**EXAMINATION 1**
**Chemistry 3A**


**Name:_____Key_____**          **SID #:_____**
            Print first name before second!
            Use capital letters!


                    **GSI (if you are taking Chem 3AL): _____**

**Peter Vollhardt**
**February 22, 2018**


**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 **18** 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***!**

I.  [30 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.)
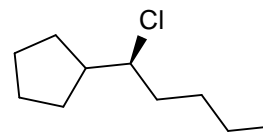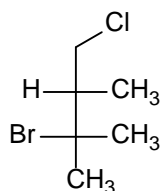
a.
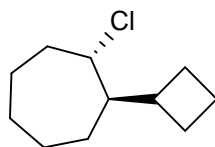


(This enantiomer)

(1*S*,2*R*)-1-Chloro-2-cyclobutylcycloheptane

b.

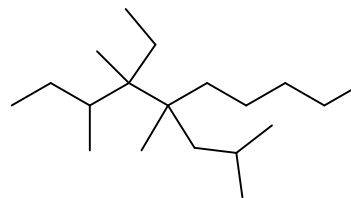(*S*)-(1-Chloropentyl)cyclopentane
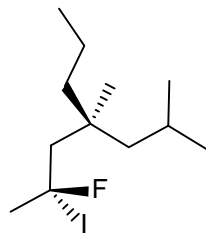


c.



(This enantiomer)

(*S*)-3-Bromo-1-chloro-2,3-dimethylbutane

d.

4-Ethyl-3,4,5-trimethyl-5-(2-methylpropyl)-decane

e.



(This enantiomer)

(2R,4S)-2-Fluoro-2-iodo-4,6-dimethyl-4-propylheptane

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

Write the best Lewis structure for each of the following molecules. **Remember to assign charges, if any, to atoms! Don't forget to draw any lone electron pairs!**
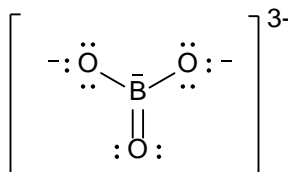
a.

$$\left[ \ :\ddot{F}\!-\!\ddot{O}\!-\!\ddot{F}: \ \right]$$
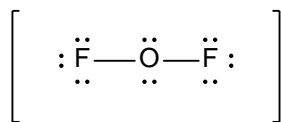
What is the geometry of FOF? Place an "x" mark into the box next to your answer.

Linear ☐

Bent ☒

b.

$$\left[ \ ^{-}:\ddot{O} \diagdown \underset{\underset{\displaystyle :\ddot{O}:}{\overset{\|}{B}}}{} \diagup \ddot{O}:^{-} \ \right]^{3-}$$

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

$$\left[ \overset{2^-}{:P} \overset{\phantom{}}{\equiv} Be \overset{\phantom{}}{-} \overset{..}{\underset{..}{S}} :^- \longleftrightarrow \overset{-}{:P} \overset{2^-}{=} Be \overset{\phantom{}}{=} \overset{..}{\underset{..}{S}} \right]^{3-}$$
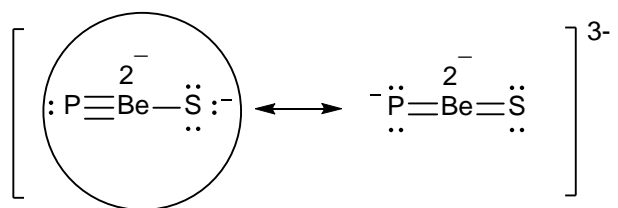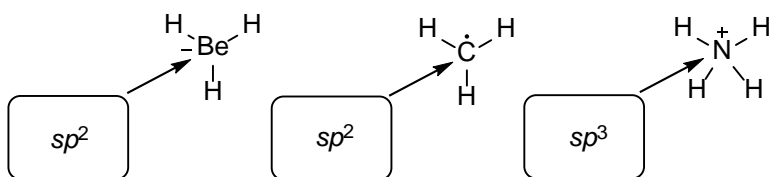
d. The following structure has three **octet** resonance forms. Circle the best one.
**Note added in grading: Because of a typo (should be "one octet resonance form", this question became intractable. Everybody got full credit on it.**
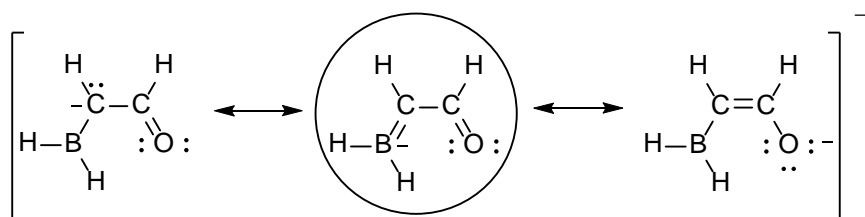
e. Enter the hybridization (*sp, sp²*, *sp³*) of the indicated atom in the box provided.

