

**Problem Set #3**

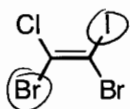
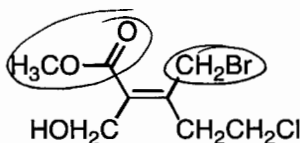
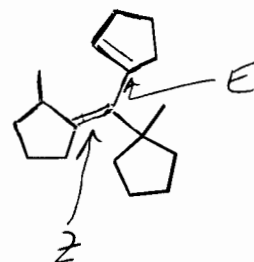
Due: March 3, 4:00 pm

1. Calculate the degree of unsaturation for
- $C_8H_{10}F_3NO$
- .

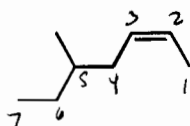
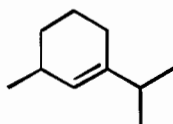
If fully saturated:  $C_8H_{18}$ 

$$18H - (10H + 3 \overset{(F)}{-1} - 1 \overset{(N)}{+1}) = \frac{6H}{2} = 3H_2 = \boxed{3}$$

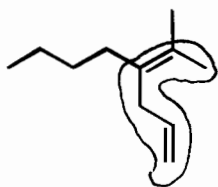
2. Assign
- E-Z*
- configuration to each alkene.

*E**Z**Z*

3. Name the following alkenes.

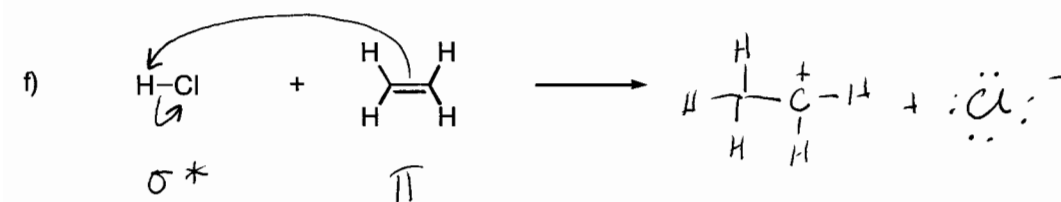
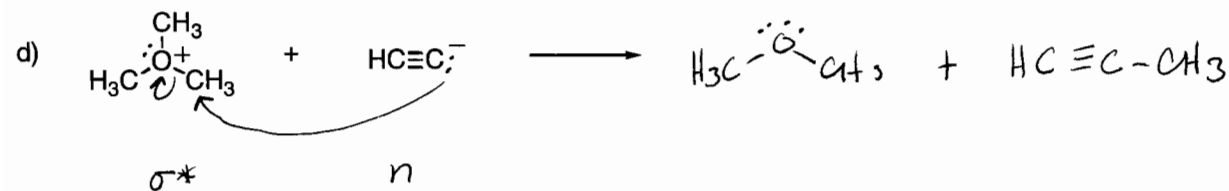
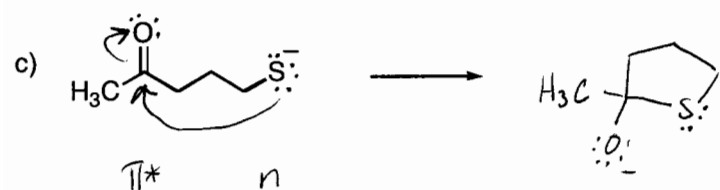
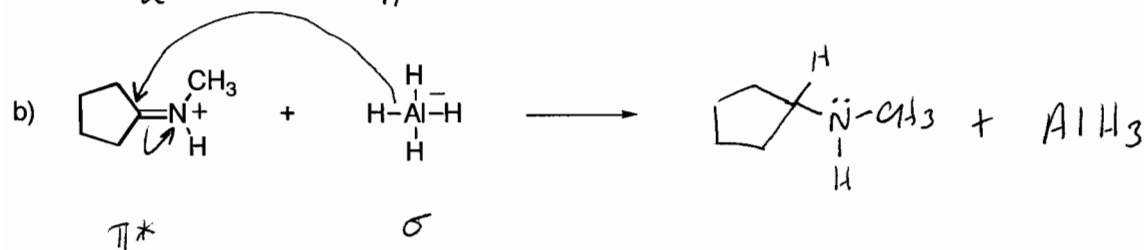
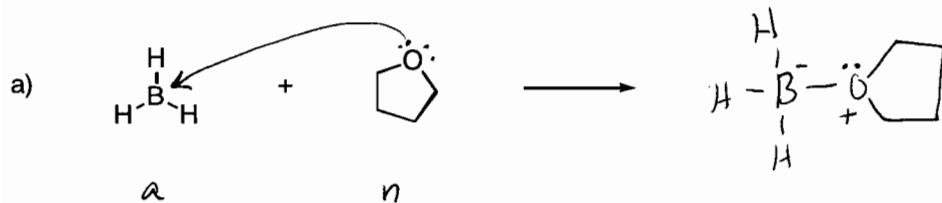
*cis*-5-methyl-2-heptene

