UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

Version

01

November 6th, 2018 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 01** 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 blue 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

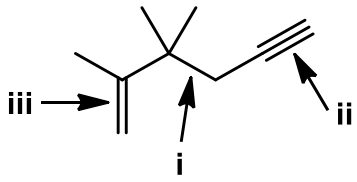
ANSWER ANY SEVEN (7) of questions 1-8 (2 marks per question)

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

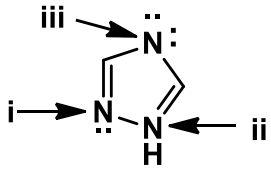
Use the following code to indicate your answers.

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

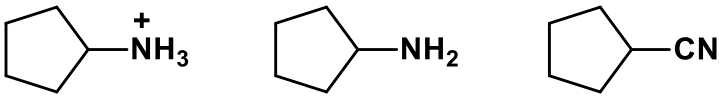
1. The relative lengths of the indicated bonds:



2. The formal charge on each of the corresponding nitrogen atoms indicated below (all required lone pairs are shown):

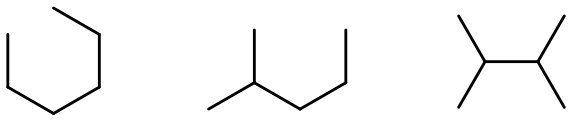


3. The relative basicity of the following compounds:



i **ii** **iii**

4. The relative stability of the following isomers:

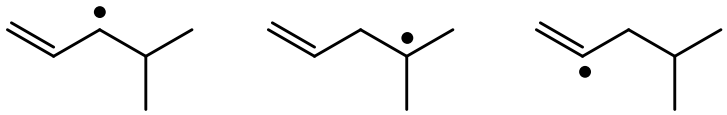


i **ii** **iii**

Use the following code to indicate your answers.

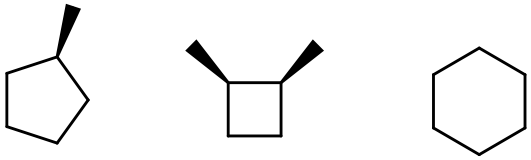
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

5. The relative stability of the following radicals:



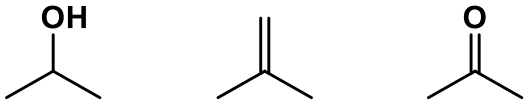
i **ii** **iii**

6. The number of different monochlorinated constitutional isomers formed by the reaction each of the following molecules with chlorine in the presence of uv light:



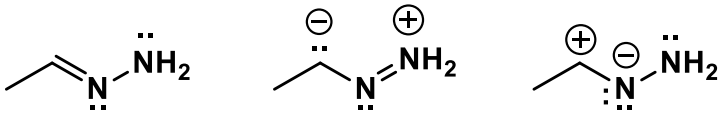
i **ii** **iii**

7. The relative acidity of the most acidic H in the molecules:



i **ii** **iii**

8. The relative importance of the resonance contributors shown below to the resonance hybrid:



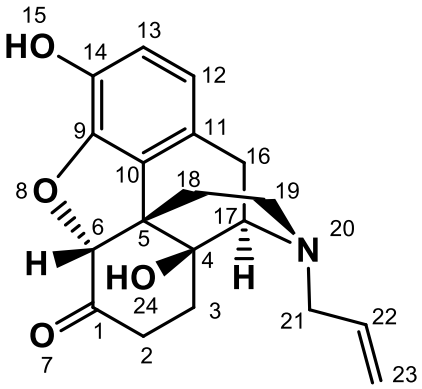
i **ii** **iii**

18% **PART 2: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 9 – 17

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.

