

UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 351

Version
01

November 1st, 2023

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 in the bubble sheet, and only Parts 5, 6, and 7 are to be answered in the exam answer booklet provided. When answering the long answer questions in the answer booklet you must record their answers within the boxes provided.

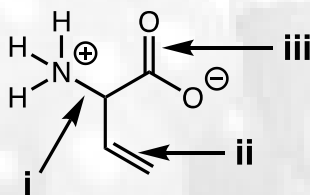
Parts 1 - 4 consist of a series of multiple-choice questions numbered 1 - 31 which are to be answered on your computer answer sheet (no extra time is provided for “bubbling” in the score sheet). Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a **pencil 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.

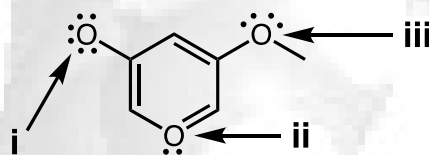
Molecular models are permitted during the exam; calculators are also permitted, **but NOT programmable calculators**. **Absolutely no other electronic devices are allowed.**

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

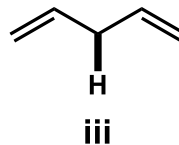
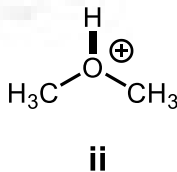
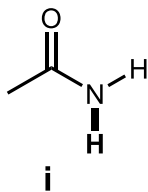
1. The relative lengths of the indicated bonds:



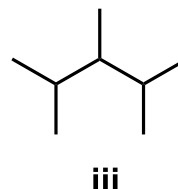
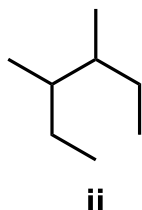
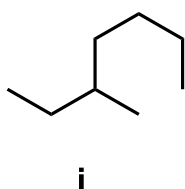
2. The formal charge on each oxygen atom below from most positive to most negative (all lone pairs are shown):



3. The relative acidities of each of the following:



4. The relative stability of each of the following isomers:



Use the following code to indicate your answers.

A. $i > ii > iii$

B. $i > iii > ii$

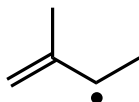
C. $ii > i > iii$

D. $ii > iii > i$

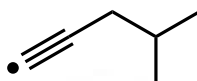
E. $iii > i > ii$

AB. $iii > ii > i$

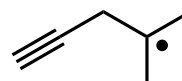
5. The relative stability of the following radicals:



i

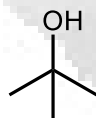


ii

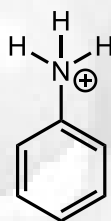


iii

6. The relative acidity of the most acidic H in each of the following:



i

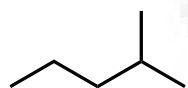


ii



iii

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



i

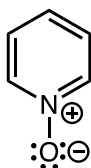


ii

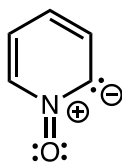


iii

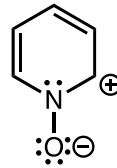
8. The relative importance of the following resonance contributors:



i



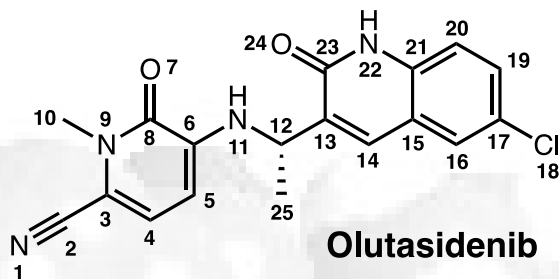
ii



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 Olutasidenib, a treatment for acute myeloid leukemia:



9. Which atom is the most basic?

- A. C2 B. O7 C. N22 D. Cl18 E. N1

10. Which bond is the strongest?

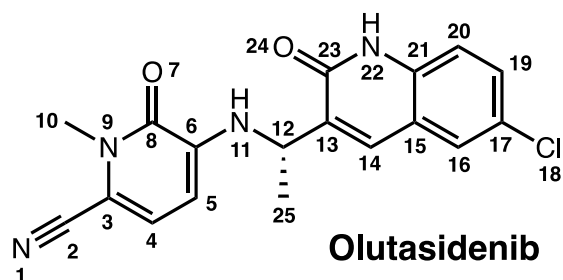
- A. C17-Cl18 B. C6-N11 C. C23-O24 D. C3-C4 E. N1-C2

