UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

November 4th, 2015 Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

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

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

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

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

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

14% PART 1: RELATIVE PROPERTIES

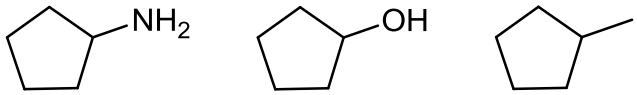
ANSWER ANY SEVEN (7) of questions 1-8 (2 marks per question)

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

Use the following code to indicate your answers.

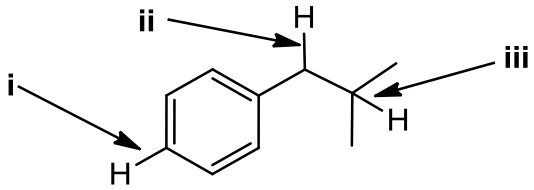
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

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

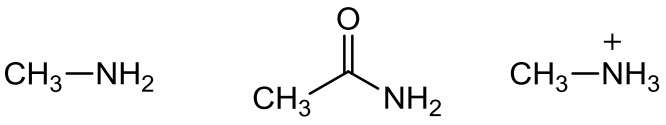


i **ii** **iii**

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

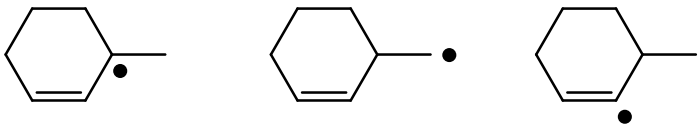


3. The relative basicity of each of the following:



i **ii** **iii**

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

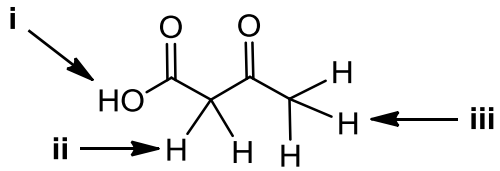


i **ii** **iii**

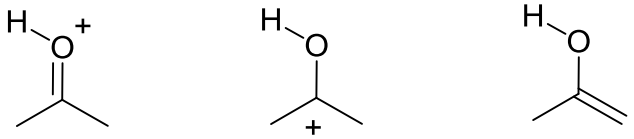
Use the following code to indicate your answers.

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 acidity of each of the hydrogens indicated below:

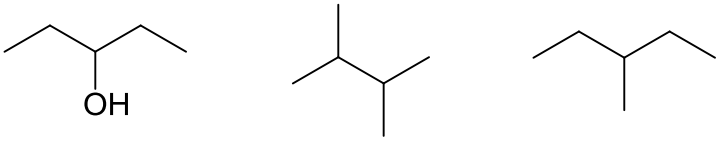


6. The relative importance of the resonance contributors shown below to the resonance hybrid of the conjugate acid of 2-propanone:



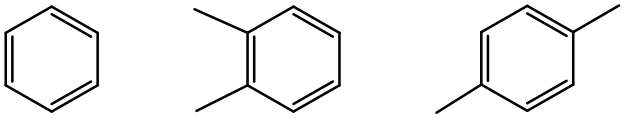
i **ii** **iii**

7. The relative boiling points of the compounds shown below:



i **ii** **iii**

8. The number of types of **C** in each of the following molecules:



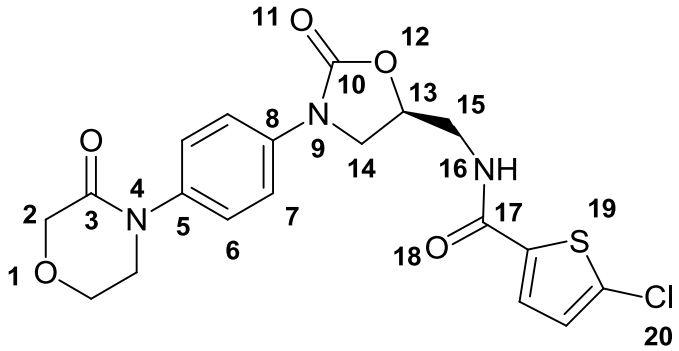
i **ii** **iii**

18% **PART 2: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 9 – 17

For each of the questions 9 - 12 select the appropriate answer(s) from the answers provided. In some cases more than one selection may be required for full credit.