Questions 9-17 all refer to Naloxone, an opioid antagonist (structure shown below):



Naloxone

9. Which atom is the most acidic hydrogen bonded to ?

A. C2 **B.** C6 **C.** O15 **D.** C21 **E.** O24

10. What type of orbital does the lone pair of **N20** occupy ?

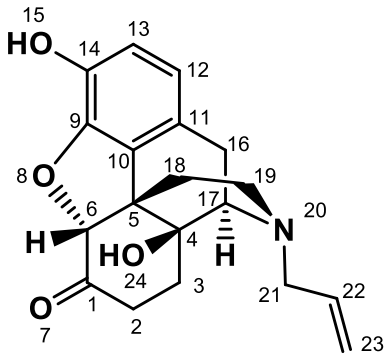
A. sp **B.** sp^2 **C.** s **D.** sp^3 **E.** p

11. What are the hybridisations of **O7** and **O15** respectively ?

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

12. What is the IHD (index of hydrogen deficiency) of Naloxone ?

A. 7 **B.** 8 **C.** 9 **D.** 10 **E.** 11



Naloxone

13. Which of the following functional groups are found in Naloxone ?

A. amide **B.** amine **C.** ester **D.** ether **E.** carboxylic acid

14. What configuration terms best describe **C6** and the **C22=C23** respectively ?

A. R, E **B.** R, Z **C.** S, E **D.** S, Z **E**. R only **AB**. S only

15. Which of the bonds listed below is the shortest ?

A. C1-C2 **B.** C2-C3 **C.** C10-C11 **D.** N20-C21 **E.** C22-C23

16. If Naloxone were reacted with TWO equivalents of NaOH, what are the best approximate percentages of deprotonations at **O15** and **O24**?

A. O15/O24 (100%, 100%) **B**. O15/O24 (100%, 50%) **C**. O15/O24 (100%, 0%)

D. O15/O24 (50%, 100%) **E**. 015/O24 (0%, 100%)

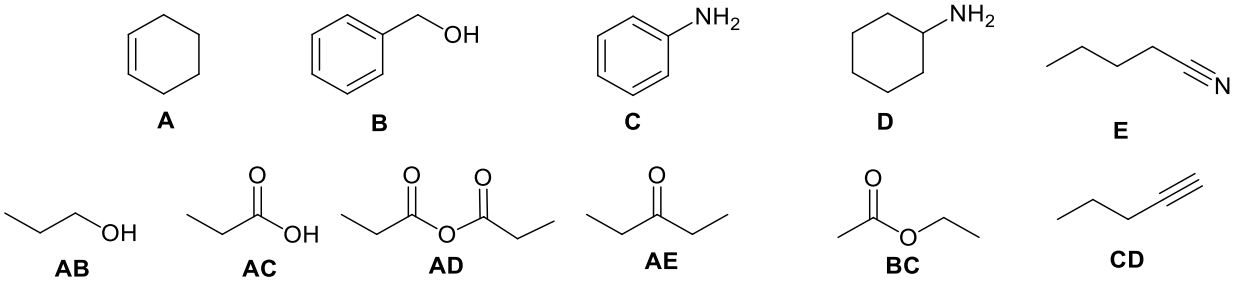
17. Which term(s) best describe **C16** ?