11. What orbitals are the lone pairs of **N1** and **N11** in, respectively?

- A. sp, sp³ B. sp², sp² C. sp, p D. p, sp³ E. p, p

12. What is the IHD of Olutasidenib?

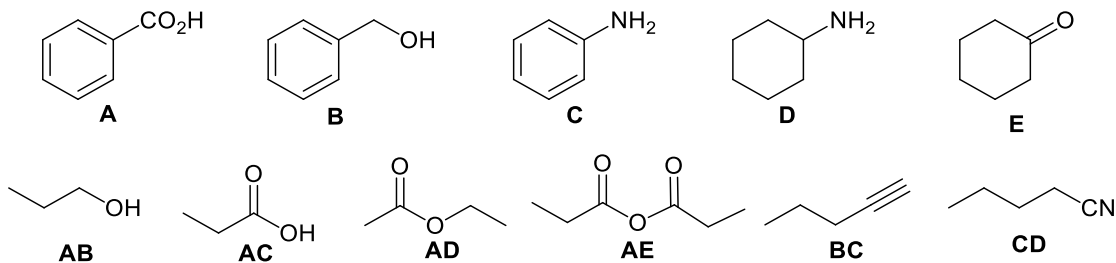
- A. 11 B. 12 C. 13 D. 14 E. 15



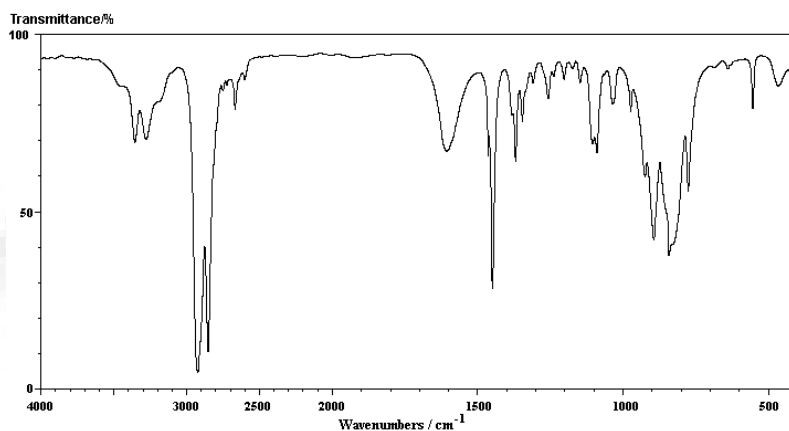
13. The most acidic hydrogen in Olutasidenib is attached to which atom?
- A. N1 B. N9 C. Cl18 D. N22 E. C12
14. Which of the following functional groups are found in Olutasidenib?
- A. amine B. alkyne C. ketone D. ether E. arene
15. Which of the following bonds would have the highest IR stretching frequency?
- A. N1-C2 B. C3-C4 C. N11-H D. C23-O24 E. C17-Cl18
16. Which of the following properly describes the configuration of Olutasidenib
- A. R B. S C. *cis* D. *trans* E. None apply
17. Which value is closest to the C10-N9-C3 bond angle?
- A. 60° B. 90° C. 109.5° D. 120° E. 180°

15% **PART 3: SPECTROSCOPY****ANSWER ALL SIX (6) OF QUESTIONS 18 – 23 (2.5 marks per question).**

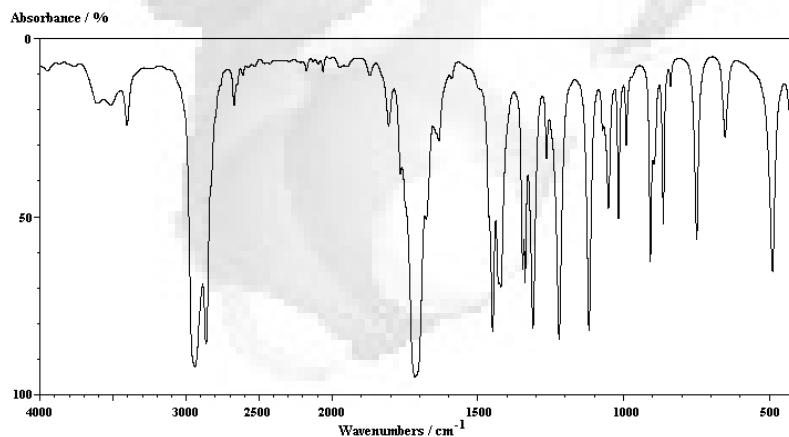
For each of the questions 18-23, match the IR spectra to a structure in the list below:



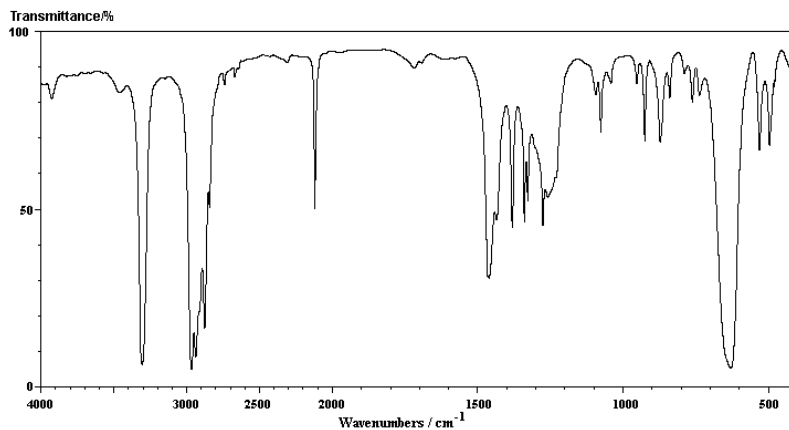
18.

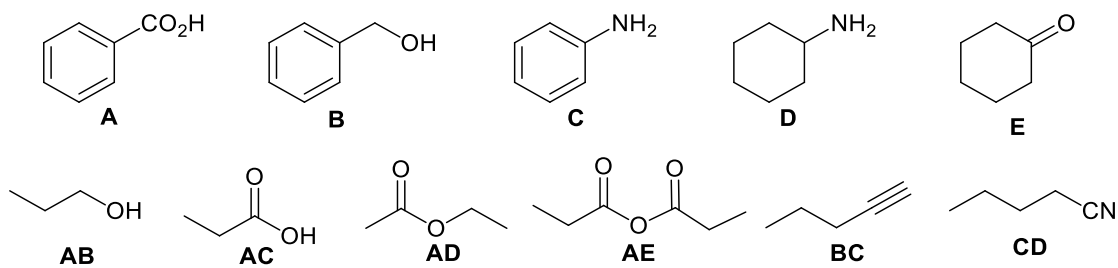


19.

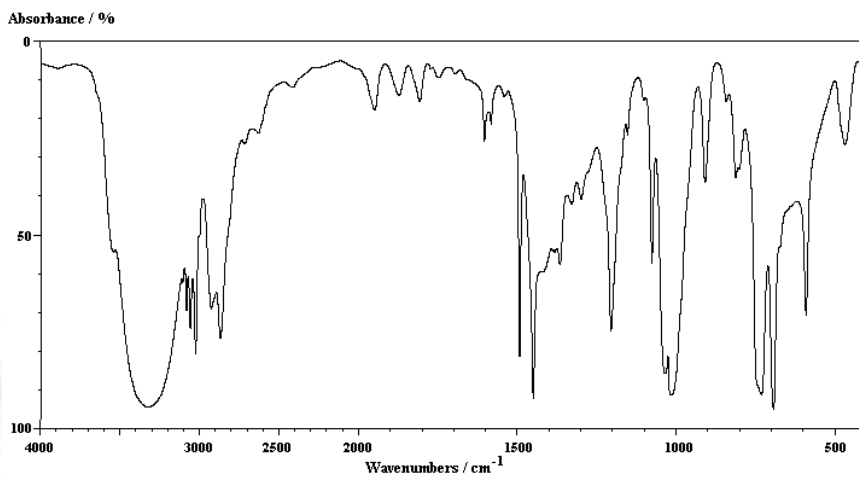


20.

