EXAMINATION 1
Chemistry 3A

Name:____Key_____   SID #:_____
     Print first name before second!   Make sure the number is correct!
     Use capital letters!

                    GSI (if you are taking Chem 3AL): _____
Peter Vollhardt
February 28, 2019

Please provide the following information if applicable.

Making up an I Grade   _____
If you are, please indicate the semester during which you took previous Chem 3A and the instructor:

_____   _____
 Semester   Instructor


Auditor _____

Please write the answer you wish to be graded in the boxed spaces provided.

Do scratch work on the back of the pages. This test should have **16** numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **Read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy now than sorry later!** *Good Luck*!

Do not remove unstaple and/or remove a page from the exam. It will compromise the consonance of scanned copies in Gradescope.

I. [36 Points]   Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (such as cis, trans, *R*, *S*, meso, hashed/wedged lines, etc.)
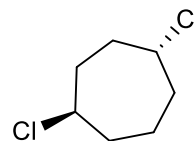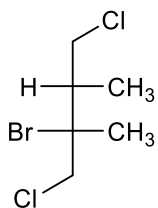
a.
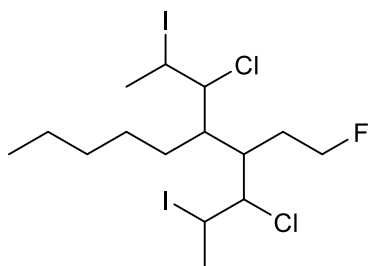
(No stereochemistry)

3-Chloro-5-(1-chloro-2-iodopropyl)-4-(2-fluoroethyl)-2-iododecane
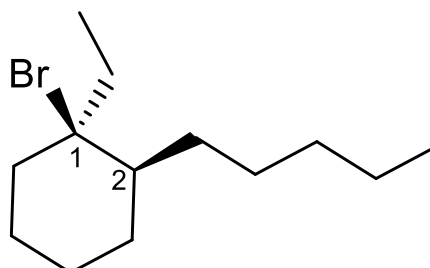
b.

(1*R*,4*R*)-1,4-Dichlorocycloheptane

c.

(Name this enantiomer)

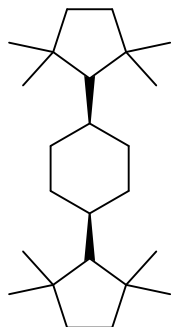(2*R*,3*S*)-2-Bromo-1,4-dichloro-2,3-dimethylbutane

d.

(1*R*,2*S*)-1-Bromo-1-ethyl-2-pentylcyclohexane
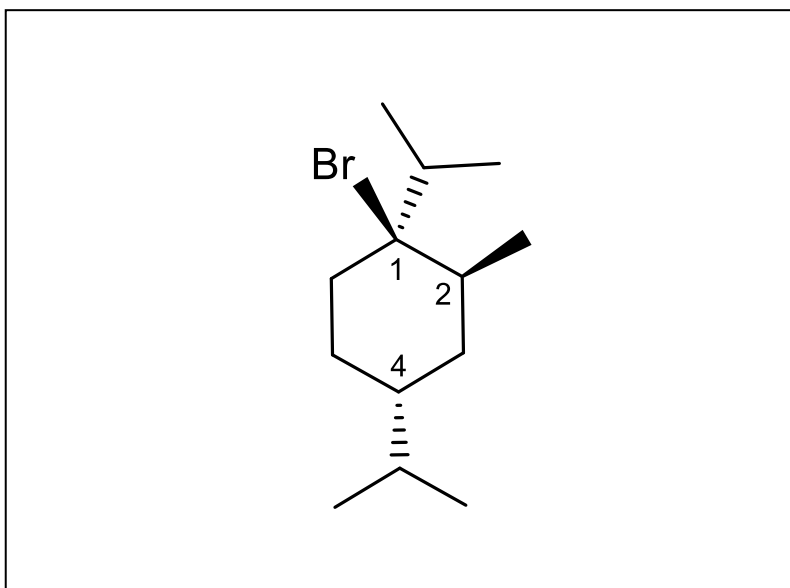
(Complete the stencil in the box)

e.

cis-1,4-Bis(2,2,5,5-tetramethylcyclopentyl)cyclohexane

f.

(1S,2S,4R)-1-Bromo-2-methyl-1,4-bis(1-methylethyl)cyclohexane

(Complete the stencil in the box)

II. [30 Points]

TABLE 1-1	Partial Periodic Table

| Period								Halogens	Noble gases
First	H^1								He^2
Second	$Li^{2,1}$	$Be^{2,2}$	$B^{2,3}$	$C^{2,4}$	$N^{2,5}$	$O^{2,6}$		$F^{2,7}$	$Ne^{2,8}$
Third	$Na^{2,8,1}$	$Mg^{2,8,2}$	$Al^{2,8,3}$	$Si^{2,8,4}$	$P^{2,8,5}$	$S^{2,8,6}$		$Cl^{2,8,7}$	$Ar^{2,8,8}$
Fourth	$K^{2,8,8,1}$							$Br^{2,8,18,7}$	$Kr^{2,8,18,8}$
Fifth								$I^{2,8,18,18,7}$	$Xe^{2,8,18,18,8}$

Note: The superscripts indicate the number of electrons in each principal shell of the atom.

