

UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

November 8th, 2016

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.  $i > ii > iii$

B.  $i > iii > ii$

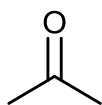
C.  $ii > i > iii$

D.  $ii > iii > i$

E.  $iii > i > ii$

AB.  $iii > ii > i$

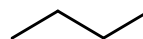
1. The relative boiling points of the compounds shown below:



i

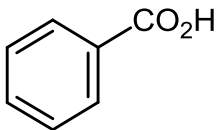


ii

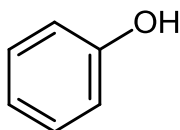


iii

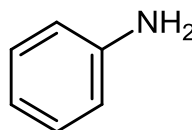
2. The relative solubility of the following in aqueous sodium bicarbonate:



i

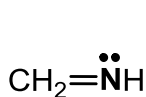


ii

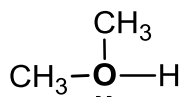


iii

3. The relative charge on the **bold** atoms in each of the following:



i

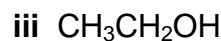
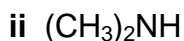
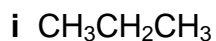


ii



iii

4. The basicity of each of the following:

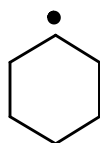


Use the following code to indicate your answers.

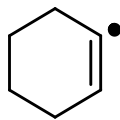
- A. i > ii > iii  
 B. i > iii > ii  
 C. ii > i > iii

- D. ii > iii > i  
 E. iii > i > ii  
 AB. iii > ii > i

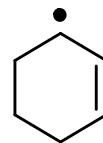
5. The relative stability of the following radicals:



**i**

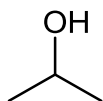


**ii**

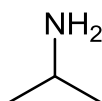


**iii**

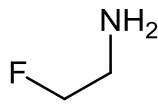
6. Rank these molecules in order of the amount of its conjugate acid that would be present in a 1 M aqueous HCl solution:



**i**



**ii**



**iii**

7. The relative rate of reaction when each of the following are reacted with Cl<sub>2</sub> / uv light:

**i** 2,2-dimethylpropane

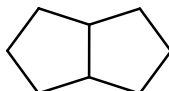
**ii** 2,2-dimethylbutane

**iii** 2,3-dimethylbutane

8. The number of types of H in each of the following:



**i**



**ii**



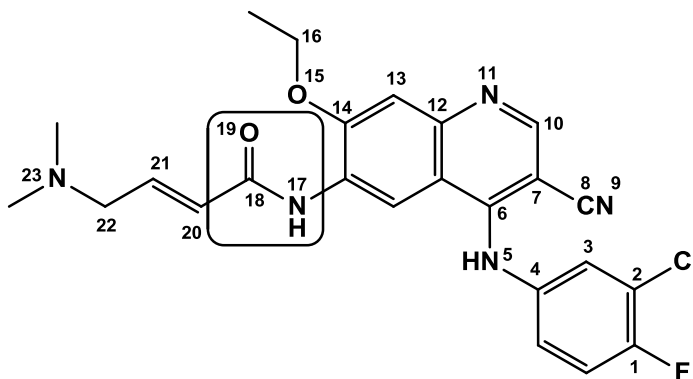
**iii**

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.**

Use the structure of **Pelitinib**, a potent irreversible epidermal growth factor receptor (EGFR) inhibitor with potential antineoplastic activity, as depicted below to answer the questions **9-17**.



9. What is the index of hydrogen deficiency (IHD) of **Pelitinib** (above) ?

- A. 12      B. 13      C. 14      D. 15      E. 16      AB. 17

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

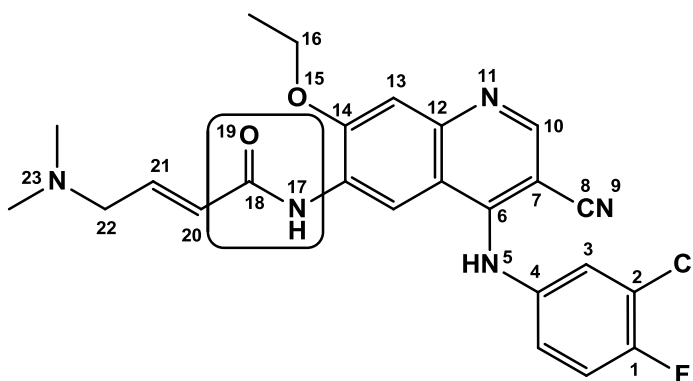
- A. -4    B. -3    C. -2    D. -1    E. 0    AB. +1    AC. +2    AD +3    BC. +4