$sp^2$

$sp^2$

$sp^3$

III.   [20 Points]

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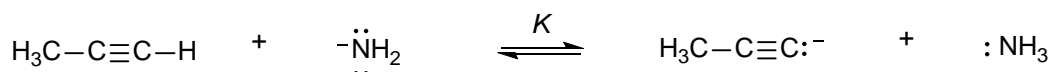
| Acid | $K_a$ | $pK_a$ |
|------|-------|--------|
| Hydrogen iodide, HI (strongest acid) | $\sim 1.0 \times 10^{10}$ | $-10.0$ |
| Hydrogen bromide, HBr | $\sim 1.0 \times 10^{9}$ | $-9.0$ |
| Hydrogen chloride, HCl | $\sim 1.0 \times 10^{8}$ | $-8.0$ |
| Sulfuric acid, $H_2SO_4$ | $\sim 1.0 \times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

Increasing acidity (upward arrow) — Increasing basicity of conjugate base (downward arrow)

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

[a]First dissociation equilibrium

Using the data in the Table above, indicate the position of the following acid-base equilibria and give the approximate equilibrium constants in the boxes provided.
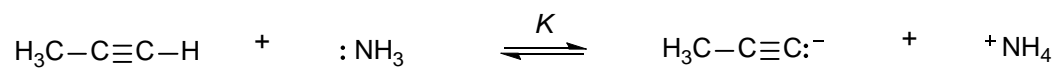
a.

$$H_3C-C{\equiv}C-H \quad + \quad {^-\ddot{N}H_2} \quad \overset{K}{\rightleftharpoons} \quad H_3C-C{\equiv}C{:}^- \quad + \quad {:}NH_3$$

Equilibrium lies to the:   left  [ ]

right  [ X ]

$K \approx$  [ $10^{10}$ ]

b.

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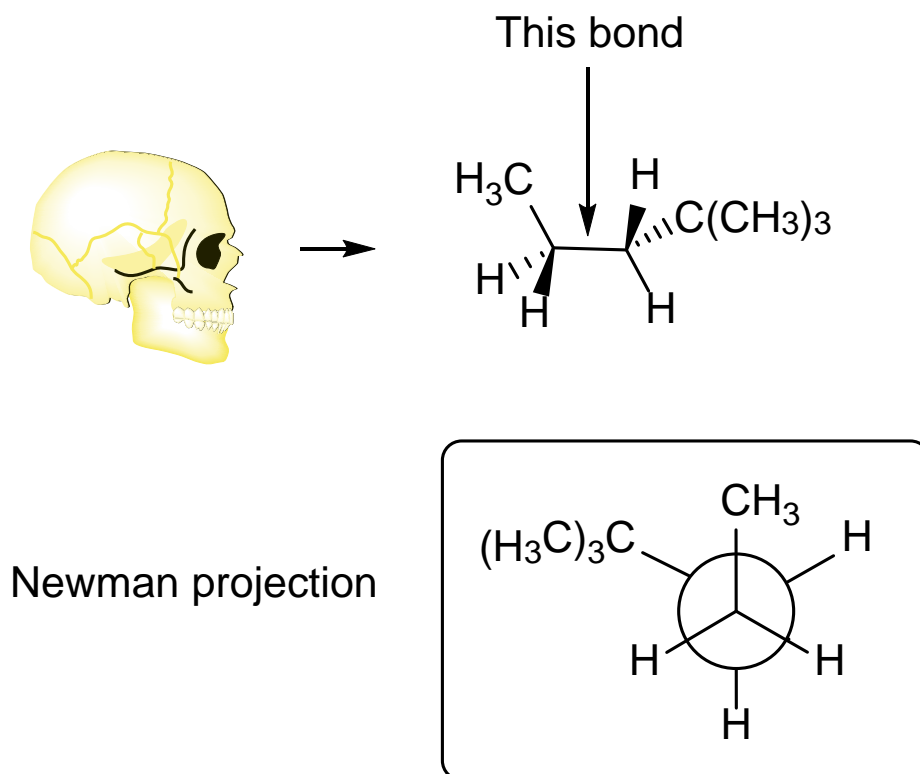
Equilibrium lies to the:  left