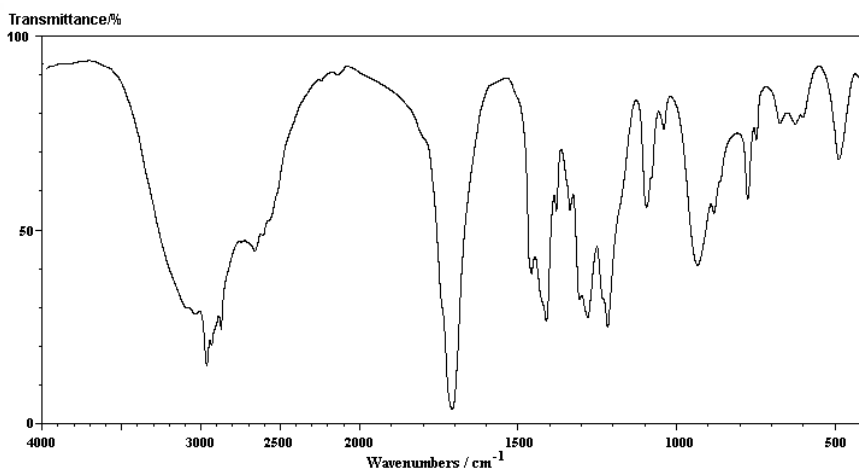




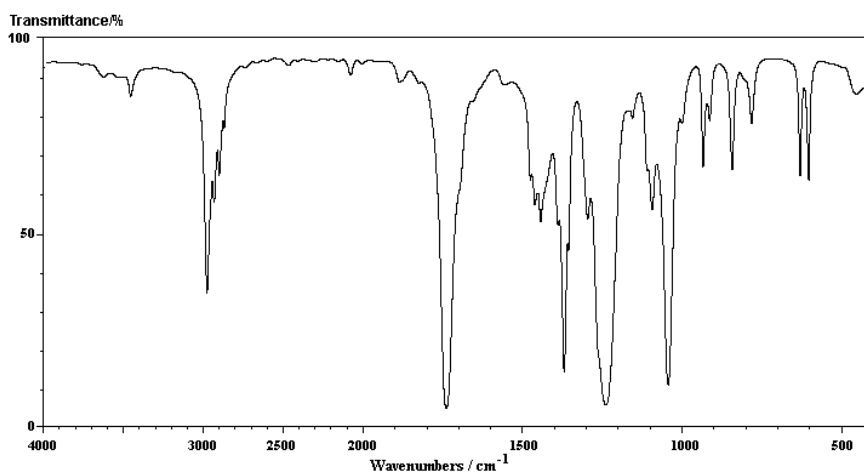
21.



22.



23.

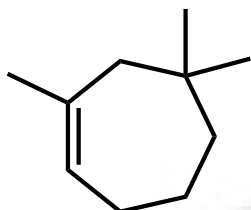


14% **PART 4: NOMENCLATURE**

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

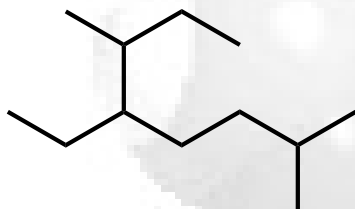
For each of questions 24 to 27, select the correct IUPAC name for the compound shown:

24.



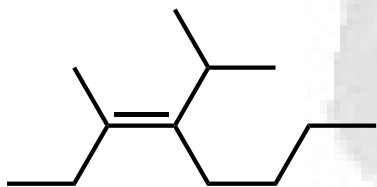
- A. 1,1,3-trimethylcyclohept-3-ene
- B. 1,1,6-trimethylcyclohept-5-ene
- C. 1,1,4-trimethylcyclohept-4-ene
- D. 2,4,4-trimethylcyclohept-1-ene
- E. 1,6,6-trimethylcyclohept-1-ene
- AB. 1,3,3-trimethylcyclohept-1-ene**

25.



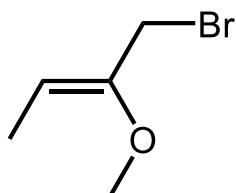
- A. 3-secbutyl-6-methylheptane
- B. 6-ethyl-3-secbutylheptane
- C. 2,6-dimethyl-5-ethyloctane
- D. 3,7-dimethyl-4-ethyloctane
- E. 4-ethyl-2,7-dimethyloctane
- AB. 5-ethyl-2,6-dimethyloctane**

26.