11. Which of the following functional groups is boxed in **Pelitinib** (above) ?

- A. ketone    B. ester    C. amide    D. amine    E. nitrile    AB. nitro

12. What type of orbital do the lone pairs of electrons on **N9** and **N11** occupy respectively ?

- A.  $sp^2, sp^2$     B.  $sp^2, sp$     C.  $sp^2, p$     D.  $sp, sp^2$     E.  $sp, sp$     AB.  $sp, p$



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.

13. What are the hybridizations of atoms **N17** and **N23** respectively?

- A.  $sp^3, sp^3$     B.  $sp^2, sp^3$     C.  $sp, sp^3$     D.  $sp^3, sp^2$     E.  $sp^2, sp^2$     AB.  $sp, sp^2$

14. Which of term(s) describe **C22** ?

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

15. Which of the following bonds is the strongest ?

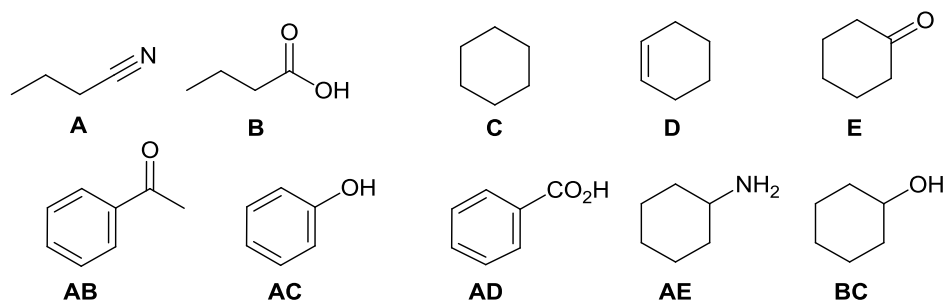
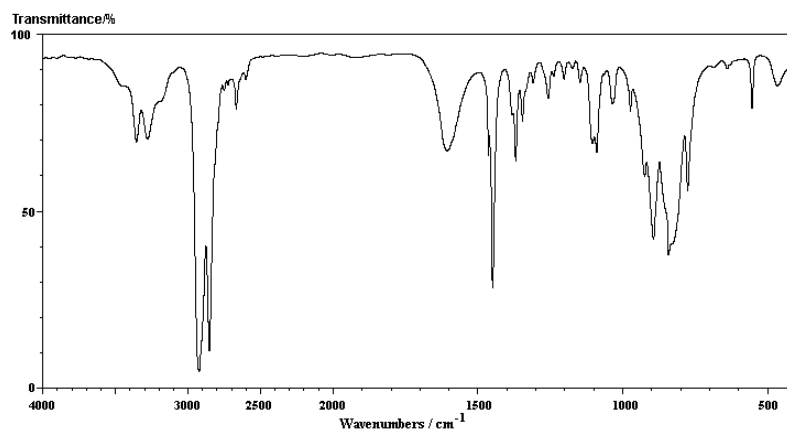
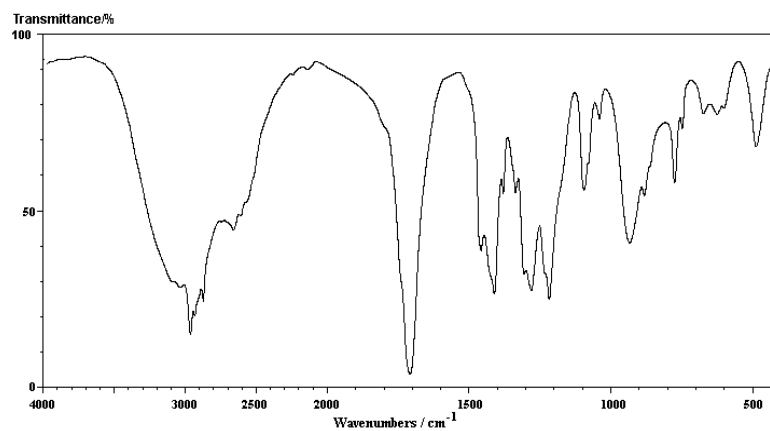
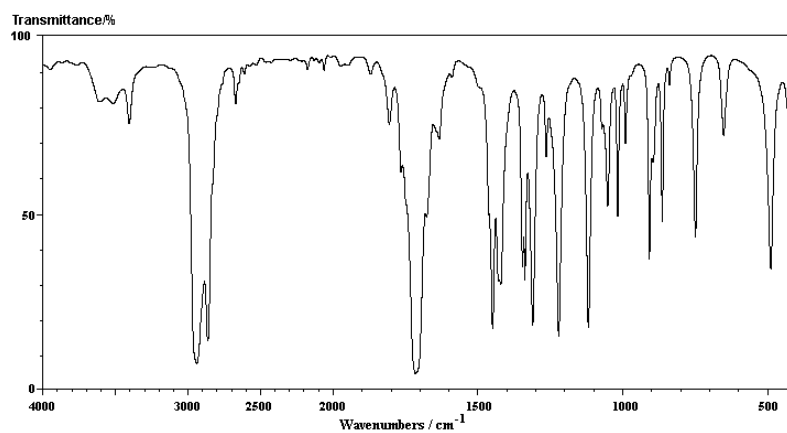
- A. C2-Cl    B. C8-N9    C. C10-N11    D. C20-C21    E. C22-N23

