UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

Version

01

November 5th, 2019 Time: 2 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** ON ***BOTH*** **YOUR BLUE BOOKLET** AND **OPTICAL SCORE ANSWER SHEET**.
ENTER **VERSION NUMBER 1** ON THE **OPTICAL SCORE 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 and **Parts 5, 6 and 7** are to be answered **IN THE BLUE BOOKLET PROVIDED**. A periodic table with atomic numbers and atomic weights and infrared data tables are located on the last two pages

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***.

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

Cont'd

14% PART 1: RELATIVE PROPERTIES

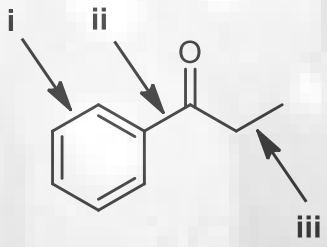
ANSWER ANY SEVEN (7) of questions 1-8 (2 marks per question)

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

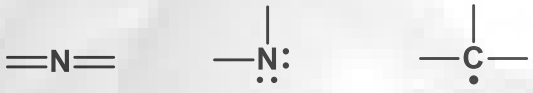
Use the following code to indicate your answers.

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:

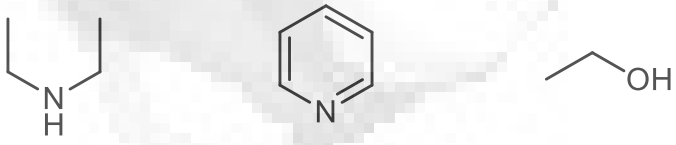


2. The formal charge on each of the bolded atoms indicated below (all required lone pairs and unpaired electrons are shown):



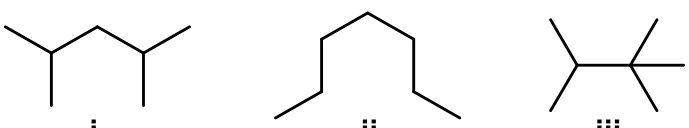
i **ii** **iii**

3. The relative basicity of the following compounds:



i **ii** **iii**

4. The relative stability of the following isomers:

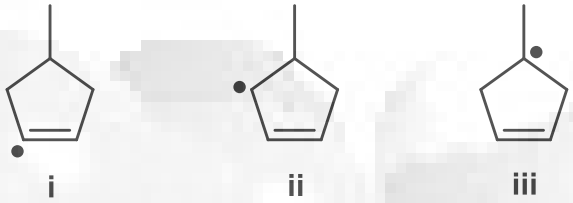


i **ii** **iii**

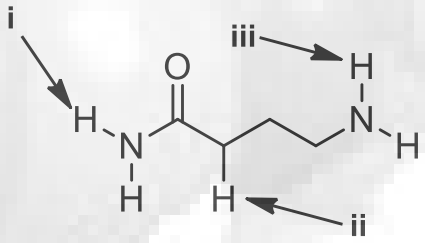
Use the following code to indicate your answers.

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

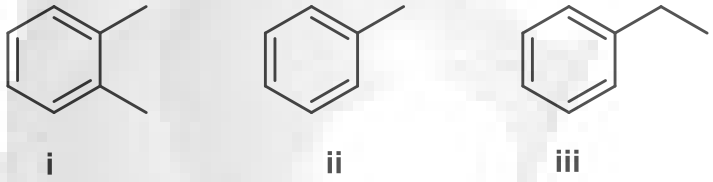
5. The relative stability of the following radicals:



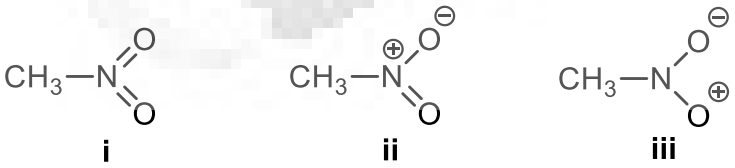
6. The relative acidity of the hydrogens indicated:



7. The number of types of H in each of the following molecules:



8. The relative importance of the resonance contributors shown:

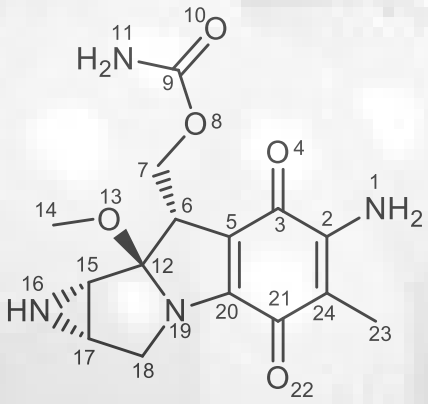


18% **PART 2: MOLECULAR PROPERTIES**

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 **Mitomycin C**, a chemotherapeutic agent to treat upper gastro-intestinal cancers, breast cancers and superficial bladder tumours:



Mitomycin C

9. Which atom is the most basic ?

A. C6 **B.** N11 **C.** O13 **D.** N16 **E.** C23

10. What type of orbital does the lone pair of **N19** occupy ?

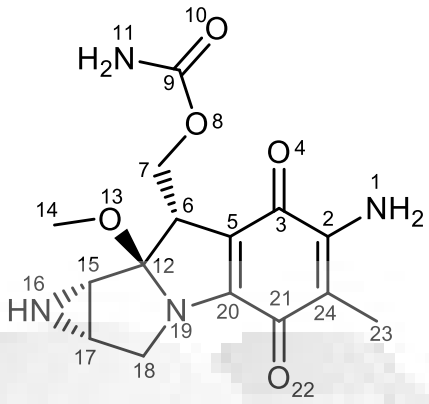
A. sp **B.** sp^2 **C.** sp^3 **D.** s **E.** p

11. What are the hybridisations of **O8** and **O13** 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 Mitomycin C ?

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



Mitomycin C

13. Which of the following functional group(s) is (are) found in Mitomycin C ?

A. arene **B.** nitrile **C.** aldehyde **D.** ketone **E.** amine

14. What configuration terms best describe **C12** and the **C5=C20** respectively ?

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

15. Which is the bond angle of O8-C7-C6 closest to ?

A. 60° **B.** 90° **C.** 109.5° **D.** 120° **E.** 180°

16. Which following terms describe **C6** ?

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

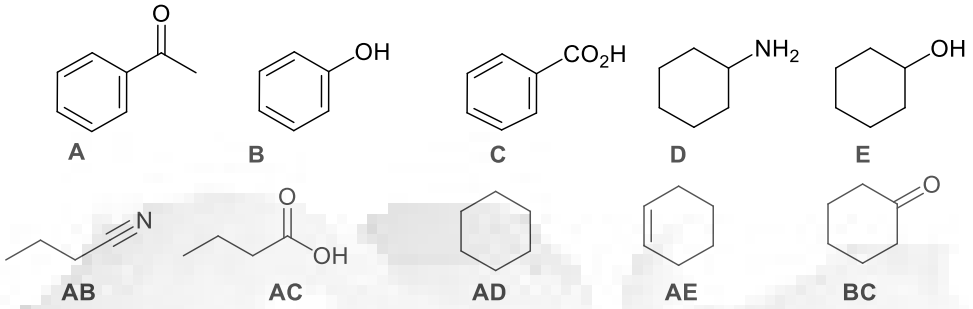
17. What is the oxidation state of **C3** ?