Pauling Electronegativities

H							He
2.1							~0
Li	Be	B	C	N	O	F	Ne
1.0	1.5	2.0	2.5	3.0	3.5	4.0	~0
Na	Mg	Al	Si	P	S	Cl	Ar
0.9	1.2	1.5	1.8	2.1	2.5	3.0	~0
K	Ca	Ga	Ge	As	Se	Br	Kr
0.8	1.0	1.6	1.8	2.0	2.4	2.8	~0

Write the Lewis octet structure for each of the following two molecules (a. and b.). **Remember to assign charges, if any, to atoms! Do not forget to draw any lone electron pairs!**

a.

$$\left[\; :\ddot{F}\!-\!\overset{+}{\underset{\cdot\cdot}{Cl}}\!-\!\ddot{F}: \; \right]^{+}$$
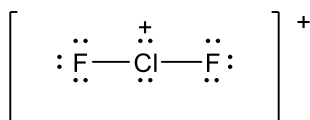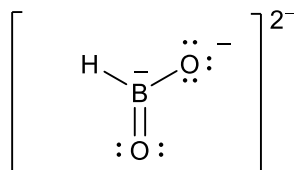
What is the geometry of $FClF^+$? Place an "x" mark into the box next to your answer.

Linear ☐

Bent ☒

b.

$$\left[\; \underset{\;\;\;\;\overset{\|}{\underset{:\ddot{O}:}{B}}}{H\diagdown \;\;\; \diagup \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:}^{-} \; \right]^{2-}$$

c. The following structure has two **octet** resonance forms. Circle the best one.

$$\left[\;\overset{-}{\underset{..}{\overset{..}{O}}}-\overset{+}{\underset{..}{O}}=\overset{..}{\underset{..}{S}}\;\longleftrightarrow\;\overset{..}{\underset{..}{O}}=\overset{+}{\underset{..}{O}}-\overset{..}{\underset{..}{S}}\overset{-}{}\;\right]$$
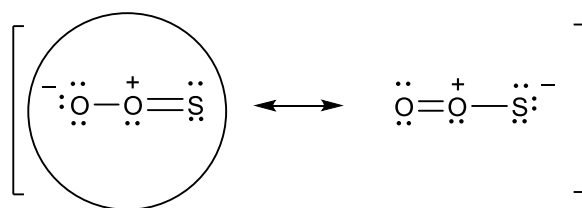
d. The following structure has three **octet** resonance forms. Circle the best one.

$$\left[\;:N\equiv\overset{+}{N}-\overset{..}{\underset{..}{O}}\overset{-}{:}\;\longleftrightarrow\;\overset{-}{:}\overset{..}{N}=\overset{+}{N}=\overset{..}{\underset{..}{O}}\;\longleftrightarrow\;\overset{2-}{\underset{..}{:N}}-\overset{+}{N}\equiv O\overset{+}{:}\;\right]$$
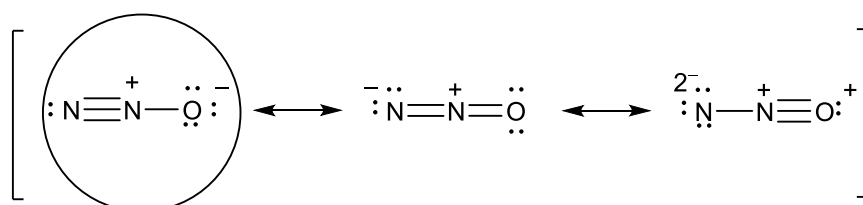
e. This picture is edited from your textbook. Label the indicated atomic orbitals (as, for example, 2*s*, 4*p*, etc.) in the boxes provided.