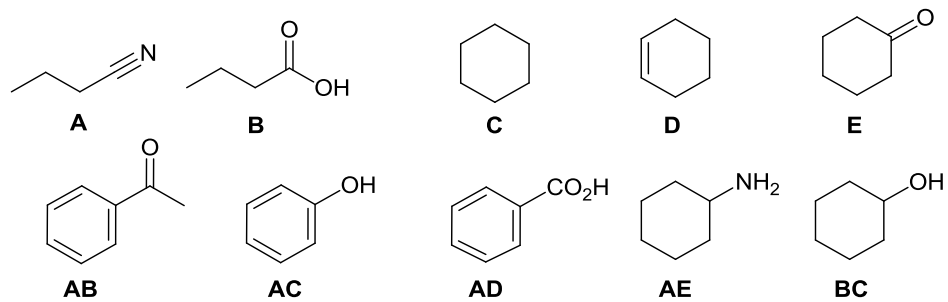
16. Which configurational term best describes **C20-C21** ?

- A. E    B. R    C. S    D. Z

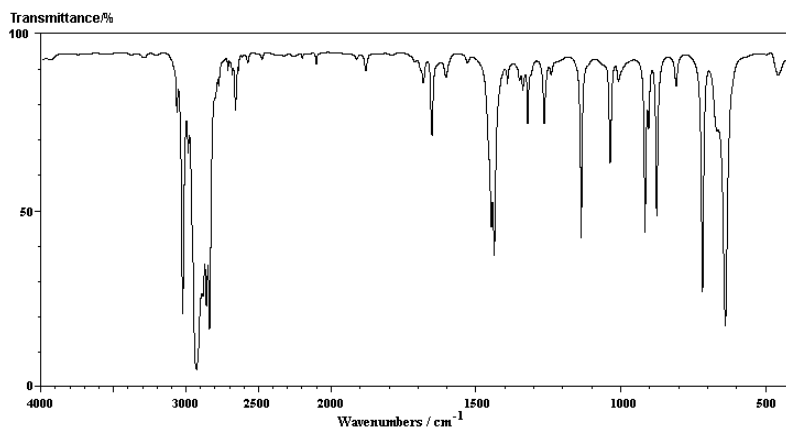
17. Which of the following atoms in **Pelitinib** (above) is the most basic ?