1-isopropyl-3-methylcyclohexene

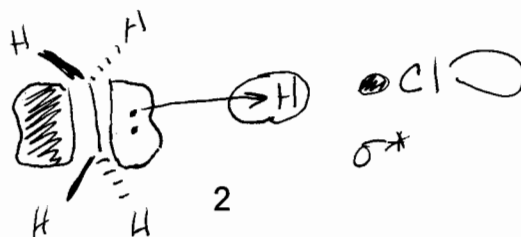


4-butyl-5-methyl-1,4-hexadiene

4. For each of the following reactions, label the type of nucleophile: lone pair (n), pi bond ( $\pi$ ), sigma bond ( $\sigma$ ), and the type of electrophile: empty atomic orbital (a), polarized pi bond ( $\pi^*$ ), polarized sigma bond ( $\sigma^*$ ). Draw in all lone pairs and use curved arrows to show how the nucleophile attacks the electrophile and show the product of these one-step reactions.

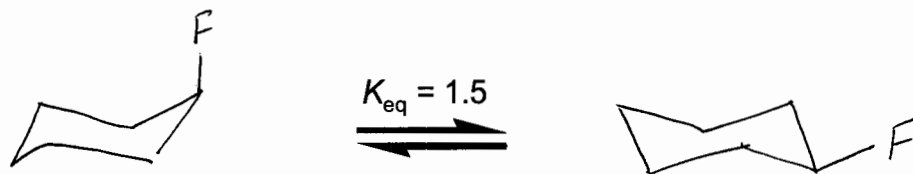


g) Show the initial orbital overlap for reaction f.



5. The equilibrium constant for the ring-inversion of fluorocyclohexane is 1.5 at 25 °C. Calculate the fraction of the axial conformer at this temperature.

a) Draw fluorocyclohexane and its ring-flipped conformer.



b) Write the equilibrium equation.

$$K_{eq} = \frac{[\text{equatorial}]}{[\text{axial}]}$$

c) Solve for the percentage of axial conformer at equilibrium.

$$\% \text{ axial} = \frac{[\text{axial}]}{[\text{axial}] + [\text{equatorial}]}$$

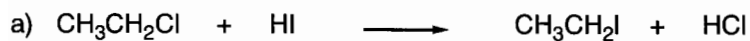
$$= \frac{[\text{axial}]}{[\text{axial}] + K_{eq}[\text{axial}]}$$

$$= \frac{[\text{axial}]}{[\text{axial}](1 + K_{eq})}$$

$$= \frac{1}{1 + K_{eq}} = \frac{1}{1 + 1.5} = \frac{1}{2.5} = \boxed{40\%}$$

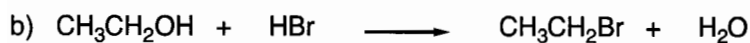
$$[\text{equatorial}] = K_{eq}[\text{axial}]$$