1*s*	1*s*	2*p*	2*p*

as in H−H   as in H−F   as in F−F

as in F−Cl

2*p*

3*p*
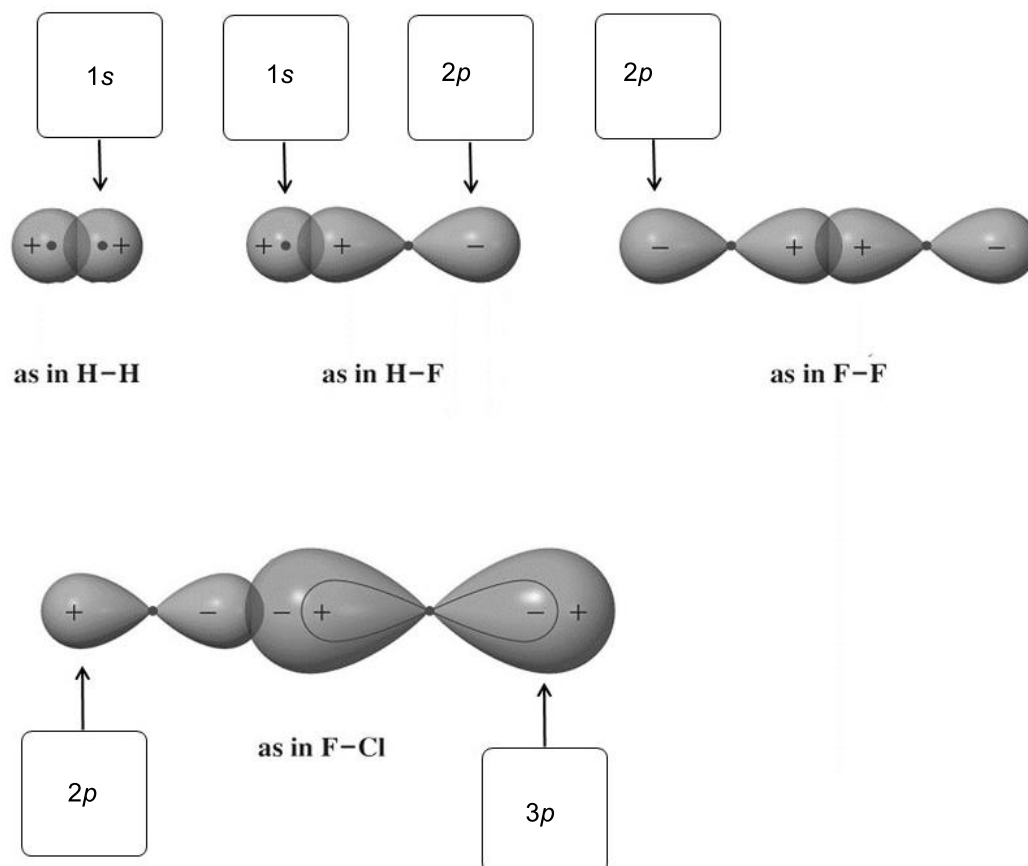
III.   [20 Points]

Table 2.2   Relative Acidities of Common Compounds (25°C)
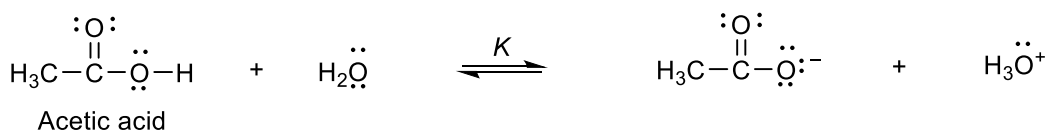
Acid	K_a	pK_a
Hydrogen iodide, HI (strongest acid)	$\sim 1.0 \times 10^{10}$	-10.0
Hydrogen bromide, HBr	$\sim 1.0 \times 10^{9}$	-9.0
Hydrogen chloride, HCl	$\sim 1.0 \times 10^{8}$	-8.0
Sulfuric acid, H_2SO_4	$\sim 1.0 \times 10^{3}$	-3.0^a
Hydronium ion, H_3O^+	50	-1.7
Nitric acid, HNO_3	25	-1.4
Methanesulfonic acid, CH_3SO_3H	16	-1.2
Hydrogen fluoride, HF	6.3×10^{-4}	3.2
Acetic acid, CH_3COOH	2.0×10^{-5}	4.7
Hydrogen cyanide, HCN	6.3×10^{-10}	9.2
Ammonium ion, NH_4^+	5.7×10^{-10}	9.3
Methanethiol, CH_3SH	1.0×10^{-10}	10.0
Methanol, CH_3OH	3.2×10^{-16}	15.5
Water, H_2O	2.0×10^{-16}	15.7
Ethyne, $HC\equiv CH$ or $RC\equiv CH$	$\sim 1.0 \times 10^{-25}$	~ 25
Ammonia, NH_3	1.0×10^{-35}	35
Ethene, $H_2C=CH_2$	$\sim 1.0 \times 10^{-44}$	~ 44
Methane, CH_4 (weakest acid)	$\sim 1.0 \times 10^{-50}$	~ 50

Note: $K_a = [H_3O^+][A^-]/[HA]$ mol L^{-1}.