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

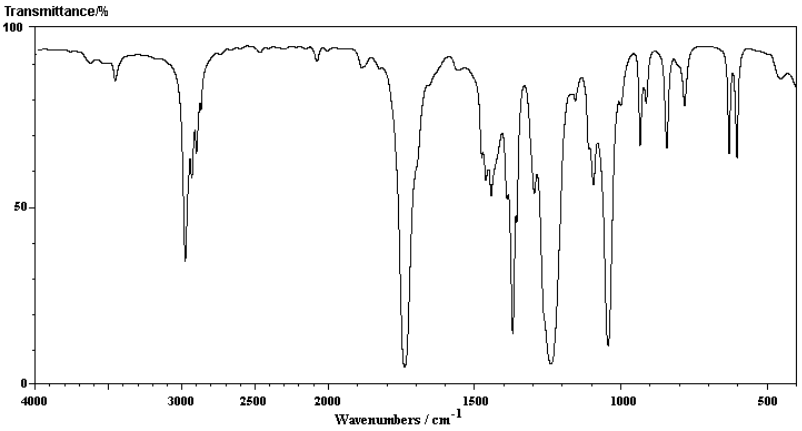
15% **PART 3: SPECTROSCOPY**

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

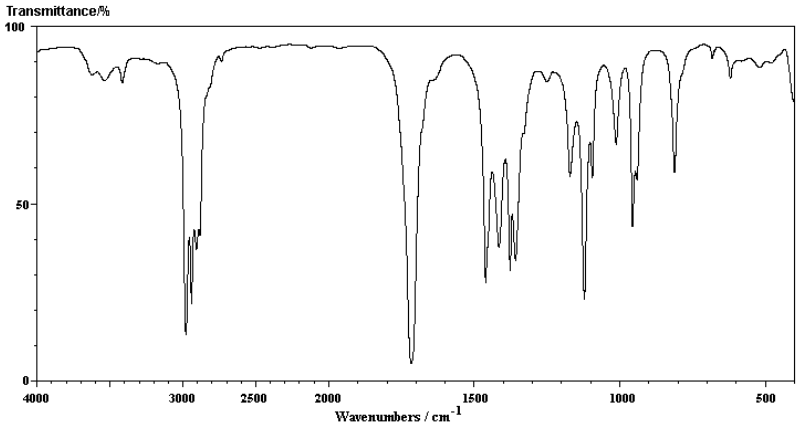
For each of the questions 18-23, match the IR spectra to a structure in the list below:



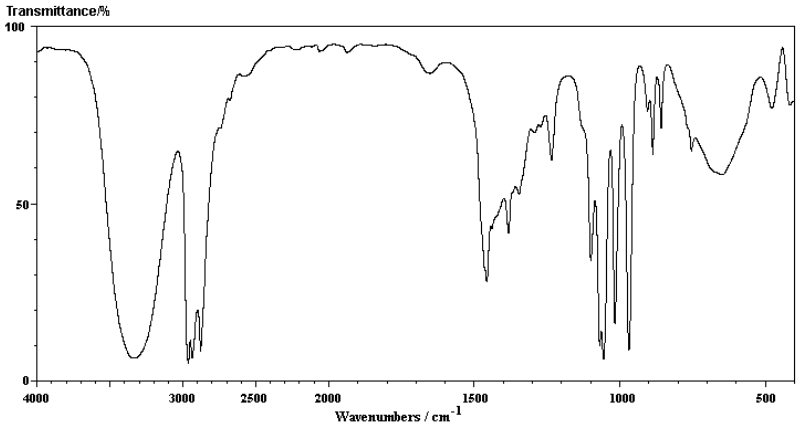
18.

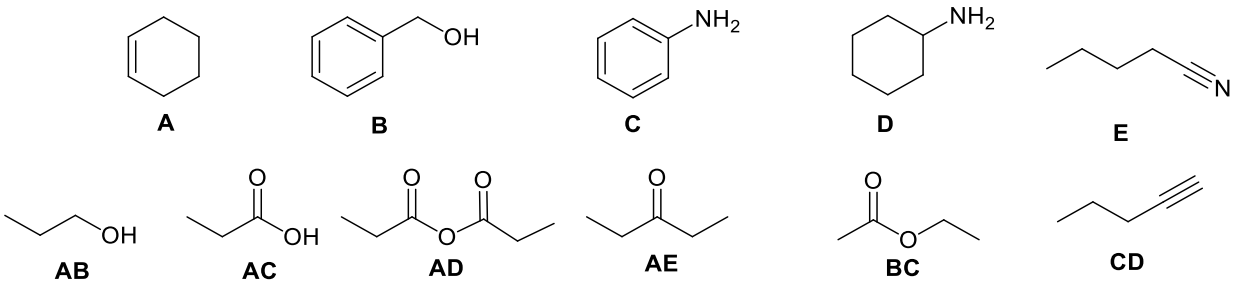


19.