6. Calculate  $\Delta H$  for each of the following reactions. (See the table at the end of this problem set).



| <u>Bonds Broken</u>                | <u>kcal/mol</u> | <u>Bonds Formed</u>               | <u>kcal/mol</u> |
|------------------------------------|-----------------|-----------------------------------|-----------------|
| $\text{CH}_3\text{CH}_2-\text{Cl}$ | 81.5            | $\text{CH}_3\text{CH}_2-\text{I}$ | 53.5            |
| $\text{H}-\text{I}$                | <u>71.3</u>     | $\text{H}-\text{Cl}$              | <u>163.0</u>    |
|                                    | 152.8           |                                   | 156.5 kcal/mol  |

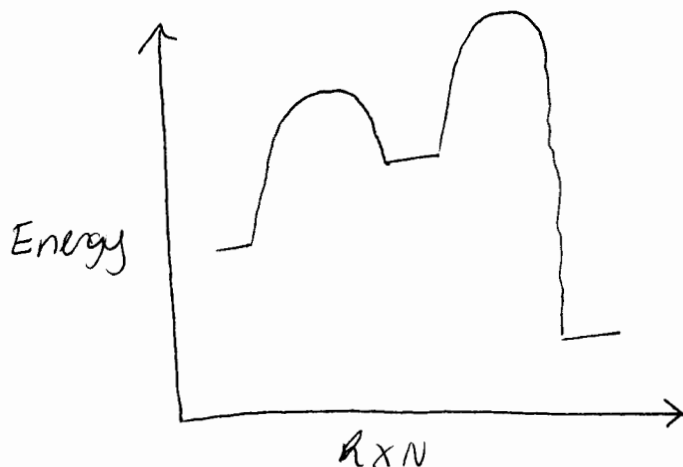
$$\Delta H = 152.8 - 156.5 = -3.7 \text{ kcal/mol}$$



| <u>Bonds Broken</u>                | <u>kcal/mol</u> | <u>Bonds Formed</u>                | <u>kcal/mol</u> |
|------------------------------------|-----------------|------------------------------------|-----------------|
| $\text{CH}_3\text{CH}_2-\text{OH}$ | 91.5            | $\text{CH}_3\text{CH}_2-\text{Br}$ | 69              |
| $\text{H}-\text{Br}$               | <u>87.5</u>     | $\text{H}-\text{OH}$               | <u>119</u>      |
|                                    | 179             |                                    | 188             |

$$\Delta H = 179 - 188 = -9.0 \text{ kcal/mol}$$

7. a) Draw an energy diagram for a two-step reaction passing through an intermediate that is less stable than both the starting material and the product, where the product is more stable than the starting material and the activation energy for proceeding from the intermediate to the product is higher than that for proceeding from the intermediate to the starting material.



b) Which species does the first transition state resemble more closely (circle one)

starting material

intermediate

c) Which species does the second transition state resemble more closely (circle one)

product

intermediate

d) Which transition state is involved in the rate determining step of the overall reaction (circle one)?

first

second

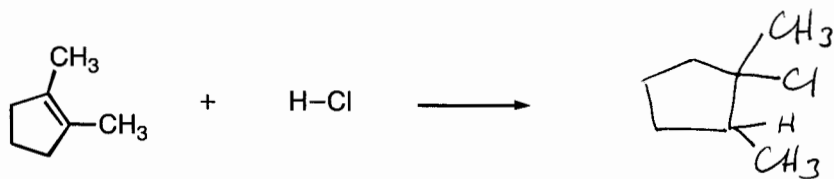
e) The reaction is: exergonic endergonic

f)  $\Delta G$  is: positive negative

g)  $K_{eq}$  is:  $>1$   $<1$  0

8. Consider the following reaction.

a) Show the product (ignore stereochemistry).