X

right

$K \approx$    $10^{-15}$

IV.   [20 Points]   Consider the rotation about the indicated bond in the alkane shown.

a. Complete the Newman projection along the view depicted by the skull below in the box provided. Note: You will need to supply the bonds to the back carbon (circle).

This bond

$H_3C$    H
        $C(CH_3)_3$
H
    H        H

Newman projection

$(H_3C)_3C$    $CH_3$    H

    H        H
        H

This rotamer is (circle all correct statements):

1. Staggered    2. Eclipsed    3. Equatorial    4. Gauche

5. Encumbered by transannular strain    6. Anti

b. Draw the most stable rotamer of the above molecule by completing the two stencils provided in the boxes.
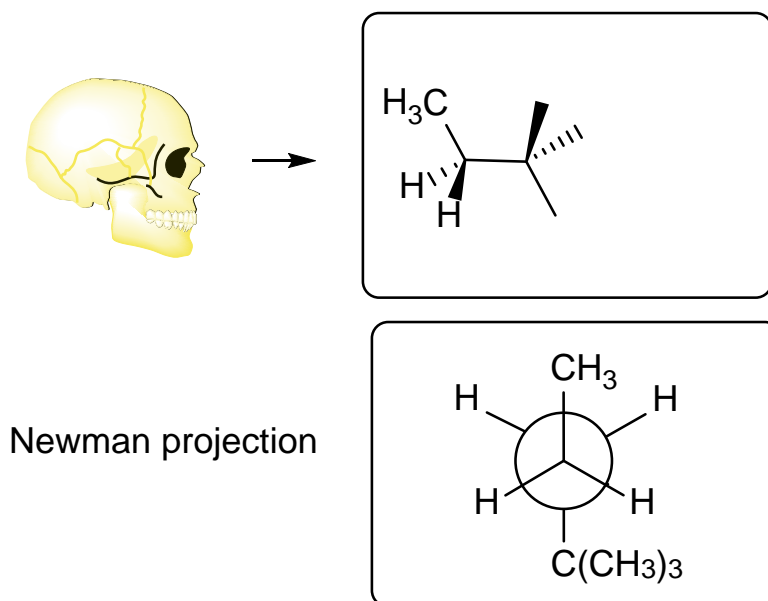


Newman projection

This rotamer is (circle all correct statements):

1. (Staggered)    2. Eclipsed    3. Equatorial    4. Gauche

5. Encumbered by transannular strain    6. (Anti)

V.     [40 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) |

A researcher wants to explore the radical amination of cyclohexane [equation (1)] using hydrazine, H$_2$N–NH$_2$, a cheap industrial chemical ($2,000/ton).
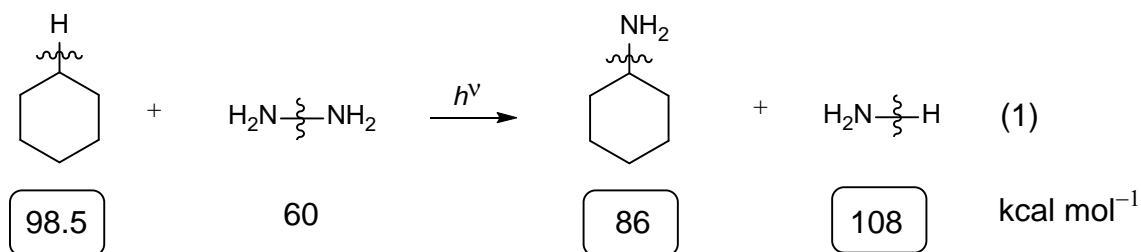


a. Give the missing bond dissociation energies in the equation above, using the data in the Table at the top of the page and the H$_2$N–NH$_2$ bond dissociation energy of 60 kcal mol$^{-1}$.

b. Calculate the $\Delta H°$ value for reaction (1). Show your work.