Use the structure of **Rivaroxaban**, an anticoagulant and a drug that reduces the risk of stroke, as depicted below to answer the questions **9-17**.



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

A. 9 **B.** 10 **C.** 11 **D.** 12 **E.** 13

10. What is the oxidation state of **C2** ?

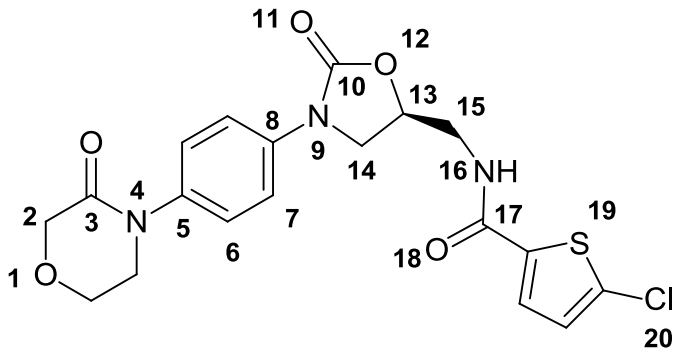
A. -4 **B.** -3 **C.** -2 **D.** -1 **E.** 0 **AB**. +1 **AC**. +2 **AD** +3 **BC**. +4

11. Which of the following functional groups is (are) found in Rivaroxaban ?

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

12. What type of orbital do the two lone pairs of electrons on **O1** occupy?

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



For each of the questions 13 - 17 select the appropriate answer(s) from the answers provided. In some cases more than one selection may be required for full credit.

13. What are the hybridizations of atoms **C14** and **N16** respectively?

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

14. Which of the following terms describe the **H** attached to **C15** ?

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

15. Which of the following terms describe **C13** ?

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

16. What configuration terms best describe **C13** ?

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

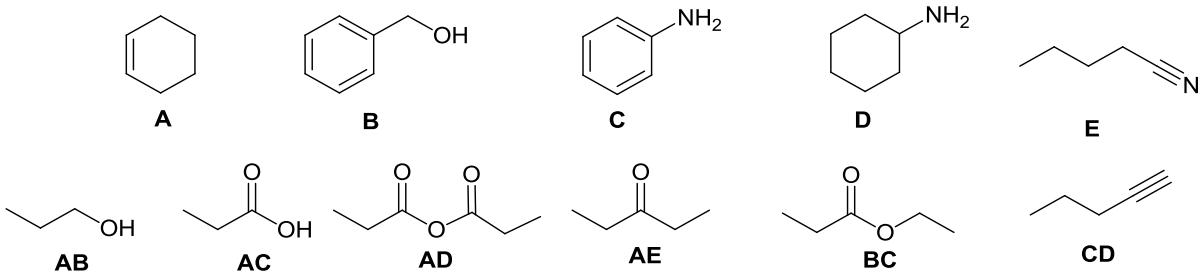
17. Which of the following atoms is the most basic ?