- A. N5    B. N9    C. N11    D. O15    E. O19  
 AB. N23    AC. Cl (on C2)    AD. F (on C1)

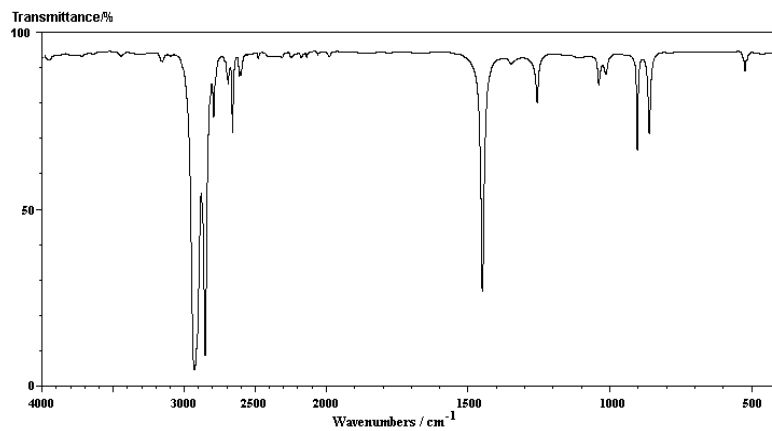
15% **PART 3: SPECTROSCOPY****ANSWER ALL SIX (6) OF QUESTIONS 18 – 23 (2.5 marks per question).****For each of the questions 18-23, match the IR spectra to a structure in the list below:****18.****19.****20.**



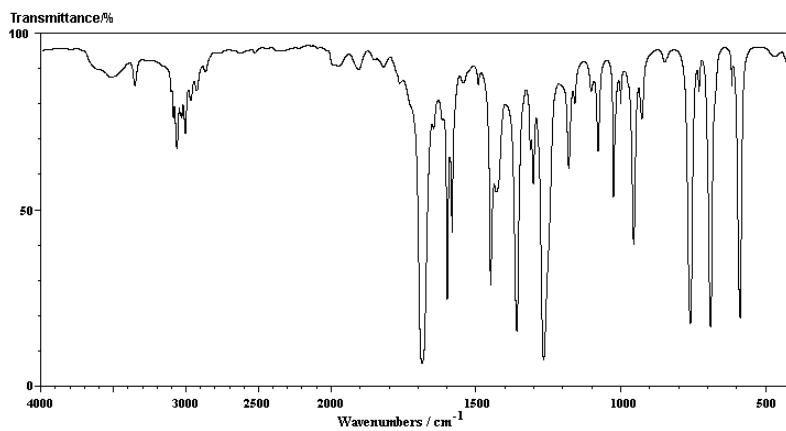
21.



22.



23.

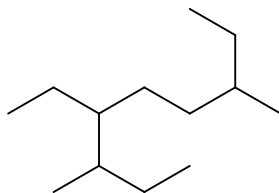


14% **PART 4: NOMENCLATURE**

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

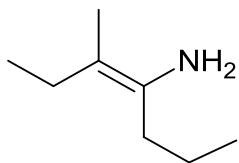
**For each of questions 24 to 27, select the correct IUPAC name for the compound shown:**

24.



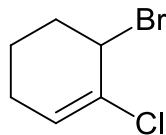
- A. 3-methyl-6-(1-methylpropyl)octane  
 B. 6-methyl-3-(1-methylpropyl)octane  
 C. 2-ethyl-5-(1-methylpropyl)heptane  
 D. 6-ethyl-3-(1-methylpropyl)heptane  
 E. 4-ethyl-3,7-dimethylnonane  
**AB. 3,7-dimethyl-4-ethylnonane**

25.



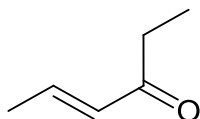
- A. (Z)-3-methyl-4-aminohept-3-ene  
 B. (E)-3-methyl-4-aminohept-3-ene  
 C. (Z)-3-methyl-4-aminohept-3-ene  
 D. (E)-4-amino-3-methylhept-3-ene  
 E. (Z)-4-amino-3-methylhept-3-ene  
**AB. (E)-4-amino-5-methylhept-4-ene**

26.



- A. 1-bromo-2-chlorocyclohex-2-ene  
 B. 2-bromo-1-chlorocyclohexene  
 C. 3-bromo-2-chlorocyclohexene  
 D. 6-bromo-1-chlorocyclohexene  
 E. 1-chloro-2-bromocyclohexene  
**AB 2-chloro-3-bromocyclohexene**

27.