- A. (E)-3-methyl-4-isopropyloct-3-ene
- B. (Z)-3-methyl-4-isopropyloct-3-ene
- C. (E)-4-isopropyl-3-methyloct-3-ene
- D. (Z)-4-isopropyl-3-methyloct-3-ene
- E. (E)-4-butyl-3,5-dimethylhex-3-ene
- AB. (Z)-4-butyl-3,5-dimethylhex-3-ene**

27.

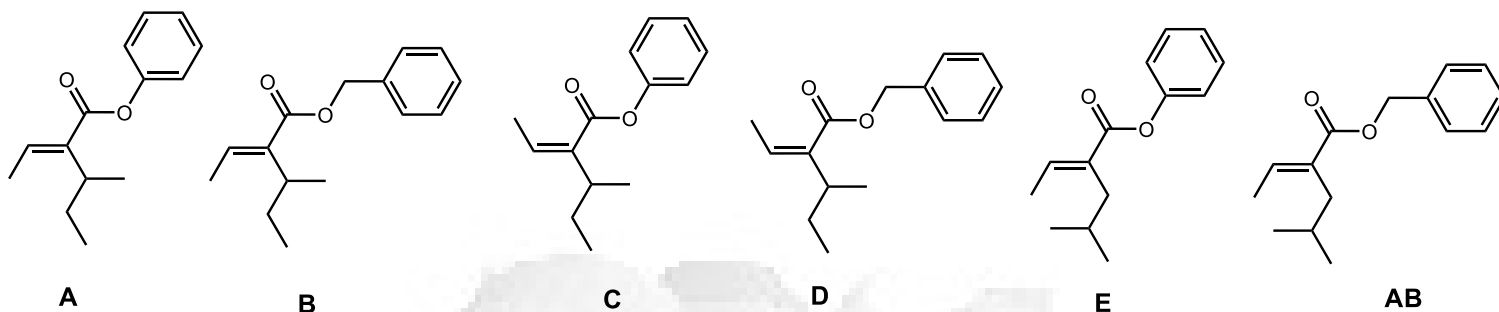


- A. (Z)-1-bromobut-2-en-2-ol
- B. (E)-1-bromobut-2-en-2-ol
- C. (Z)- 1-bromo-2-methoxy-2-butene
- D. (Z)-4-bromo-3-hydroxy-2-butene
- E. (E)-1-bromo-2-methoxy-2-butene
- AB. (E)-4-bromo-3-hydroxy-2-butene**

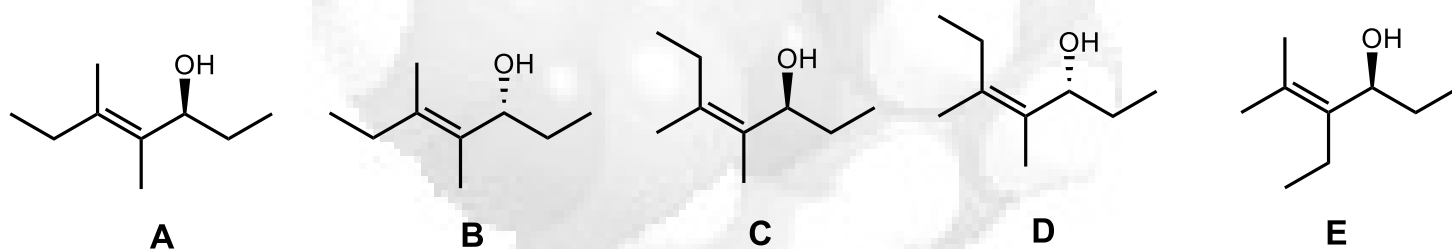
ANSWER ANY SEVEN (7) of the questions 24-31 (2 marks per question).