A. N4 **B. N9** **C. O12** **D. N16** **E. O18** **AB. Cl 20**

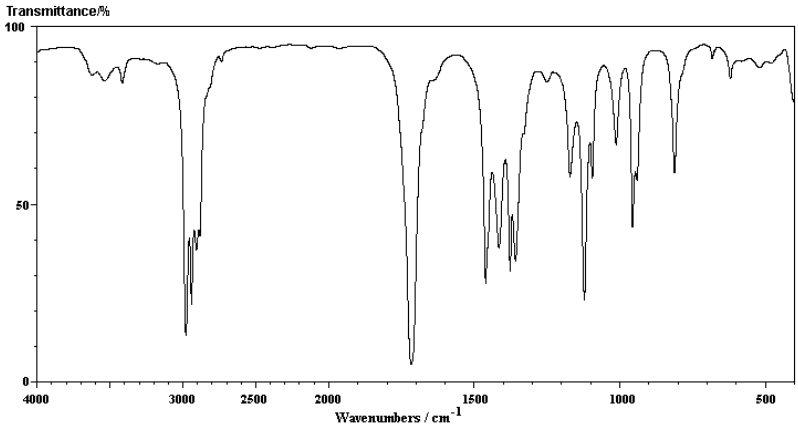
15% **PART 3: SPECTROSCOPY**

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

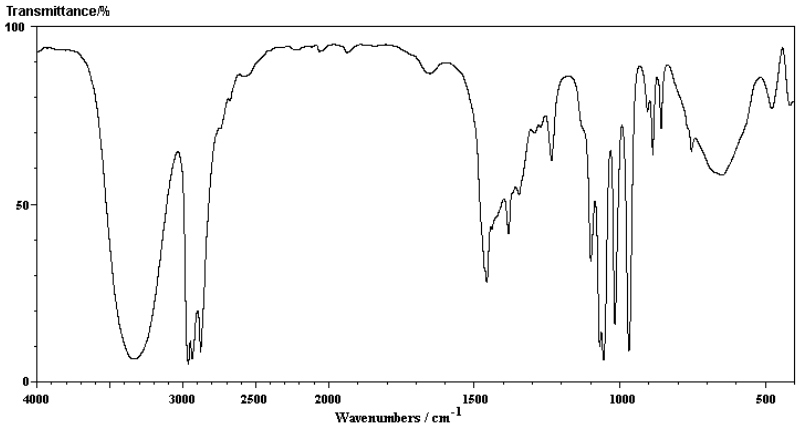
For each of the questions 18-23, match the IR spectra to a structure in the list below:



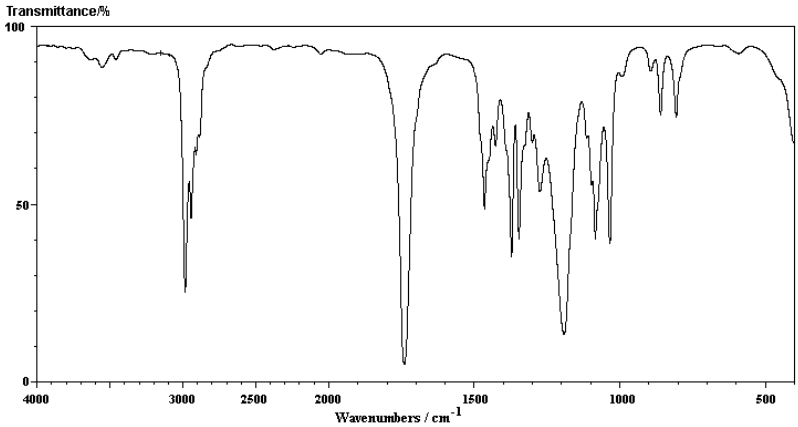
18.

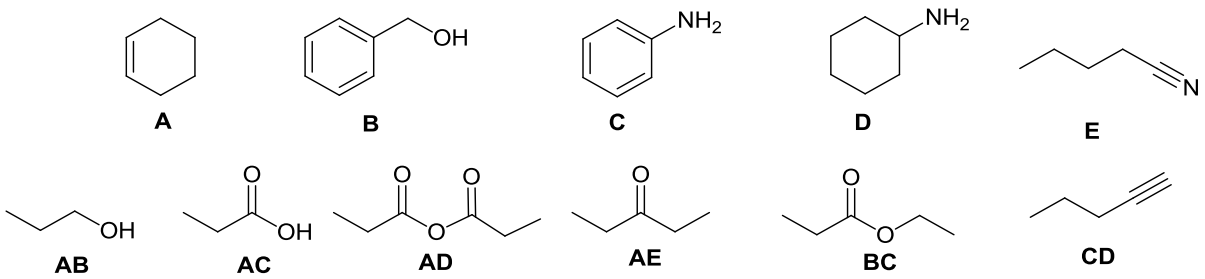


19.

