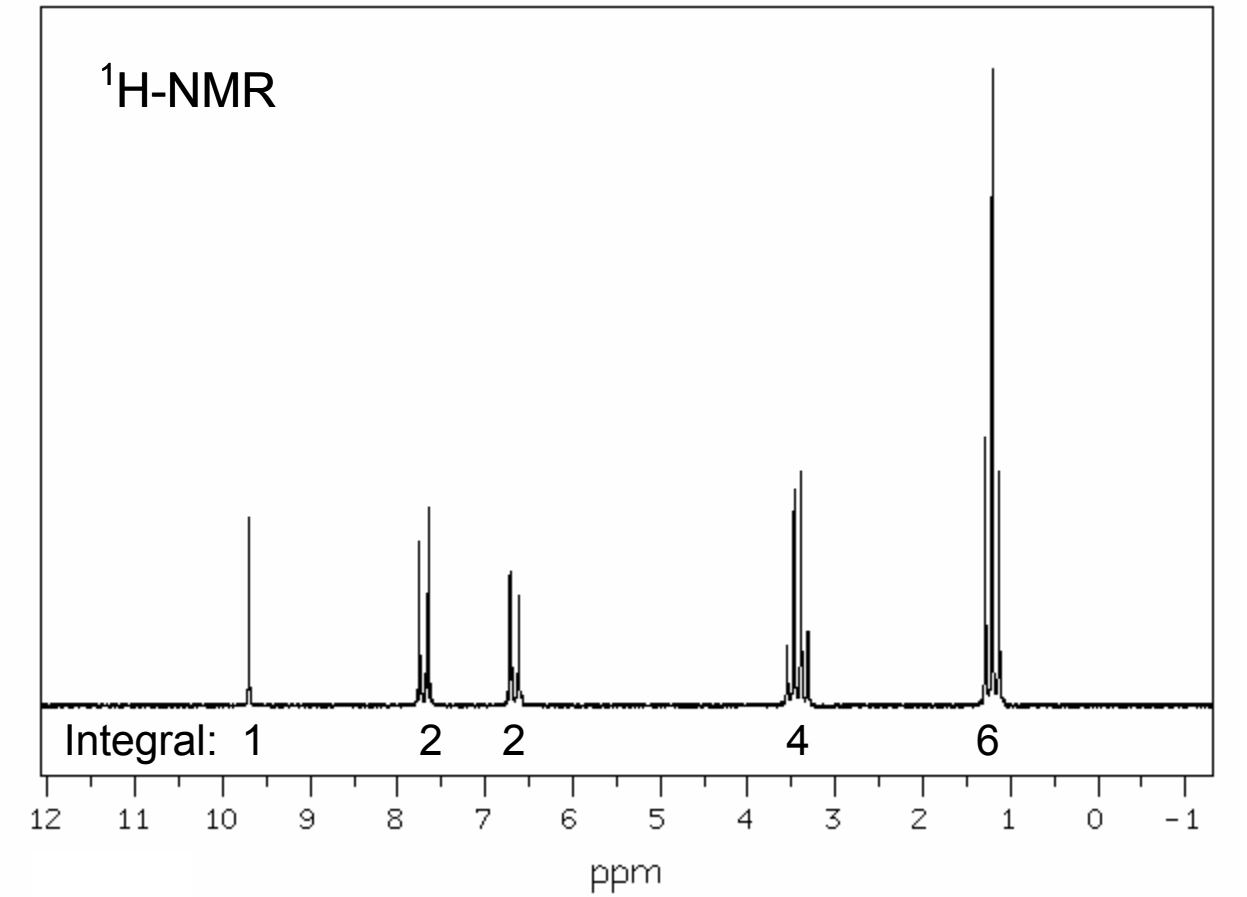
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

From the spectral data provided below, identify the **structure** of a molecule with the **molecular formula $C_{11}H_{15}NO$.**






^{13}C-NMR
200
180
160
140
120
100
80
60
40
20
0
ppm


^{1}H-NMR
Integral: 1
2
2
4
6
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

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 alkene, 2-methylpropene, reacts with methanol in the presence of an acid catalyst to give t-butyl methyl ether.

Step 1. Protonation of the alkene π-bond in 2-methylpropene by sulfuric acid to create the more stable tertiary carbocation and the bisulfate ion.

Step 2. Attack on the electrophilic carbocation by a molecule of methanol acting as a nucleophile to generate an oxonium ion.

Step 3. Deprotonation of the oxonium ion by the bisulfate ion acting as a base to give the ether, t-butyl methyl ether, and regenerating the catalyst, sulfuric acid.