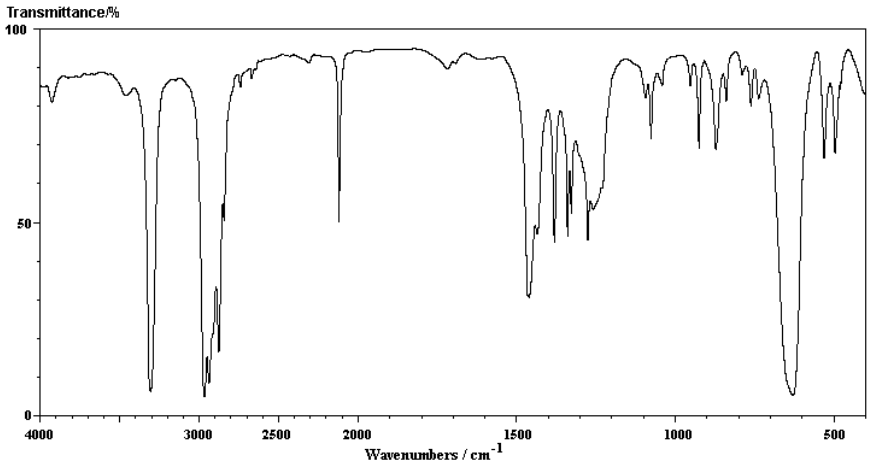


20.

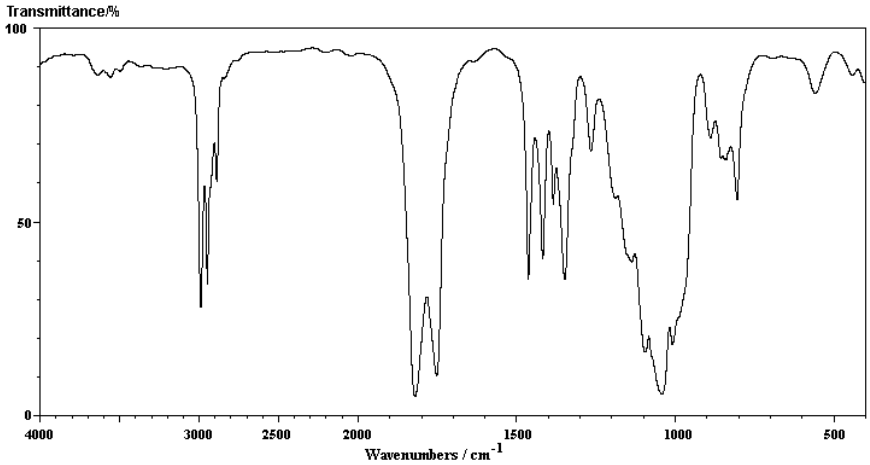




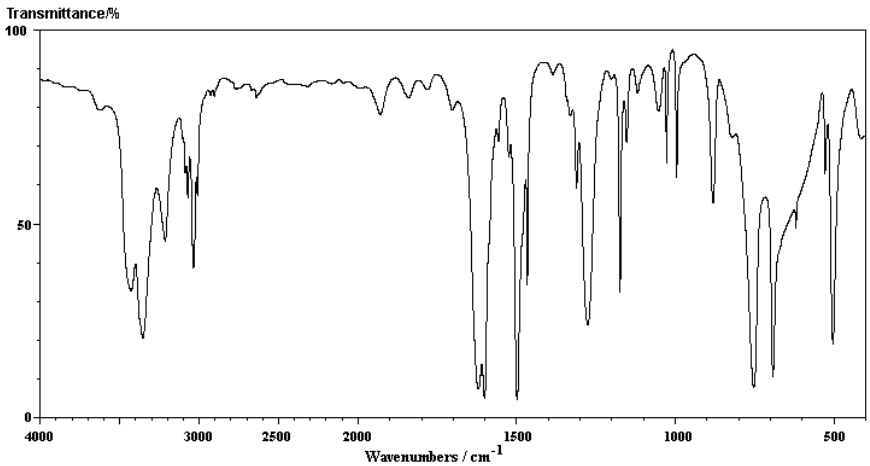
21.



22.



23.

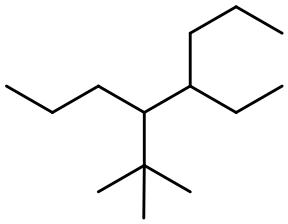


14% **PART 4: NOMENCLATURE**

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

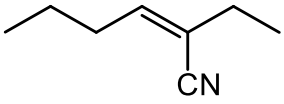
For each of questions 24 to 27, select the correct IUPAC name for the compound shown:

24.