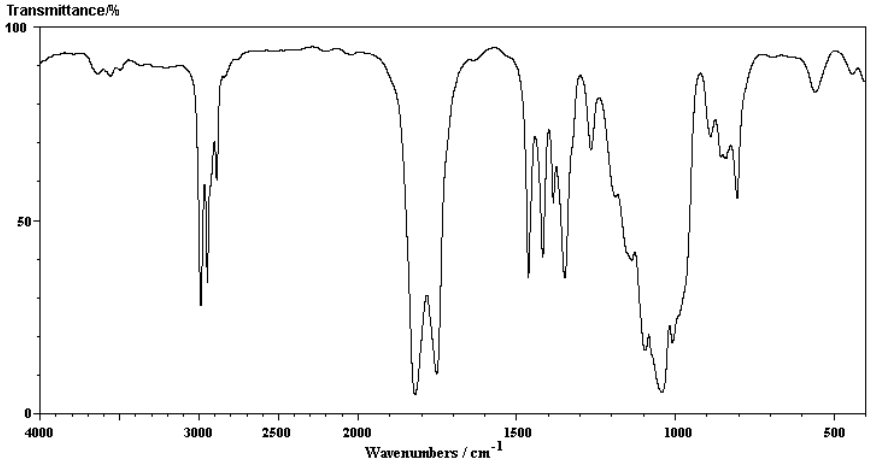


20.

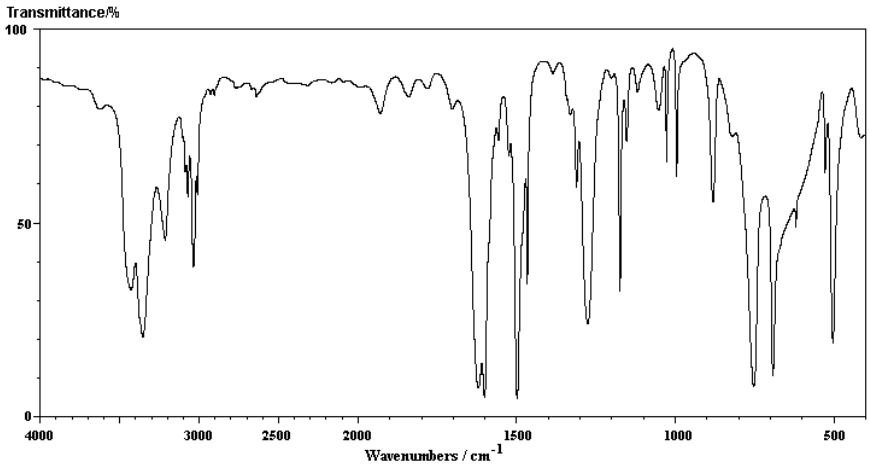




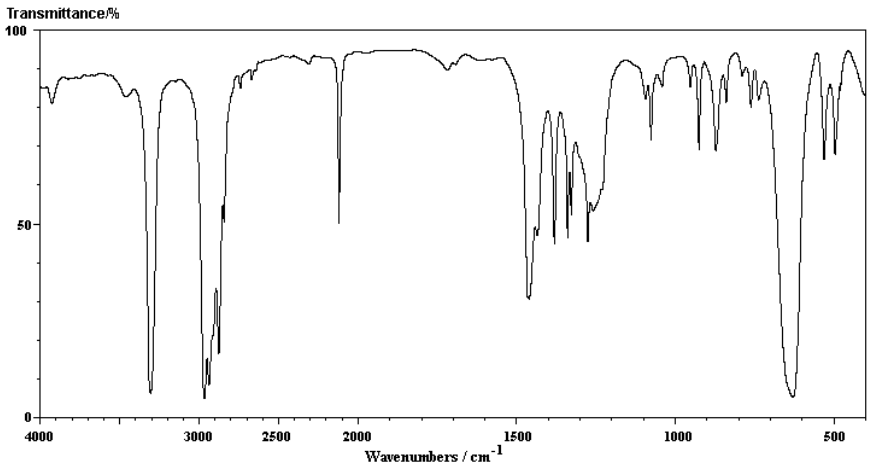
21.



22.



23.



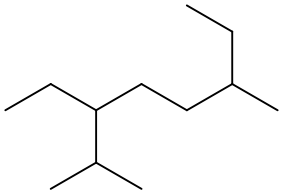
Cont'd

14% **PART 4: NOMENCLATURE**

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

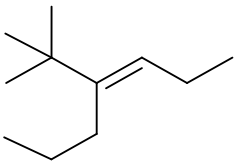
For each of questions 24 to 27, select the correct IUPAC name for the compound shown:

24.



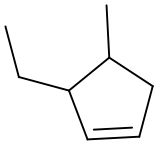
A. 3-isopropyl-6-ethylheptane
B. 2,6-dimethyl-3-ethyloctane
C. 3,7-dimethyl-6-ethyloctane
D. 2-ethyl-5-isopropylheptane
E. 3-ethyl-2,6-dimethyloctane
AB.3,6-diethyl-2-methylheptane

25.