[a]First dissociation equilibrium

Using the data in the Table above, circle "left" or "right" to indicate the position of the following acid-base equilibria and give the approximate equilibrium constants (namely in the form of 10^x) in the respective boxes provided.
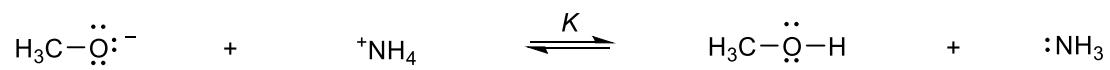
a.

$$H_3C-\overset{\overset{\textstyle :O:}{\|}}{C}-\overset{..}{\underset{..}{O}}-H \quad + \quad H_2\overset{..}{\underset{..}{O}} \quad \underset{\longleftarrow}{\overset{K}{\longrightarrow}} \quad H_3C-\overset{\overset{\textstyle :O:}{\|}}{C}-\overset{..}{\underset{..}{O}}:^- \quad + \quad H_3\overset{..}{O}^+$$

Acetic acid

Equilibrium lies to the: (left)

right

$K \approx$ $\boxed{10^{-6.4}}$

b.

$$H_3C-\overset{..}{\underset{..}{O}}:^{-} \quad + \quad ^{+}NH_4 \quad \overset{K}{\rightleftharpoons} \quad H_3C-\overset{..}{\underset{.}{O}}-H \quad + \quad :NH_3$$
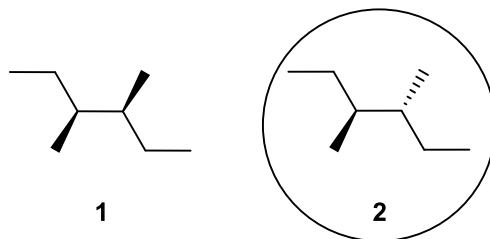
Equilibrium lies to the: left

(right)

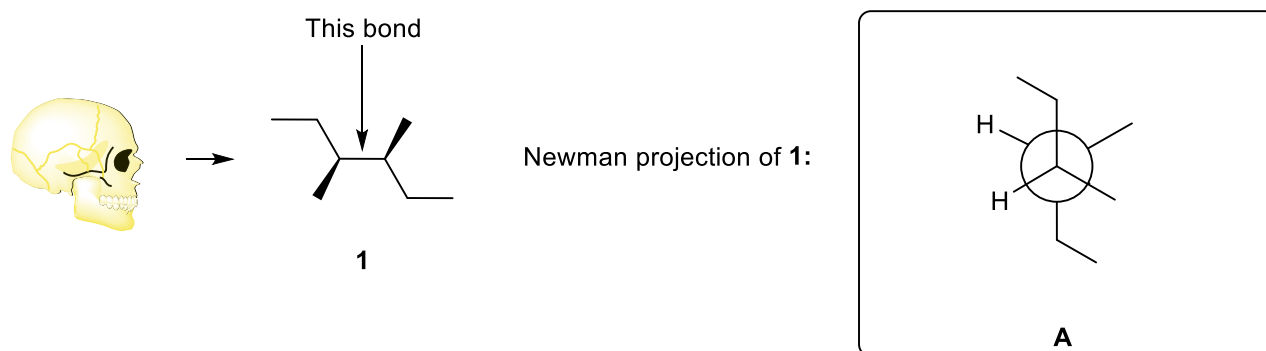$K \approx$ $\boxed{10^{6.2}}$

IV.   [36 Points]   Consider the two diastereomers of 2,3-dimethylhexane, **1** and **2**, shown below.
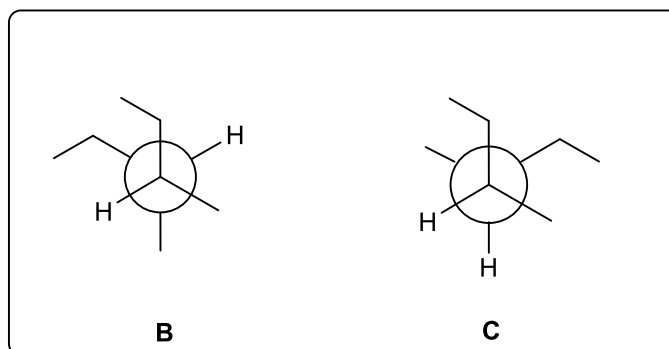
1   **2**

a. One of them has a meso structure. Circle which one.