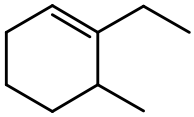
A. 4-ethyl-5-t-butyloctane
B. 4-(1,1-dimethylethyl)-5-ethyloctane
C. 4-(1,1-dimethylethyl)-3-propylheptane
D. 5-(1,1-dimethylethyl)-4-propylheptane
E. 5-ethyl-4-(1,1-dimethylethyl)-octane
AB. 3-propyl-4-(1,1-dimethylethyl)-heptane

25.



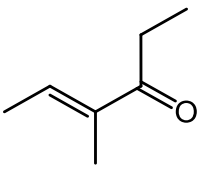
A. (Z)-2-ethylhex-2-enenitrile
B. (E)-2-ethylhex-2-enenitrile
C. (Z)-3-cyanohex-3-ene
D. (E)-3-cyanohex-3-ene
E. (Z)-4-cyanohex-3-ene
AB.(E)-4-cyanohex-3-ene

26.



A. 1-ethyl-2-methylcyclohexene
B. 2-methyl-1-ethylcyclohexene
C. 2-ethyl-1-methylcyclohexene
D. 1-methyl-2-ethylcyclohexene
E. 1-ethyl-6-methylcyclohexene
AB 6-ethyl-1-methylcyclohexene

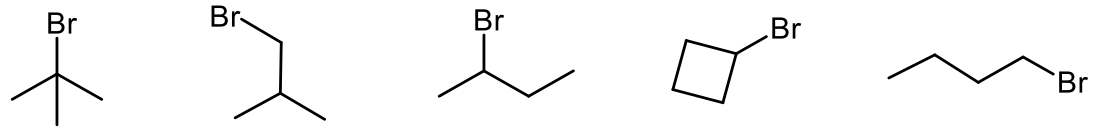
27.



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

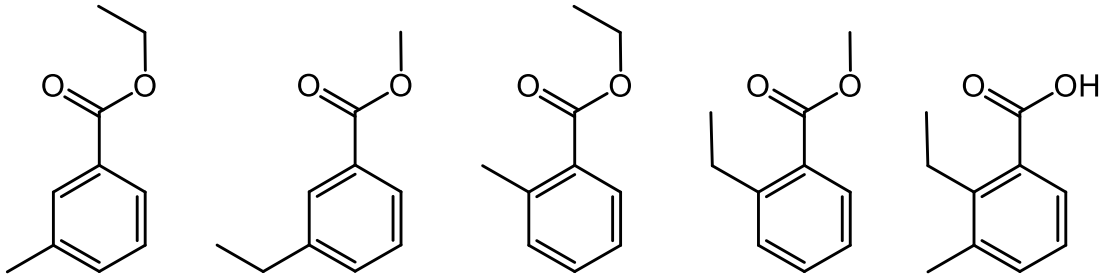
For each of questions 28 to 31, select the correct structure for the IUPAC name provided:

28. sec-butyl bromide



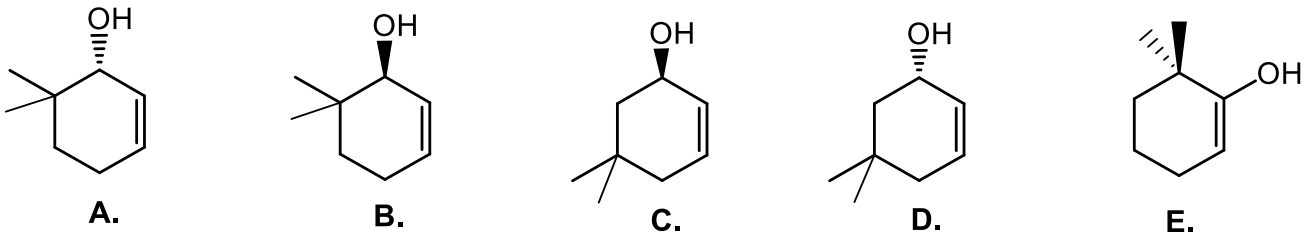
A. **B.** **C.** **D.** **E.**

29. ethyl o-methylbenzoate



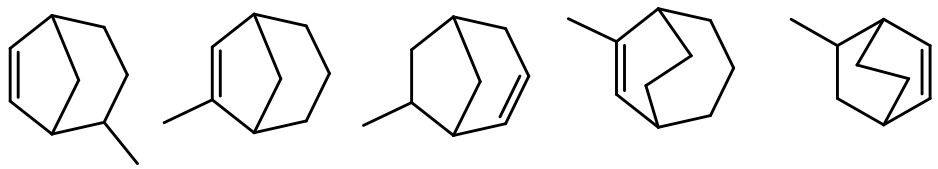
A **B** **C** **D** **E**

30. (S)-6,6-dimethylcyclohex-2-en-1-ol



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

31. 7-methylbicyclo[3.2.1]oct-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.

Each of the following questions needs to be answered based on compound **X** which has the molecular formula $C_6H_{10}O$.

a) What is the molecular weight of compound **X** ?

b) What is the index of hydrogen deficiency of compound **X**?

c) Name 3 oxygen containing functional groups that could be present in isomers of **X**.

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

e) Draw a structure for **X** where the most acidic proton has a pKa ~25

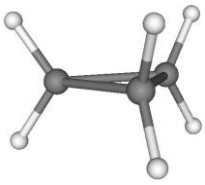
f). Draw a structure for **X** that has resonance-stabilisation and exists in a (Z,Z) configuration.

g) Draw a structure for **X** that contains a ring and a chiral centre using the 3D wedge-hash representation.

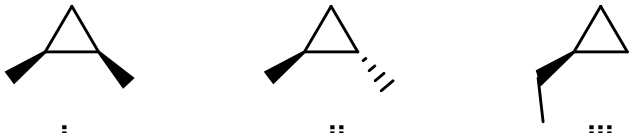
13% **PART 6: THERMODYNAMICS**

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

A 3D representation of cyclopropane is shown below.



Three structures of substituted derivatives of cyclopropane are shown below:



i **ii** **iii**

a) Write a balanced reaction equation for the complete combustion of isomer **i**.

b) Calculate $\Delta H_f°$ of isomer **iii**, given that the following heats of combustion:

$\Delta H_C°$,C (graphite) = -93.9 kcal/mol

$\Delta H_C°$,H_2 (gas) = -68.4 kcal/mol

$\Delta H_C°$,isomer iii = -805.9 kcal/mol

c) Given that the heats of formation, $\Delta H_f°$ of the other two isomers are -6.3 kcal/mol and -7.3 kcal/mol: match each of the two isomers **i**-**ii** to their corresponding $\Delta H_f°$ values;

d) Draw an energy diagram to illustrate the relative energy difference between all three isomers **i**-**iii**, with clearly labeled reactants, products, and all $\Delta H_f°$ values, and indicate which one is the most stable isomer and which one is the lease stable.

e) Use the principles of bonding, and conformational analysis (models lab experiment) to explain the trend that you observed in **d** above.

f) A fourth isomer, **iv**, another substituted cyclopropane, reacts with chlorine and UV light to give two monochlorinated constitutional isomers. Draw the structure of isomer **iv**.

 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 reaction sequence described verbally by the following points in which 3-bromobut-1-ene (substrate), is placed in water (reagent), to give but-3-en-2-ol and (E)-but-2-en-1-ol.

Step 1. The loss of bromine from 3-bromobut-1-ene gives a secondary carbocation and a bromide ion.

Step 2. Resonance stabilization of the secondary carbocation shows a primary carbocation contributor.

Step 3. The attack of water as a nucleophile on one of the carbocations in one of the resonance contributors produces an oxonium ion.

Step 4. An acid-base reaction of the oxonium ion with a molecule of water to give (E)-but-2-en-1-ol and a hydronium ion.

b) 3-bromobut-1-ene can be synthesized by radical bromination of but-2-ene with N-bromosuccinimide and heat. However, a second product is also obtained. What is that product and briefly explain why it is formed (mechanism not required).

c) *Based on the information provided in this question*, what substrate and reagent would you use if you wanted to prepare 3-ethoxycyclohexene ? (mechanism not required)

**** THE END ****

IRH / CCL / RP F2018

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)