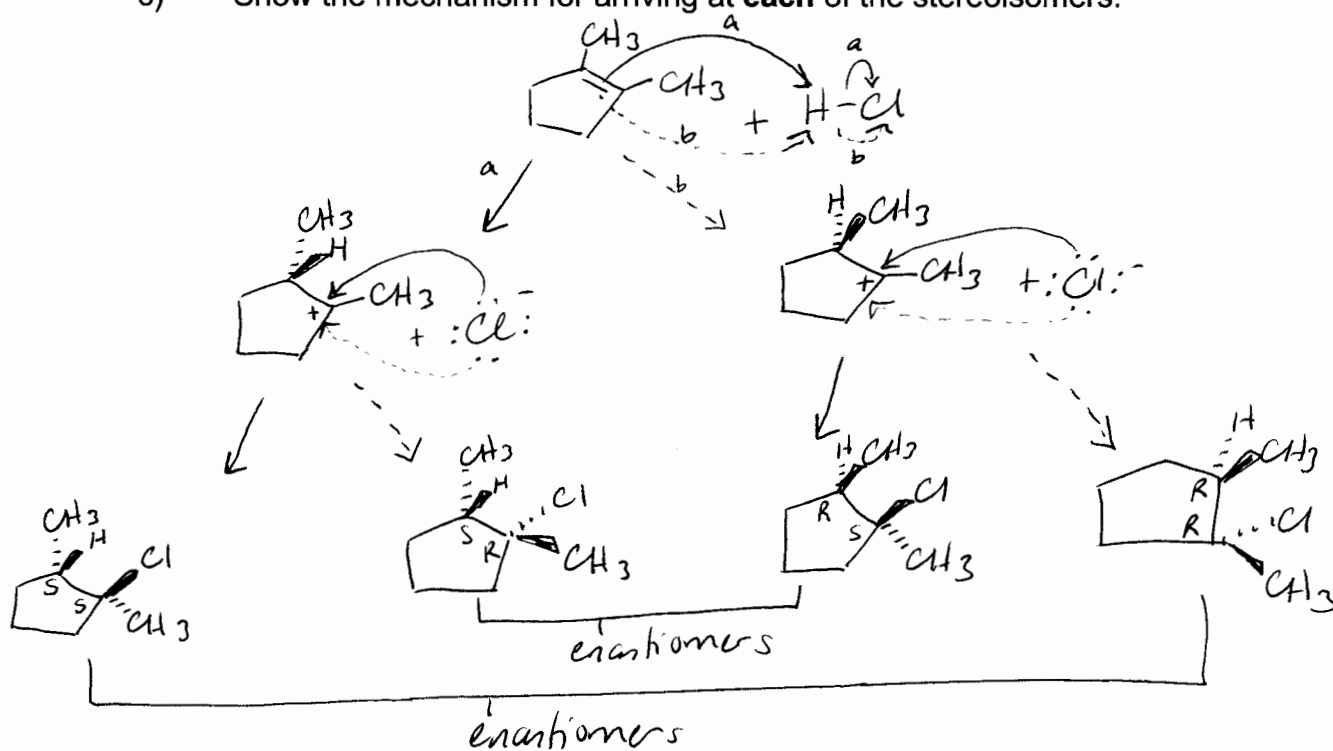


b) How many stereoisomers will form during this reaction?

2 chirality centers

$2^2 = 4$  stereoisomers

c) Show the mechanism for arriving at **each** of the stereoisomers.