b. Draw the Newman projection **A** of **1** along the view depicted by the skull below by completing the Newman stencil in the box provided.
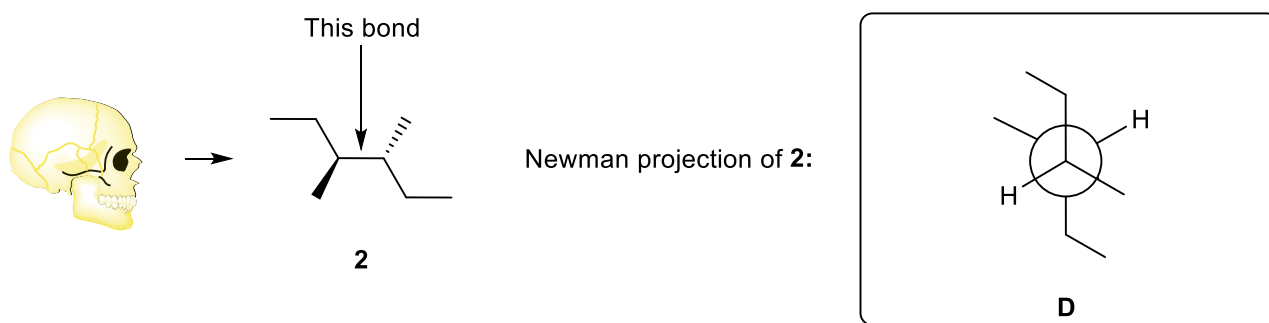
This bond

1

Newman projection of **1**:

A

c. Draw the Newman projections **B** and **C** arising from the **clockwise** rotation of the back carbon by successive 120°.
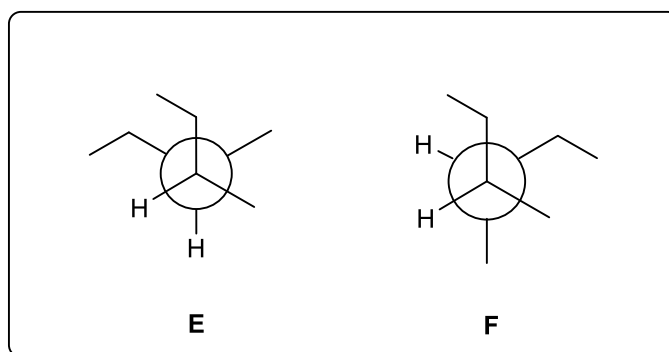
B   **C**

d. Which one of these staggered rotamers would you consider to be the **most** hindered and therefore of highest energy? Circle your answer below.

A   B   C

e. Draw the Newman projection **D** of **2** along the view depicted by the skull below by completing the Newman stencil in the box provided.

This bond

2

Newman projection of **2**:

D

f. Draw the Newman projections **E** and **F** arising from the **clockwise** rotation of the back carbon by successive 120°.

E   **F**

g. Which one of these staggered rotamers would you consider to be the **least** hindered and therefore of lowest energy? Circle your answer below.

D   E   F

V.   [28 Points]

Table **3.1**   Bond-Dissociation Energies of Various A–B Bonds in the Gas Phase [$DH°$ in kcal mol^{-1} (kJ mol^{-1})]

A in A–B	**B in A–B**						
	–H	**–F**	**–Cl**	**–Br**	**–I**	**–OH**	**–NH$_2$**
H—	104 (435)	136 (569)	103 (431)	87 (364)	71 (297)	119 (498)	108 (452)
CH$_3$—	105 (439)	110 (460)	85 (356)	70 (293)	57 (238)	93 (389)	84 (352)
CH$_3$CH$_2$—	101 (423)	111 (464)	84 (352)	70 (293)	56 (234)	94 (393)	85 (356)
CH$_3$CH$_2$CH$_2$—	101 (423)	110 (460)	85 (356)	70 (293)	56 (234)	92 (385)	84 (352)
(CH$_3$)$_2$CH—	98.5 (412)	111 (464)	84 (352)	71 (297)	56 (234)	96 (402)	86 (360)
(CH$_3$)$_3$C—	96.5 (404)	110 (460)	85 (356)	71 (297)	55 (230)	96 (402)	85 (356)

We have learned in class that the radical iodination of methane is endothermic by 13 kcal mol^{-1}. Hoping to render these thermodynamics more favorable by tackling a relatively weaker C–H bond, a researcher explored the iodination of 2-methylpropane [equation (1)].

a. Give the missing bond dissociation energies in the equation below in the three boxes provided, using the data in the Table at the top of the page.

| 96.5 | | 36 | | 55 | | 71 kcal mol^{-1} |
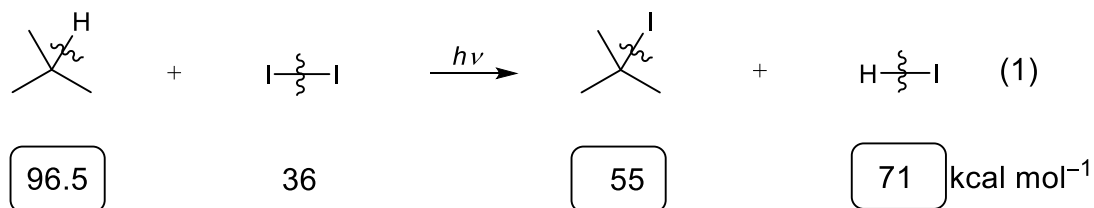
b. Calculate the $\Delta H°$ value for reaction (1). Show your work.