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

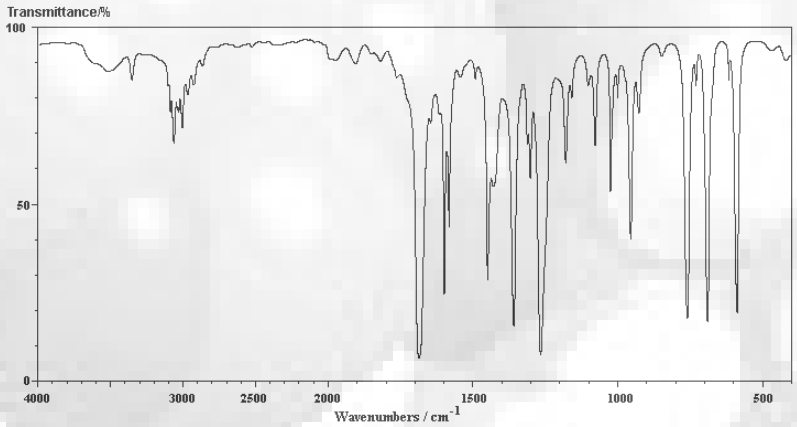
15% **PART 3: SPECTROSCOPY**

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

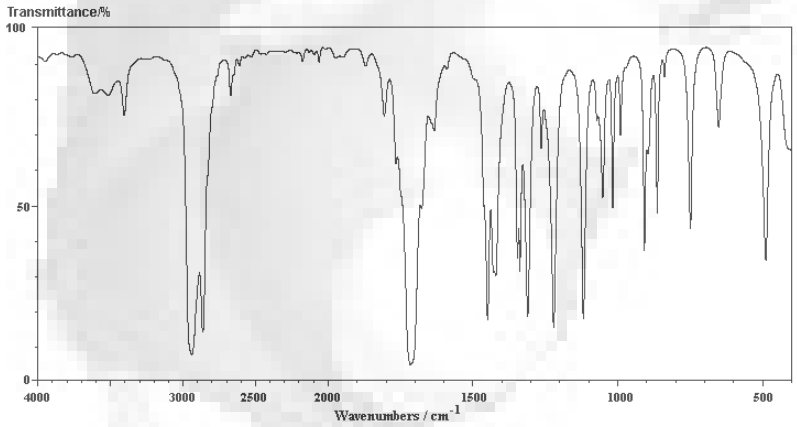
For each of the questions 18-23, match the IR spectra to a structure in the list below:



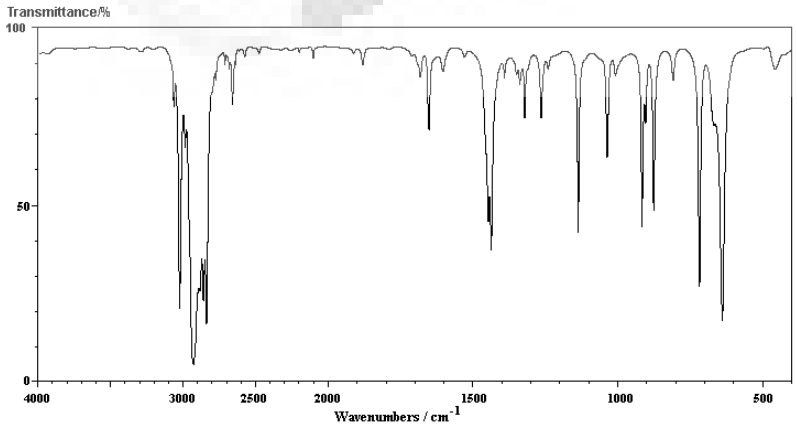
18.

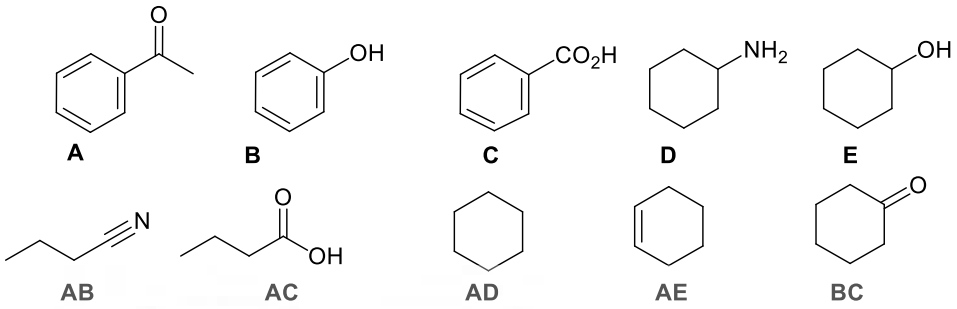


19.