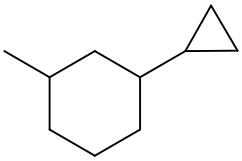
A. E-4-(1,1-dimethylethyl)hept-3-ene
B. Z-4-(1,1-dimethylethyl)hept-3-ene
C. E-4-(1,1-dimethylethyl)hept-4-ene
D. Z-4-(1,1-dimethylethyl)hept-4-ene
E. E-2,2-dimethyl-3-propylhex-3-ene
AB. Z-2,2-dimethyl-3-propylhex-3-ene

26.



A. 3-methyl-4-ethylcyclopentene
B. 4-ethyl-3-methylcyclopentene
C. 3-methyl-2-ethylcyclopentene
D. 2-ethyl-3-methylcyclopentene
E. 4-methyl-3-ethylcyclopentene
AB 3-ethyl-4-methylcyclopentene

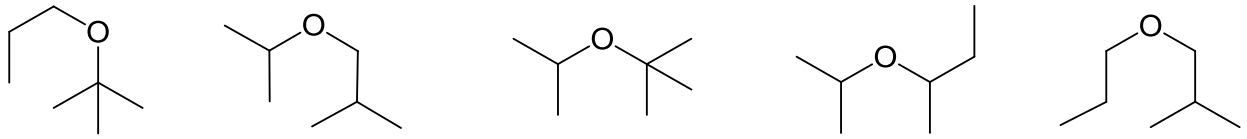
27.



A. 1-cyclopropyl-3-methylcyclohexane
B. 3-cyclopropyl-1-methylcyclohexane
C. 1-methyl-3-cyclopropylcyclohexane
D. 3-methyl-1-cyclopropylcyclohexane
E. 1-(3-methylcyclohexyl)cyclopropane
AB. (3-methylcyclohexyl)cyclopropane

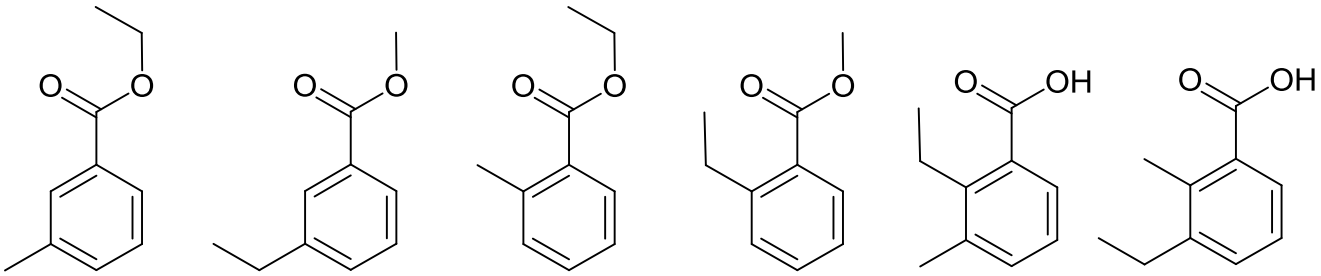
For each of questions 28 to 31, select the correct structure for the IUPAC name provided:

28. t-butyl isopropyl ether



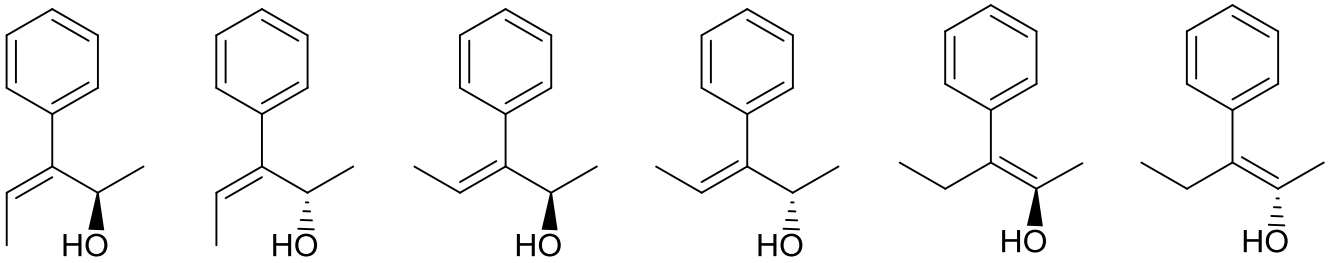
A. **B.** **C.** **D.** **E.**

29. ethyl m-methylbenzoate



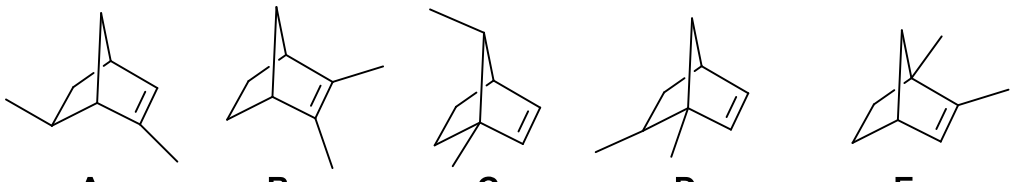
A **B** **C** **D** **E** **AB**

30. (2S,3Z)-3-phenylpent-3-en-2-ol



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

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.

Answer the following questions about molecule **X**, molecular formula C_8H_{10}.

a. What is the empirical formula of this molecule ?

b. What is the index of hydrogen deficiency of **X** ?

c. The IR spectrum of compound **X** shows medium absorptions at ~1500 cm^{-1} and ~1600 cm^{-1} and also 2900-3100 cm^{-1}. When **X** was reacted with bromine and UV light it gave predominantly one monobromination product **Y** with one chiral center. **Y** has 5 types of hydrogen and 6 types of carbon. What is the structure of **X** ?

d. Give a balanced equation showing the structures of **X** and **Y** for the bromination of **X** with Br_2 in the presence of light to give **Y**. Explain why **Y** is the expected major product.

e. Draw a 3D representation of one enantiomer of **Y.** What is the systematic IUPAC name of **Y**?

f. Draw **Z,** a constitutional isomer of **X** that has 3 types of hydrogen and 4 types of carbons and has the following characteristic IR absorptions: 2120 cm^{-1} and 3300 cm^{-1}

g. Identify a base that is strong enough to deprotonate the most acidic proton in **Z**.

13% **PART 6: THERMODYNAMICS**

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

Some of the thermodynamic data (heats of combustion, ΔH_C^o and heats of formation, ΔH_F^o) for but-1-yne and two of its isomers, buta-1,2-diene and buta-1,3-diene are listed in the following table:

Thermodynamic Data / kcal mol^{-1}		
compound	ΔH_C^o	ΔH_F^o
but-1-yne	-620.64	?
buta-1,2-diene	-619.93	?
buta-1,3-diene	?	+26.00

a) What term can be used to describe the isomerism involved in the three isomers?

b) Write a balanced chemical reaction equation to illustrate the complete combustion of buta-1,2-diene.

c) Calculate the heats of formation for but-1-yne and buta-1,2-diene as well as the heat of combustion for buta-1,3-diene using the following heats of combustion: $\Delta Hc^0_{(graphite)}$ = -94.05 kcal mol^{-1}, $\Delta Hc^0_{(H2)}$ = -68.32 kcal mol^{-1}.

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

e) Provide a molecular level explanation to explain the bonding in buta-1,2-diene and buta-1,3-diene, and how this can explain their relative stability.

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 propanal, undergoes nucleophilic addition when reacted with methanal in the presence of sodium hydride, followed by treatment with H_3O^+ to form 3-hydroxy-2-methylpropanal.

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

Step 2. The lone pair of the carbanion attacks the electrophilic carbon in methanal, to give the alkoxide conjugate base of 3-hydroxy-2-methylpropanal.

Step 3. The alkoxide conjugate base of 3-hydroxy-2-methylpropanal is reacted with H_3O^+ in an acid-base reaction to give 3-hydroxy-2-methylpropanal and water.

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

c) What is the most acidic hydrogen in 3-hydroxy-2-methylpropanal and what is its approximate pKa?

**** THE END ****

INFRA-RED GROUP ABSORPTION FREQUENCIES

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

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

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

Cont'd

PERIODIC TABLE

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

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