$\Delta H°$ (1)  :  (98.5 + 60) − (86 + 108) = −35.5 kcal mol$^{-1}$

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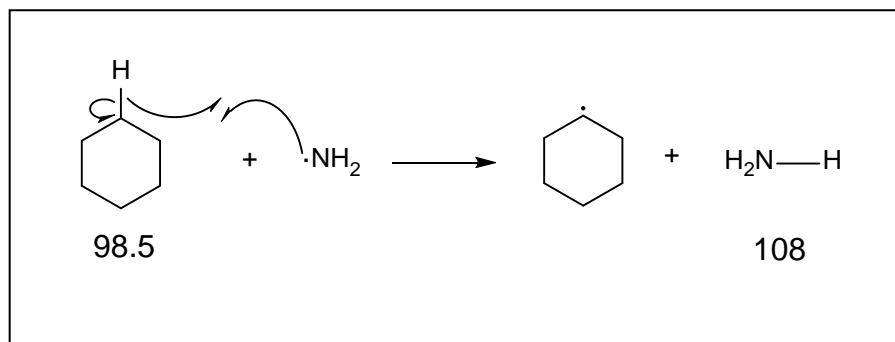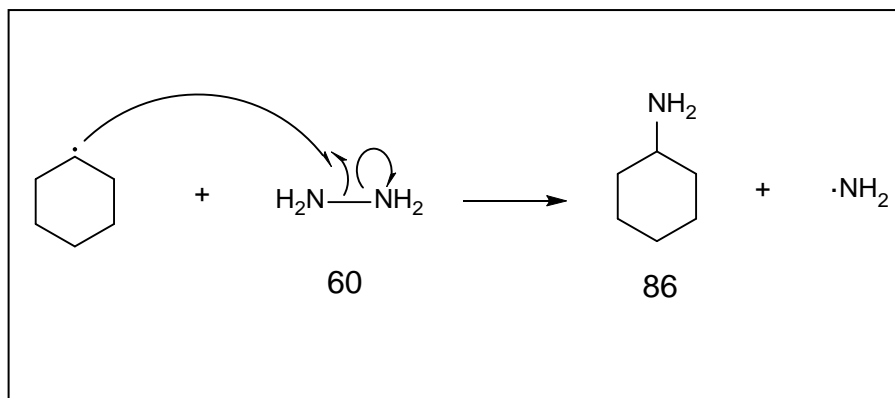
Answer:          Yes              No

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

1$^{st}$ Propagation step:

2nd Propagation step:



60

86

e. Calculate the respective $\Delta H^\circ$ values for the two propagation steps. Show your work.

$\Delta H^\circ$ (1st propagation step):  $\Delta H^\circ = 98.5 - 108 = -9.5$ kcal mol$^{-1}$

$\Delta H^\circ$ (2nd propagation step):  $\Delta H^\circ = 60 - 86 = -26$ kcal mol$^{-1}$

f. The first (and rate determining) propagation step in the radical *chlorination* of cyclohexane is less exothermic than that of the above amination. In comparison, would you expect aminations with hydrazine to be (circle your answer):

1. More selective?

2. Less selective?

VI.      [30 Points]

a. (*S*)-2-Chloro-1,1-dimethylcyclobutane shown below undergoes single chlorination at the methyl and 2-, 3-, and 4-positions. In the boxes and stencils provided, draw the respective products. Note: There are more stencils in each box than you will need. Add the missing chlorines and indicate stereochemistry clearly.
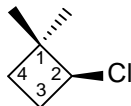