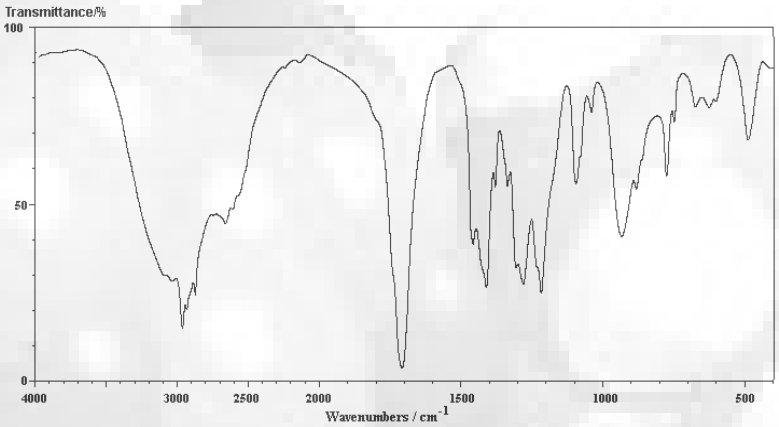


20.

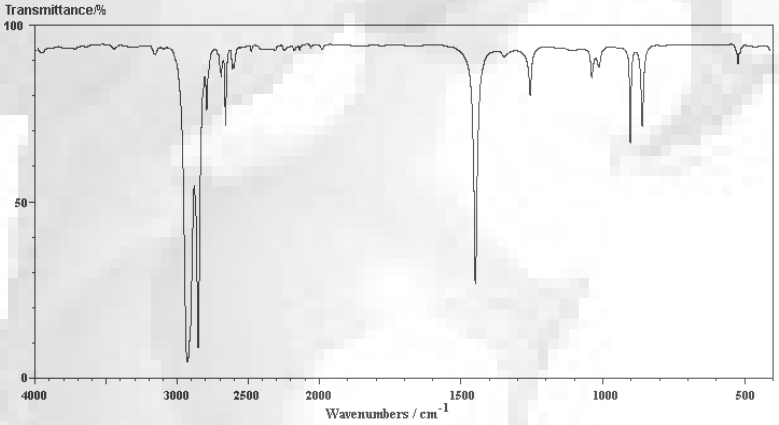




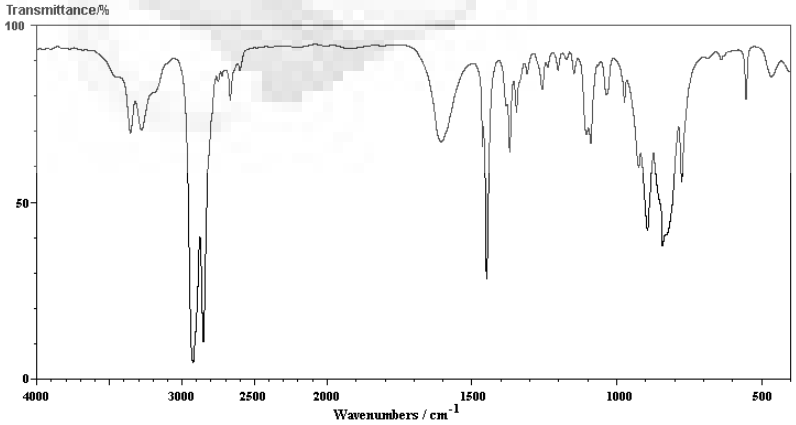
21.



22.



23.

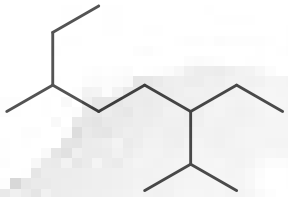


14% **PART 4: NOMENCLATURE**

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-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. 6-ethyl-3-isopropylheptane

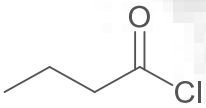
25.