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

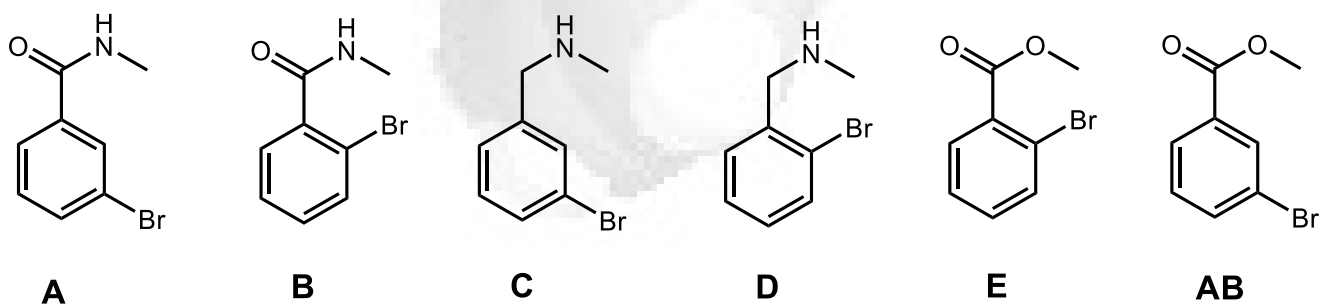
28. Benzyl trans-2-isobutylbut-2-enoate



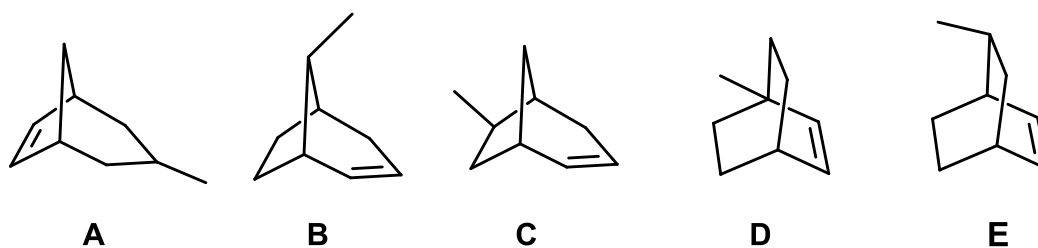
29. (3S,4Z)-4,5-dimethylhept-4-en-3-ol



30. N-methyl meta-bromobenzamide



31. 8-methylbicyclo[3.2.1]oct-2-ene:



13% **PART 5: STRUCTURE DETERMINATION**

Write your answers within the boxes provided in the answer booklet provided.

PARTIAL marks may be awarded.

ALL of the following questions need to be answered using the molecular formula **C₅H₁₁NO**.

- a) What is the molecular weight ?
- b) What is the index of hydrogen deficiency (IHD) ?
- c) Name two nitrogen containing functional groups that could be present.
- d) Draw a structure **D** that contains no sp² atoms and has 3 types of C and 3 types of H
- e) Draw a structure **E** that would have a characteristic IR peak near 1650 cm⁻¹, and where the most acidic proton has a pK_a ~30.
- f) Draw a structure **F** where the most acidic proton has a pK_a ~15.
- g) Draw a structure **G** that contains a tri-substituted alkoxy alkene that has Z stereochemistry.

13% **PART 6: THERMODYNAMICS**

Write your answers within the boxes provided in the answer booklet provided.

PARTIAL marks may be awarded.

a) What type of isomers are **i** and **ii**? (state which type or say not isomers)

b) What type of isomers are **i** and **iii**? (state which type or say not isomers)



c) What is the IUPAC name for **iii**?

d) Write a balanced equation for the complete combustion of species **ii**.

e) Isomer **ii** has a heat of combustion (ΔH_c°) = -1095.44 kcal mol⁻¹. Calculate ΔH_f° for this isomer using the following heats of combustion:

$$\Delta H_c^\circ \text{ C (graphite)} = -93.9 \text{ kcal mol}^{-1}$$

$$\Delta H_c^\circ \text{ H}_2 \text{ (gas)} = -68.4 \text{ kcal mol}^{-1}$$

f) If the other two species had ΔH_f° of -26.94 kcal/mol, and -23.90 kcal/mol. Draw an Energy diagram (with clearly labelled reactants, products, compounds **i**, **ii**, and **iii** and all ΔH values) to illustrate the relative energy difference between these three isomers.

g) On your energy diagram compare the three isomers by clearly indicating which one is the most stable and which one is the least stable.

h) Use the principles of bonding to explain the stability trend observed above.

13% **PART 7: MECHANISM**

Write your answers within the boxes provided in the answer booklet provided.