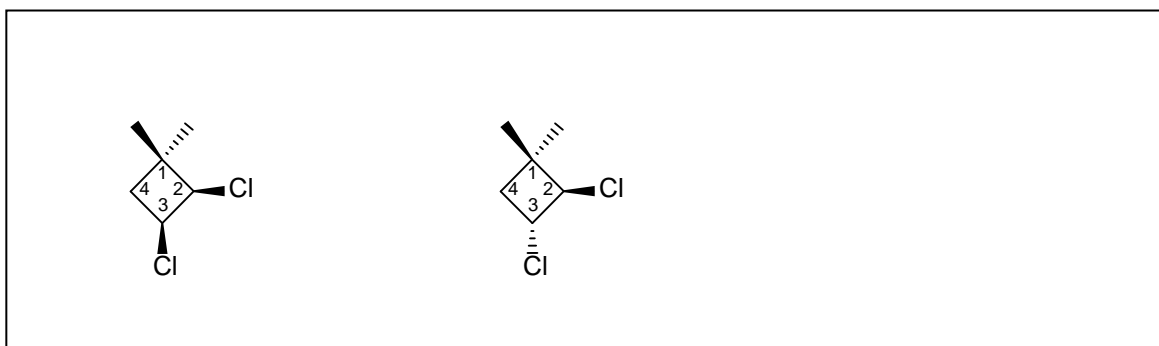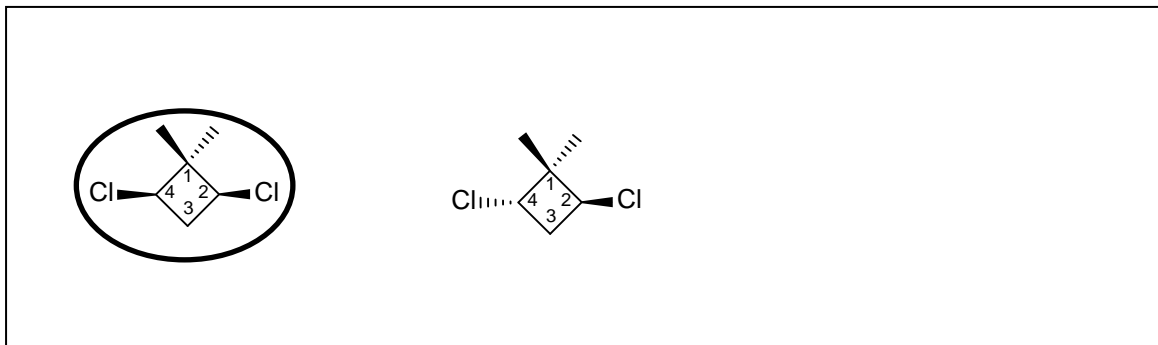(*S*)-2-Chloro-1,1-dimethylcyclobutane

Methyls:
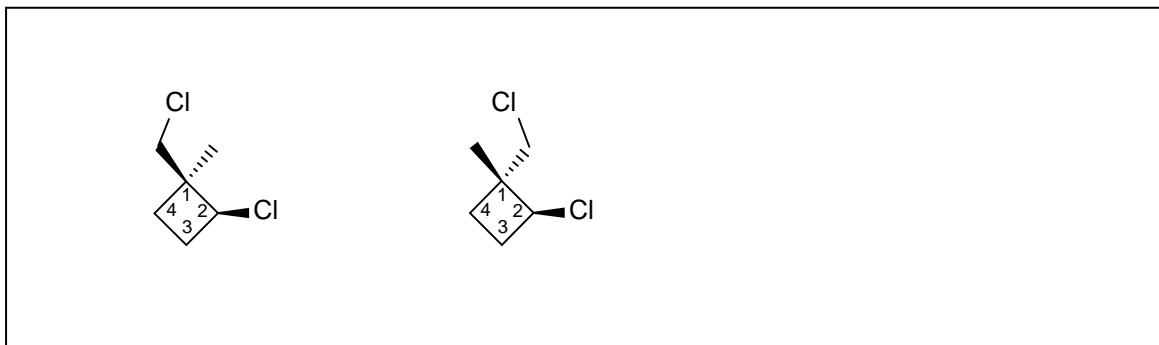


Position 2:



Position 3:

Position 4:



b. Does the above radical chlorination of (*S*)-2-chloro-1,1-dimethylcyclobutane give any optically **inactive** products? Circle your answer.
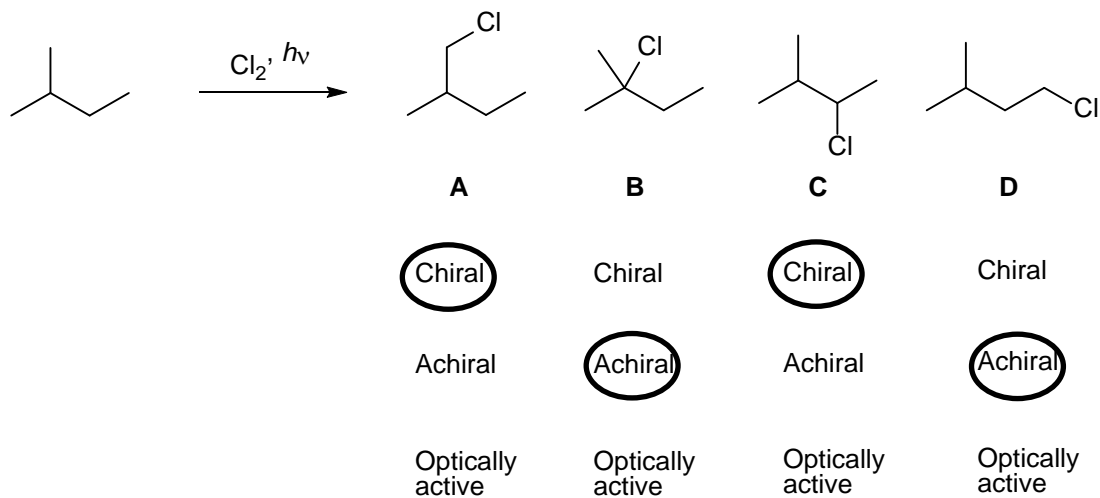
Answer:　　　　　　( Yes )　　　　　　No

If your answer is yes, circle the structures of the optically **inactive** substances in your boxes above.

VII.   [20 Points]

The chlorination of 2-methylbutane gives products **A**–**D**.

a. Circle the properties written below each product molecule that are associated with it.



|  | A | B | C | D |
|---|---|---|---|---|
| | (Chiral) | Chiral | (Chiral) | Chiral |
| | Achiral | (Achiral) | Achiral | (Achiral) |
| | Optically active | Optically active | Optically active | Optically 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.

Ratio of **A** : **B** : **C** : **D** = 6 : 5 : 8 : 3

VIII.   [15 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$\overset{O}{\overset{\|}{C}}$ | 1.41   (5.90) | HO | 0.94   (3.93) |
| | | $CH_3O$ | 0.75   (3.14) |
| | | $H_2N$ | 1.4     (5.9) |
| $CH_3O\overset{O}{\overset{\|}{C}}$ | 1.29   (5.40) | | |

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

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, calculate the change in free energy on "ring flip" to the less stable conformer. Make sure to "cap off" all axial and equatorial bonds with substituents and H atoms. Enter your calculated energy of "ring flip" (kcal mol$^{-1}$) in the box provided.
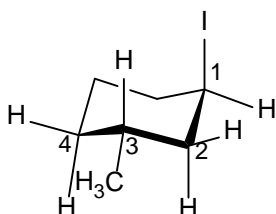
**A:** *cis*-2-Ethyl-1-methylcyclohexane
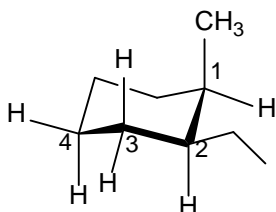
+ 0.05