A. *cis*-1,2-dimethylpent-1-ene
B. *trans*-1,2-dimethylpent-1-ene
C. *cis* -3-methylhex-2-ene
D. *trans*-3-methylhex-2-ene
E. *cis* -3-methylhept-2-ene
AB.*trans*-3-methylhept-2-ene

26.

A. 1-ethyl-3-methylcyclohexene
B. 3-methyl-1-ethylcyclohexene
C. 3-ethyl-1-methylcyclohexene
D. 1-methyl-3-ethylcyclohexene
E. 1-ethyl-5-methylcyclohexene
AB 5-ethyl-1-methylcyclohexene

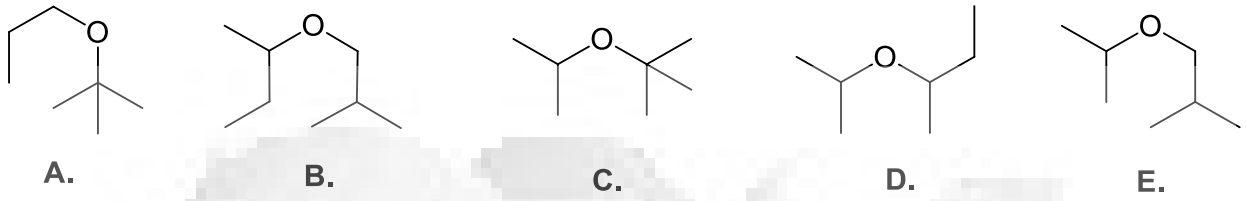
27.



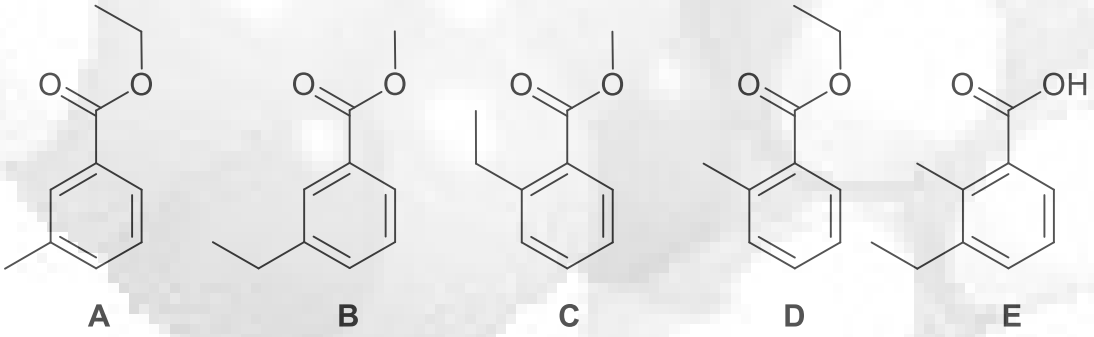
A. 1-chlorobutan-1-one
B. 1-chlorobutan-1-al
C. butanoyl chloride
D. 1-oxo-n-butyl chloride
E. butan-1-one chloride
AB.butan-1-al chloride