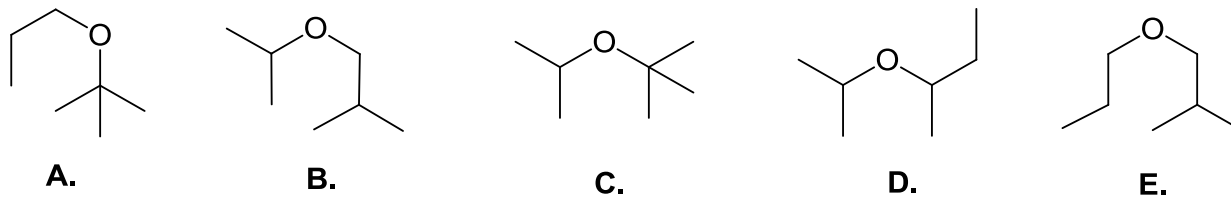


- A. *trans*-hex-4-on-2-ene  
 B. *trans*-hex-4-en-3-one  
 C. *trans*-hex-2-en-4-one  
 D. *cis*-hex-4-on-2-one  
 E. *cis*-hex-4-en-3-one  
**AB. *cis* -hex-2-en-4-one**

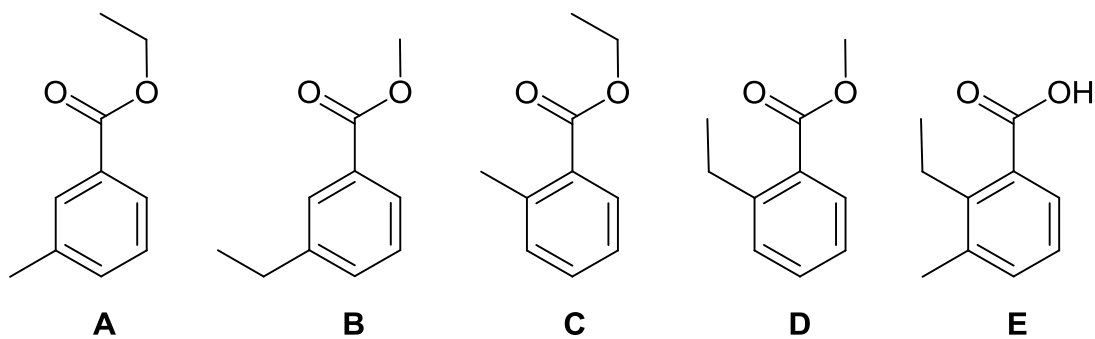


For each of questions 28 to 31, select the correct structure for the IUPAC name provided:

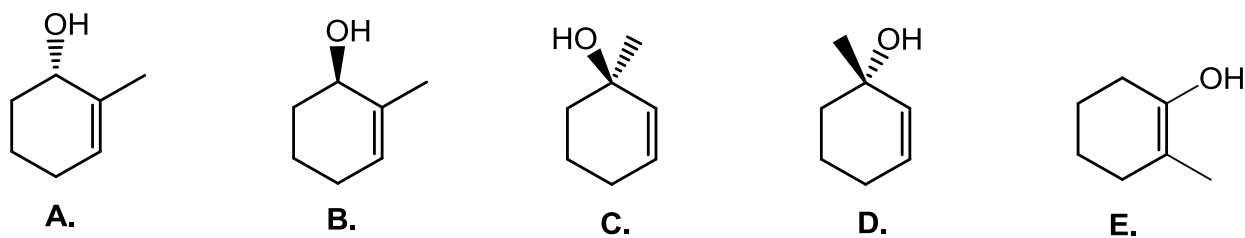
28. isobutyl isopropyl ether



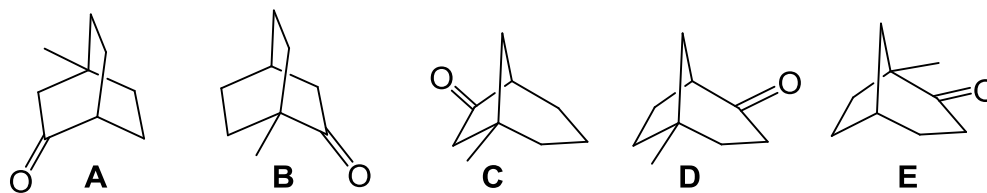
29. methyl o-ethylbenzoate



30. (S)-1-methylcyclohex-2-en-1-ol



31. 1-methylbicyclo[3.2.1]octan-2-one:



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** that contains 5 carbons, 10 hydrogens and 1 oxygen:

- a) What is the molar molecular weight of **X** ?
- b) What is the index of hydrogen deficiency of **X** ?
- c) **X** has 4 types of hydrogen and 3 types of carbon. The IR spectrum of compound **X** shows a strong broad absorption between  $3200\text{-}3600\text{ cm}^{-1}$ . What is the structure of **X** ?
- d) Identify a base that would give >90% deprotonation of the most acidic proton in **X** when 1 equivalent of the base was reacted with **X**.
- e) **Y** is a constitutional isomer of **X**. **Y** contains a chiral center and is an ether.  
Draw a 3D wedge-hash representation of **Y**.  
What is the systematic IUPAC name of **Y** ?
- f) **Z** is a constitutional isomer of **X**. **Z** has 2 types of hydrogen and 3 types of carbon, and the most acidic proton of **Z** has a  $pK_a \sim 20$ . Draw the structure of **Z**.

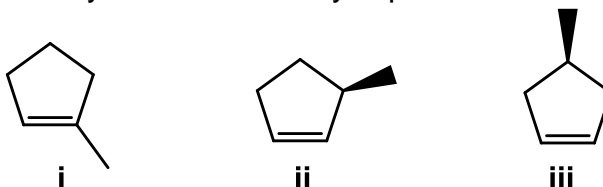
13% **PART 6: THERMODYNAMICS**

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

Two 3D representations of cyclopentene are shown below. The diagram on the right has the alkene unit directly towards you.



The structures of three methyl derivatives of cyclopentene are shown below:



- a) Give the IUPAC names of the molecules **i**, **ii**, **iii**
- b) What type of isomers are these three molecules ?
- c) Calculate  $\Delta H_f^\circ$ , for isomer **i**, given that the following heats of combustion:
- $$\Delta H_c^\circ, \text{C (graphite)} = -93.9 \text{ kcal/mol}$$
- $$\Delta H_c^\circ \text{H}_2 \text{ (gas)} = -68.4 \text{ kcal/mol}$$
- $$\Delta H_c^\circ \text{ for isomer i} = -904.1 \text{ kcal/mol}$$
- d) Given that the heats of formation,  $\Delta H_f^\circ$  of the other two isomers are +2.1 kcal/mol and +3.5 kcal/mol: match each of the three isomers **i-iii** to their corresponding  $\Delta H_f^\circ$  values and clearly indicate which is the most and least stable isomer.
- e) Use the principles of conformational analysis (models lab experiment) to explain your choices in part **d** above.
- f) A fourth isomer of methylcyclopentene that is not shown above was found to have a  $\Delta H_f^\circ$  of +2.1 kcal/mol, draw the structure of this isomer.

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 a ketone, propan-2-one undergoes alkylation to give a new ketone, hexan-2-one when reacted with a base and then an alkylating agent, 1-bromopropane.

**Step 1.** An acid-base reaction in which a proton is removed from the propan-2-one using potassium t-butoxide to give a resonance stabilised carbanion and t-butanol.

**Step 2.** Reaction of the carbanion as a nucleophile on the electrophilic carbon of 1-bromopropane, leading to the formation of a new CC sigma bond and causing the simultaneous loss of a bromide ion as a leaving group.

**b)** Draw the significant resonance contributors of:

- i) the starting material propan-2-one
- ii) the carbanion formed from propan-2-one

**c)** The pKa for the H atom removed in propan-2-one is about 20, yet in propane the pKa is over 50. Explain why there is such a large difference in acidity.

**d)** Based on the information provided in this question, what reagents would you use if you wanted to prepare octan-2-one ?

**\*\* THE END \*\***

**INFRA-RED GROUP ABSORPTION FREQUENCIES**

	<u>TYPE OF VIBRATION</u>	<u>FREQUENCY (cm<sup>-1</sup>)</u>	<u>WAVELENGTH (μ)</u>	<u>INTENSITY (1)</u>
C-H	Alkanes (stretch)	3000-2850	3.33-3.51	s
-CH <sub>3</sub>	(bend)	1450 and 1375	6.90 and 7.27	m
-CH <sub>2</sub> -	(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 <sub>2</sub> )	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

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

## Lanthanides \*

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

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