**B:** 1-(1,1-Dimethylethyl)-1-methylcyclohexane
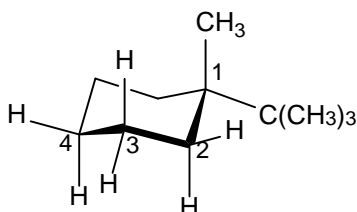
+ 3.30

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

+ 1.24

VII. [45 Points]

a. Mark the box next to your choice of an answer with an X.
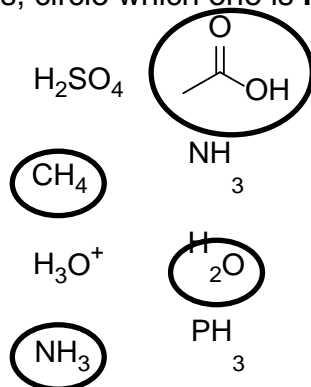Acidity increases from left to right of a row in the periodic table, because

☐      steric hindrance decreases

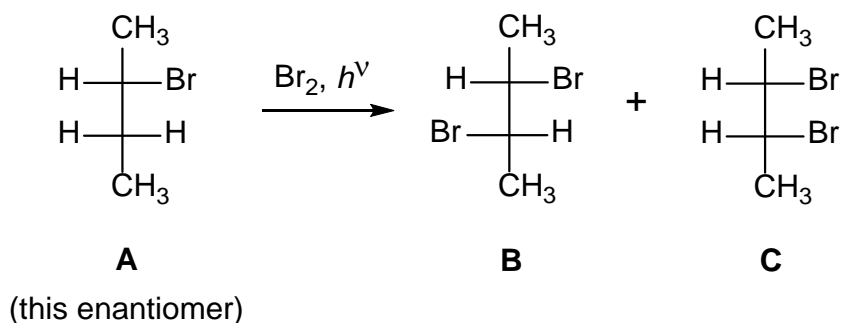☐      the product radicals increase in stability

☒      the electronegativity of deprotonated atom increases

☐      hybridization changes from $sp^3$ to $sp$

b. In the following pairs of compounds, circle which one is **less** acidic.

$H_2SO_4$    (circled: acetic acid $CH_3COOH$)

(circled) $CH_4$    $NH_3$

$H_3O^+$    (circled) $H_2O$

(circled) $NH_3$    $PH_3$

c. Consider the bromination of enantiomer **A** to give **B** and **C**.



A
(this enantiomer)

B

C

$Br_2, h^v$

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

*R*    (circled) *S*

2. The products are with respect to each other (circle the correct answer):

(circled) Diastereomers      Enantiomers      Identical      A racemate

3. The products are formed (circle the correct answer):

In equal amounts      (circled) In unequal amounts

4. The products exhibit the following properties (circle the correct answer):
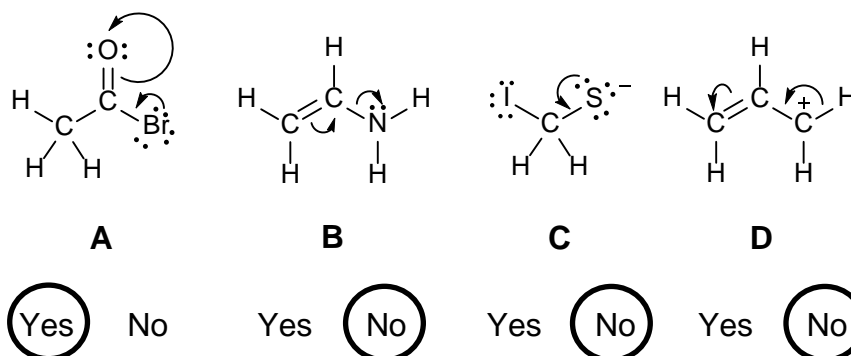
Both are optically active           Both are optically inactive
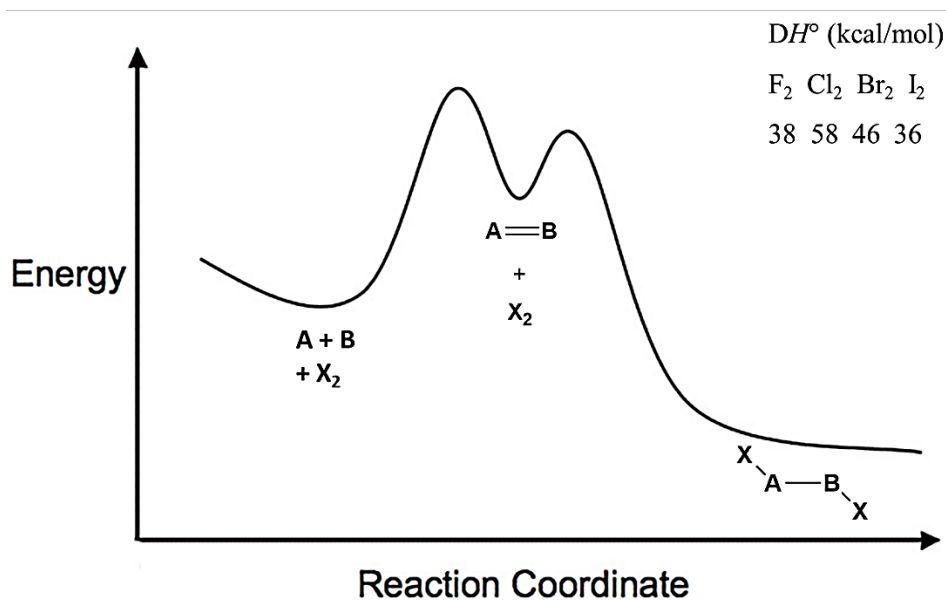
(**B** is optically active and **C** is not)           **C** is optically active and **B** is not