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

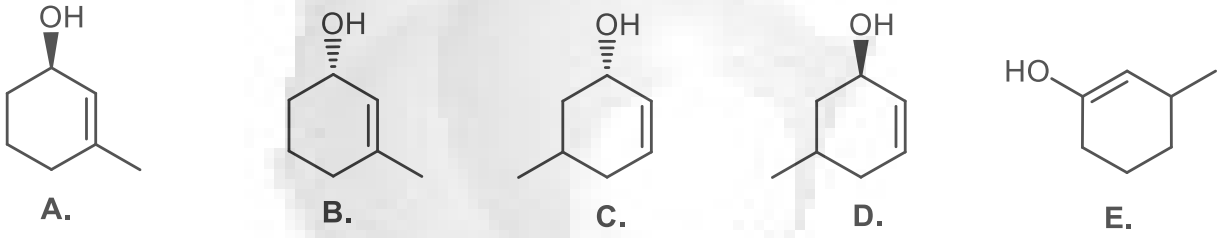
28. sec-butyl isopropyl ether



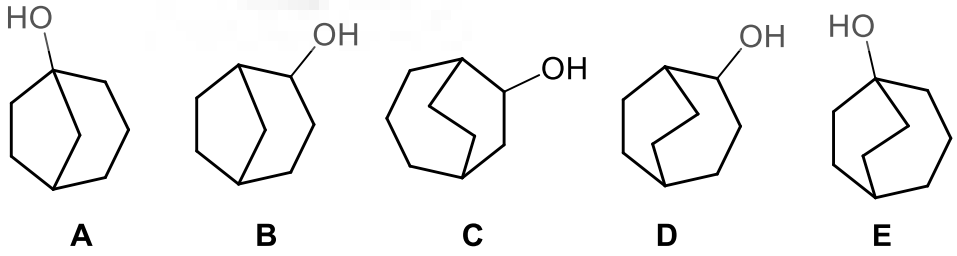
29. Methyl m-ethylbenzoate



30. (S)-3-methylcyclohex-2-en-1-ol



31. Bicyclo[3.2.1]octan-1-ol:



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 $C_5H_8O_2$.

a) What is the weight percentage of C in this molecule ?

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

c) Name three functional groups that could be present in isomers of **X**.

d). Draw a structure for **X** that contains three types of carbon and two types of hydrogen.

e) Draw an acyclic structure for **X** that has a characteristic IR peak at 1735 cm^{-1} and has the most acidic proton with pKa ~25.

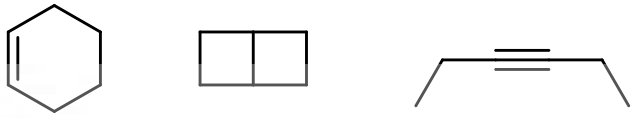
f). Name a base that can be used to cause >99.9% deprotonation of the most acidic proton in e).

g) Draw a structure for **X** that contains one ring and two chiral centers with a meso configuration, use the 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.

The structures of three isomers are shown to the right:



i **ii** **iii**

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

b) Given the thermodynamic data below, calculate the heat of combustion for isomer **ii**, and the heat of formation for isomer **iii** using the following heats of combustion:

ΔH_c^o (graphite) = –94.05 kcal mol^{-1} ΔH_c^o (H_2) = –68.32 kcal mol^{-1}

Thermodynamic Data for compounds i-iii (kcal mol^{-1})

Compound	ΔH_f^o	ΔH_c^o
i	–1.0	–904.9
ii	29.8	**?**
iii	**?**	–935.0

c) Draw an energy diagram (with clearly labeled reactants, products, and all ΔH values) to illustrate the relative energy difference between these three isomers.

d) Draw another constitutional isomer for these molecules **iv**, where this new molecule has a C-H bond that is certainly **weaker** than *every* C-H bond in **i-iii**. Clearly label which C-H bond in your new structure is the weakest.

e) Draw another constitutional isomer for these molecules **v**, where this new molecule has a C-H bond that is certainly **stronger** than *every* C-H bond in **i-iii**. Clearly label which C-H bond in your new structure is the strongest.

f) Draw another constitutional isomer for these molecules **vi**, where this new molecule would give exactly three different monochlorination products after reaction with Cl_2/UV light.

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 a carboxylic acid, benzoic acid, is alkylated using ethyl iodide in the presence of a base, ammonia, to yield ethyl benzoate.

Step 1. Deprotonation of benzoic acid by ammonia to create the conjugate base of benzoic acid (which is a carboxylate ion).

Step 2. Attack of the carboxylate ion as a nucleophile on the electrophilic carbon of ethyl iodide producing ethyl benzoate with the simultaneous loss of an iodide ion as the leaving group.

b) NAME another base that could be used to deprotonate benzoic acid for this reaction.

c) Based on the above sequence, what reagents could be used to synthesize isopropyl benzoate ?

d) Based on the above sequence, what reagents could be used to prepare ethoxybenzene ?

e) Is a phenol more or less acidic than a carboxylic acid ? Briefly explain why.

**** THE END ****

IRH / CCL / JvH F2019

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)