PARTIAL marks may 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 the C=C double bond in (S)-2-methylbut-3-enal is 'isomerized' by the action of a catalytic amount of base (sodium hydroxide), to make a more stable product.

Step 1. Removal of the most acidic proton in (S)-2-methylbut-3-enal by hydroxide to make a water molecule, along with a resonance-stabilized anion.

Step 2. The resonance-stabilized anion can share the negative charge amongst *three* different atoms. Draw the resonance structures that show this to be true, using curly arrows to indicate the movement of electrons.

Step 3. From one of those resonance structures, a lone pair in the organic anion removes a proton from water to regenerate the hydroxide base. The final product should contain a C=O double bond and a C=C double bond that is ***more stable*** than the C=C double bond found in the starting material.

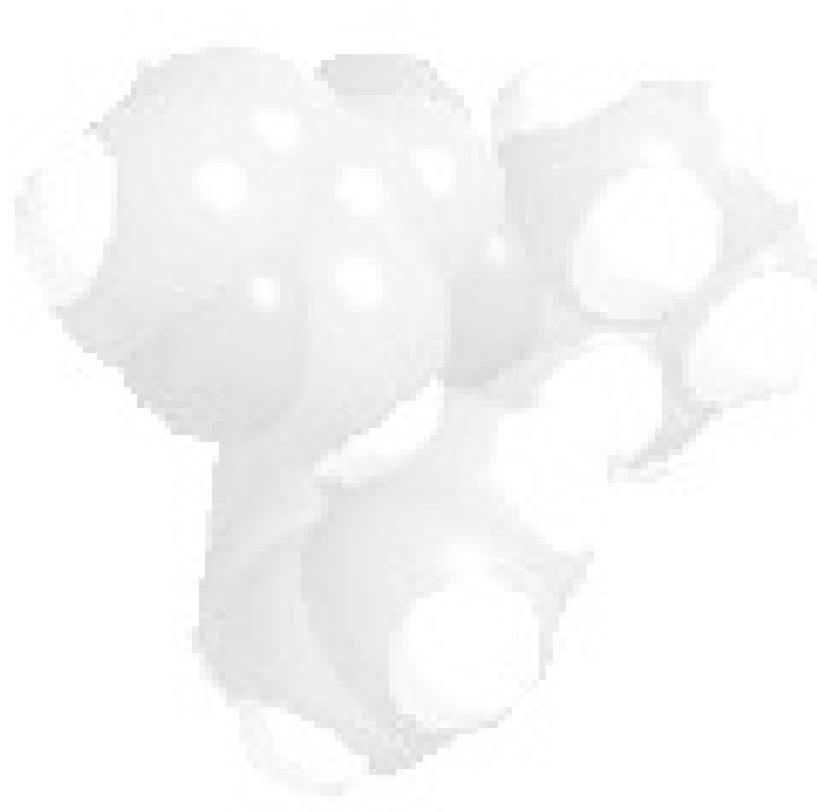
b) For the product that you have drawn, choose ***one*** of the following to describe the geometry of the new double bond: '*cis*', '*trans*', (E), (Z), or 'none apply'. If you chose 'none apply', explain why that is true. If you chose any of the other 4 options, explain how you 'ranked' the substituents on the double bond according to the proper rules.

c) Would an analogous reaction sequence be possible if the starting material was (S)-2-methylbut-3-en-1-ol? Would you be able to convert the C=C double bond in this molecule into a more stable isomer? Why or why not?

**** THE END ****

SCRAP PAPER

Remember that ALL final answers need to be in your answer booklet within the boxes provided, NOT on the scrap paper.



SCRAP PAPER

Remember that ALL final answers need to be in your answer booklet within the boxes provided, NOT on the scrap paper.



INFRA-RED GROUP ABSORPTION FREQUENCIES

		<u>TYPE OF VIBRATION</u>	<u>FREQUENCY (cm⁻¹)</u>	<u>WAVELENGTH (μ)</u>	<u>INTENSITY (1)</u>
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		3500-3100	2.86-3.23	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 may be very broad

PERIODIC TABLE

1																18	
1A																8A	
1 H 1.008	2										13	14	15	16	17	2	
	2A										3A	4A	5A	6A	7A	He	
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
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)

Actinides **