$\Delta H°$ (1) : $\Delta H°$ = 132.5 – 126 = +6.5 kcal mol^{-1}

c. Is the reaction (1) exothermic? Circle your answer.
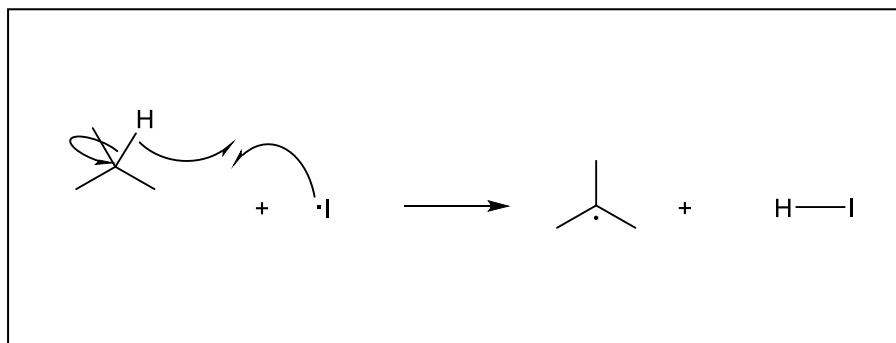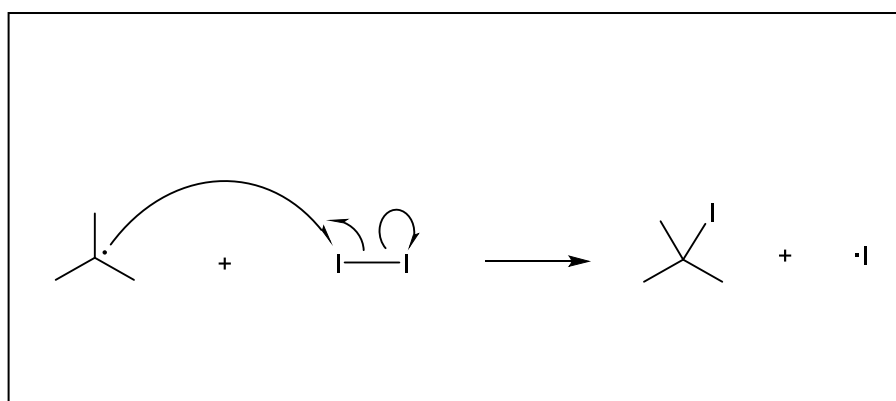
Answer: Yes   No

d.   Formulate the two propagation steps for reaction (1). Show electron-pushing fishhook arrows.

1st Propagation step:

2nd Propagation step:

e. Calculate the respective ΔH° values for the two propagation steps. Show your work.

ΔH° (1st propagation step): ΔH° = 96.5 – 71 = 25.5 kcal mol^{-1}

ΔH° (2nd propagation step): ΔH° = 36 – 55= –19 kcal mol^{-1}
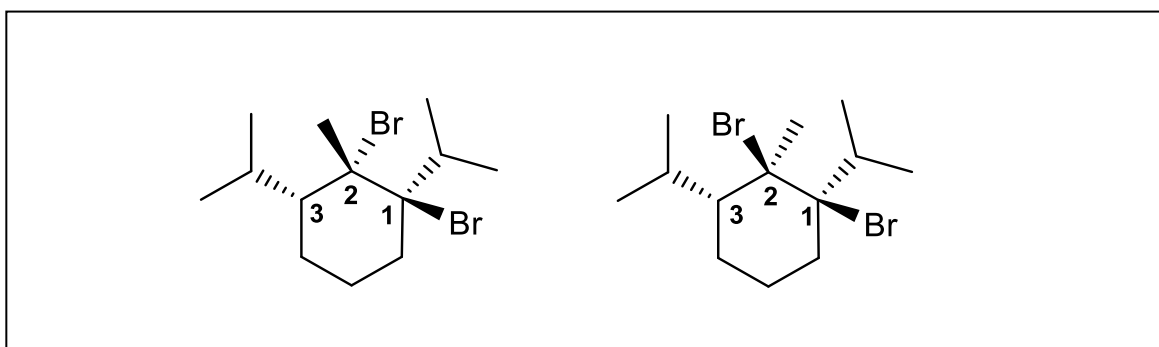
VI.   [24 Points]