d. Does the arrow pushing in the following molecules **A–D** lead to an acceptable resonance form? Circle your answers.



|      A      |      B      |      C      |      D      |

(Yes)   No         Yes   (No)         Yes   (No)         Yes   (No)

e. The following potential-energy diagram shows the reaction of **A + B** in the presence of a halogen **X₂** to generate an unobserved intermediate double-bonded species **A=B**, which is trapped by the halogen to give the final product **X-A-B-X**. The profile of this transformation is the same for X = F, Cl, Br, and I.



$\Delta H°$ (kcal/mol)

$F_2$   $Cl_2$   $Br_2$   $I_2$

38   58   46   36

Energy

A=B
+
X₂

A + B
+ X₂

X
A—B
X

Reaction Coordinate

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

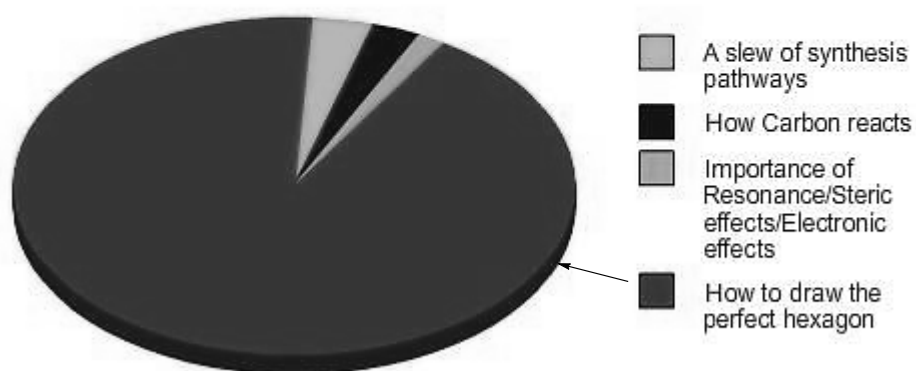☐ The rate of the reaction □ increases when changing **X** from **Cl** to **Br**.

☐ The rate of the reaction □ decreases when changing **X** from **Cl** to **Br**.

[X] The rate of the reaction □ is unaffected when changing **X** from **Cl** to **Br**.

2. The reaction of **A** with **B** follows second order kinetics. If you double the concentration of **A** and simultaneously double the concentration of **B** what would be the effect on the rate of the reaction? Place an "X" mark in the appropriate box.

| | No effect | | The rate doubles | X | The rate fourfolds | | The rate diminishes |

## Things learned in Organic Chemistry



- A slew of synthesis pathways
- How Carbon reacts
- Importance of Resonance/Steric effects/Electronic effects
- How to draw the perfect hexagon

♫ The End ♫