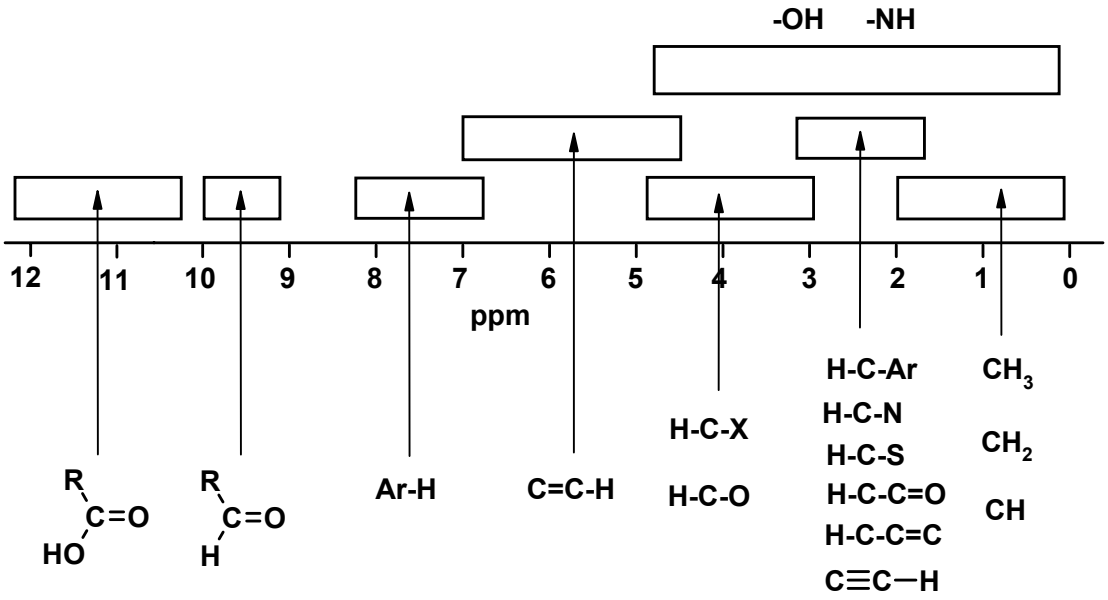
(b) Based on the sequence described in part **a**, draw the product of the reaction sequence if in step 1 the less stable isomeric primary carbocation is formed instead. Give the systematic IUPAC name of this product.

(c) Based on the sequence described in part **a**, predict the product of the reaction of 1-phenylpropene with methanol in the presence of an acid catalyst. Briefly rationalise your choice.

** THE END **

SPECTROSCOPIC TABLES

^{1}H NMR

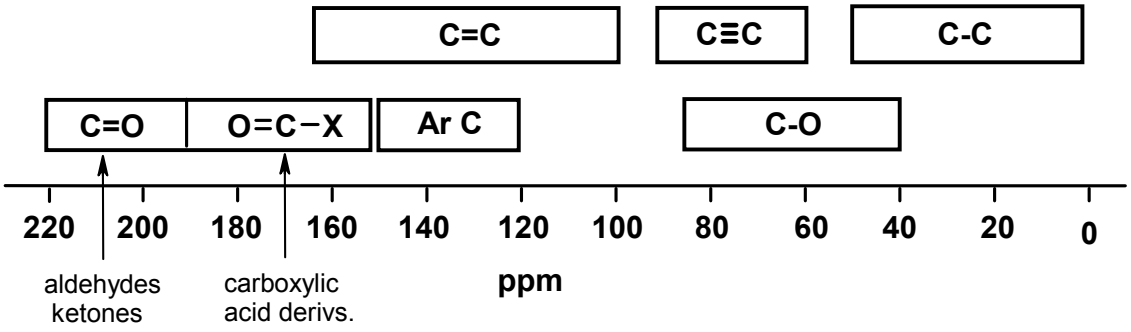


^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

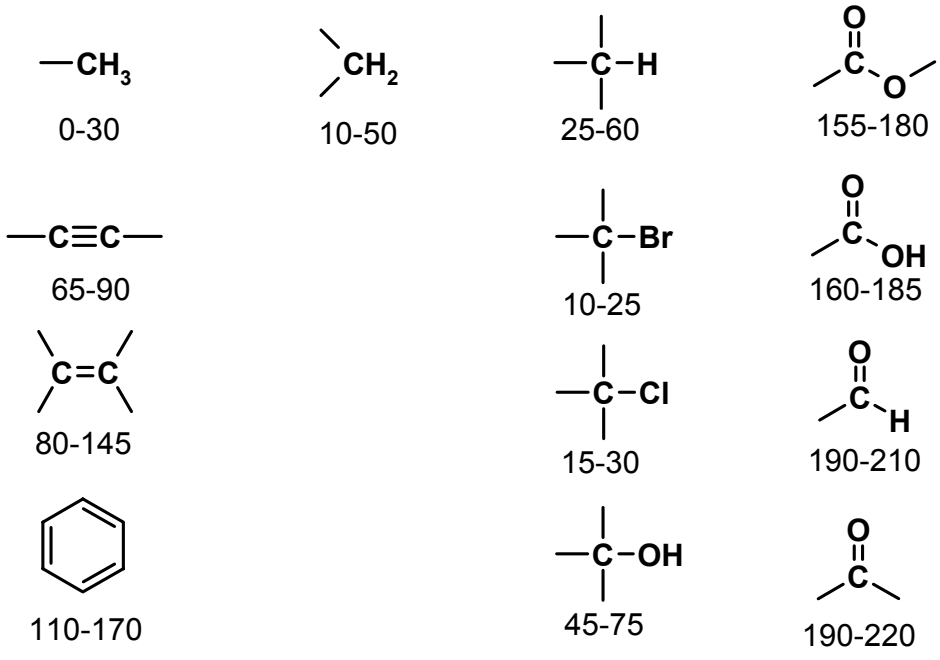
	methyl CH_3-	methylene $-CH_2-$	methyne CH
R−C—	0.9	1.4	1.5
R C=C	1.6	2.3	2.6
R C=O	2.1	2.4	2.5
R−N	2.2	2.5	2.9
R-Ar	2.3	2.7	3.0
R−Br	2.7	3.3	4.1
R−Cl	3.1	3.4	4.1
R−O—	3.3	3.4	3.7

other	
-OH	1-5
-NH	1-3
C≡CH	2.5
C=C H	5.5
Ar-H	7.3
R C=O H	10
R C=O OH	9-12

^{13}C NMR



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



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
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

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)