a. Enantiomer **A** shown below undergoes radical bromination either at carbon 2 or at carbon 3. In the boxes and using the stencils provided, draw the respective products. Note: There may be more stencils in each box than you will need. Add the missing substituents and indicate stereochemistry clearly.
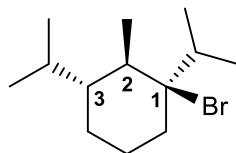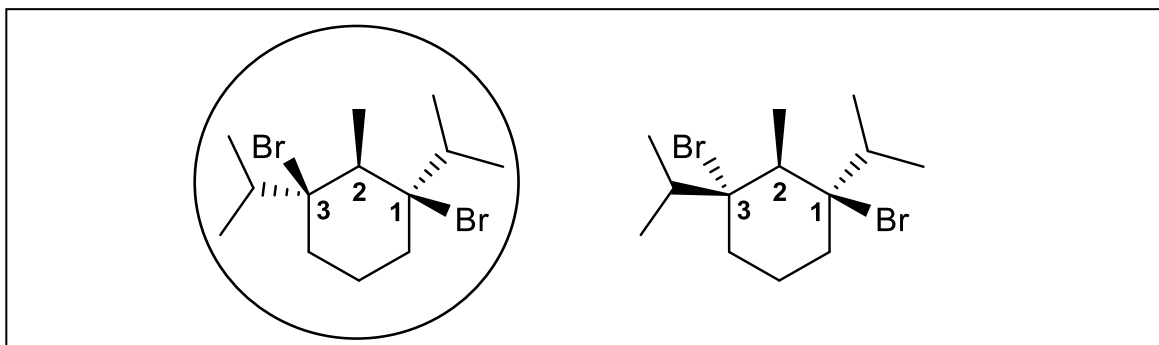

A
(this enantiomer)

Bromination at carbon 2:

Bromination at carbon 3:

b. Does the above radical bromination of **A** give any optically **inactive** products? Circle your answer.

Answer: Yes   No

If your answer is yes, circle the structures of the optically **inactive** substance(s) in your boxes above.

VII.   [22 Points]
The chlorination of hydrocarbon **1** gives products **A–F**.
a. Circle the properties written below each product molecule that are associated with it.

1   **A**   **B**   **C**

(Chiral)   (Chiral)   Chiral

Achiral   Achiral   (Achiral)

Optically   Optically   Optically
active   active   active

None are optically active, since
the starting material is achiral.

D   **E**   **F**

Chiral   (Chiral)   (Chiral)

(Achiral)   Achiral   Achiral

Optically   Optically   Optically
active   active   active

b. The selectivity for the respective hydrogens in this chlorination is tert : sec : prim = 5 : 4 : 1.
In the box below, give the expected product ratio in whole numbers (in other words, no need to normalize the ratios).

Ratio of **A : B : C : D : E : F** = 12 : 10 : 5 : 5 : 16 : 6

VIII.   [18 Points]

Table 4-3	Change in Free Energy on Flipping from the Cyclohexane Conformer with the Indicated Substituent Equatorial to the Conformer with the Substituent Axial			
Substituent	$\Delta G°$ [kcal mol^{-1} (kJ mol^{-1})]		Substituent	$\Delta G°$ [kcal mol^{-1} (kJ mol^{-1})]
H	0 (0)		F	0.25 (1.05)
CH_3	1.70 (7.11)		Cl	0.52 (2.18)
CH_3CH_2	1.75 (7.32)		Br	0.55 (2.30)
$(CH_3)_2CH$	2.20 (9.20)		I	0.46 (1.92)
$(CH_3)_3C$	≈ 5 (21)			
			HO	0.94 (3.93)
HOC (O)	1.41 (5.90)		CH_3O	0.75 (3.14)
			H_2N	1.4 (5.9)
CH_3OC (O)	1.29 (5.40)			

Note: In all examples, the more stable conformer is the one in which the substituent is equatorial.

(Increasing size) (Increasing $\Delta G°$)

Using the values in the Table above and the cyclohexane stencils provided, show the structures of the most stable conformers of **A**, **B**, and **C**. For each, place an "X" in the box next to the correct change in free energy on "ring flip". Make sure to "cap off" all axial and equatorial bonds that are explicitly shown with substituents and H atoms.
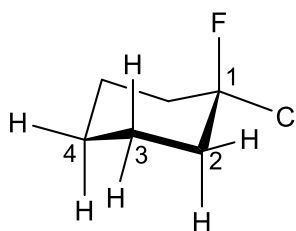
A: *cis*-1,2-Diethylcyclohexane
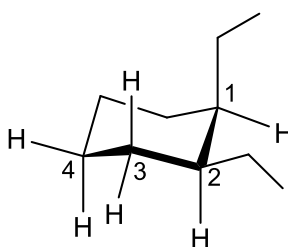
$\Delta G°$ ring flip (kcal mol^{-1})
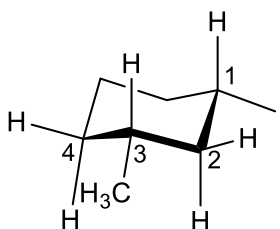
[X]	0
[ ]	+3.5
[ ]	−3.5

B: 1-Chloro-1-fluorocyclohexane

$\Delta G°$ ring flip

[ ]	−0.25
[X]	+0.27
[ ]	−0.77

C: *cis*-1-Iodo-3-methylcyclohexane

$\Delta G°$ ring flip

[X]	+2.16
[ ]	−2.16
[ ]	+1.24

IX.   [36 Points]

a. Mark the box next to your choice of a correct statement. Leave blank the boxes next to incorrect statements.

1. Acidity increases from left to right of a row in the periodic table, because steric hindrance decreases. ☐

2. Hybridization of atomic orbitals costs energy, because occupying electrons are further removed from the nucleus. ☒
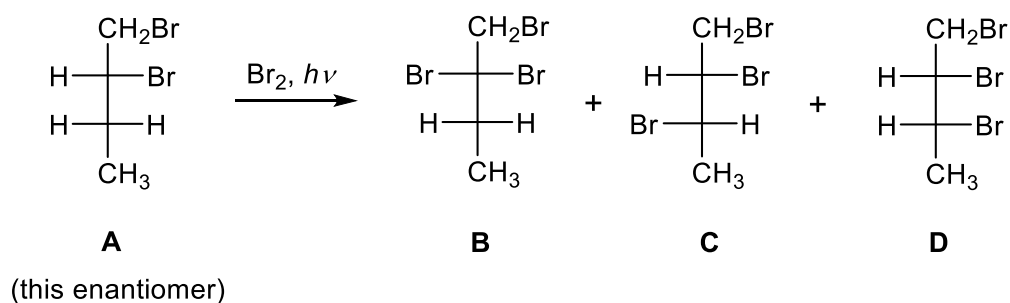
3. Bond strengths increase down a column of the periodic table. ☐

4. Acetate is less basic than methoxide, because its negative charge is delocalized. ☒

5. 2,3-Dimethylbutane is meso. ☐

6. In radical brominations, increasing the concentration of bromine will increase the rate. ☒

b. Consider the bromination of enantiomer **A** to give **B**, **C**, and **D**.

| A | B | C | D |
| (this enantiomer) | | | |

1. What is the absolute configuration of **A** (*R* or *S*)? Circle the correct answer.

Ⓡ   *S*

2. The products are formed (circle the correct answer):
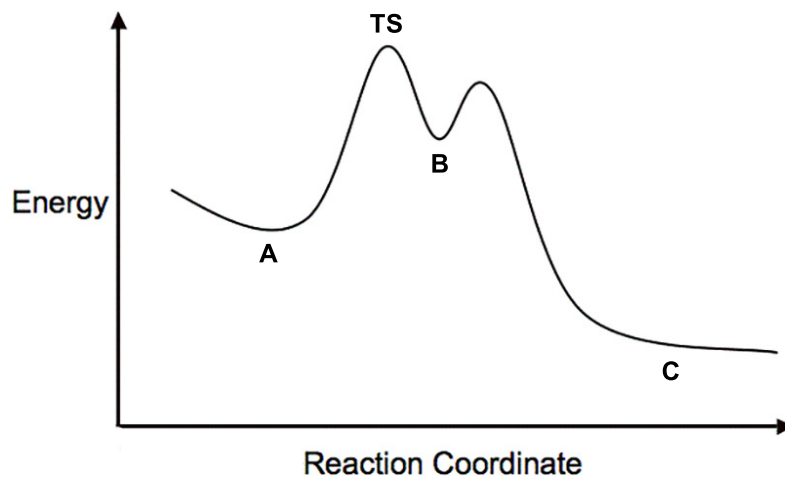
In equal amounts   (In unequal amounts)

3. The products exhibit the following properties (circle the correct answer):

All are optically active   (Two are optically inactive and a third is not)

c. The following potential-energy diagram shows the unimolecular thermal isomerization of **A** to **B** and **C**.

Reaction Coordinate

1. Label the rate determining transition state as "TS".

2. Place an "X" mark into the box next to the best statement.

☐	The rate of the reaction decreases with increasing concentration of **A**.	☒	The rate of the reaction decreases on lowering the temperature.	☐	The rate of the reaction is unaffected by increasing the concentration of **A**.

3. Place an "X" mark into the box next to the best statement.

☐	Monitoring the reaction by spectroscopy will reveal the quantitative appearance of **B**, before revealing **C**.	☒	Monitoring the reaction by spectroscopy will reveal very little of **B**, as **C** is formed.	☐	Running the reaction at low temperatures should allow the isolation of **B**.

♫ The End ♫