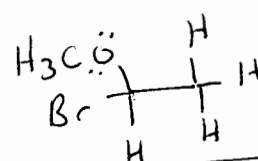
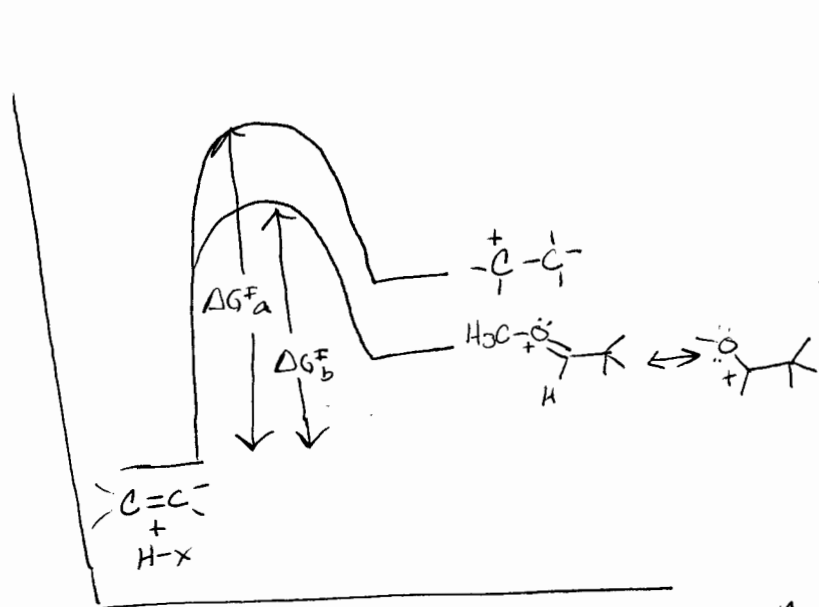
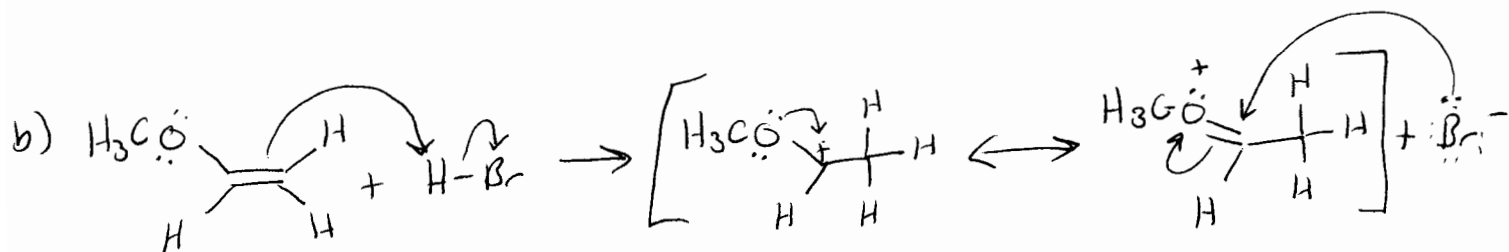
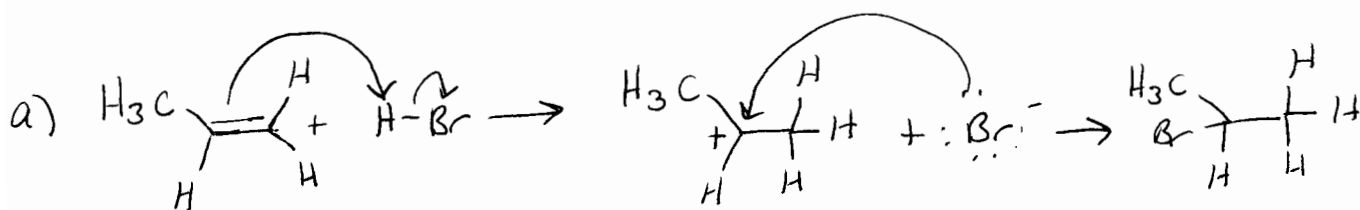
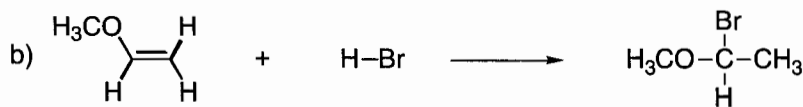
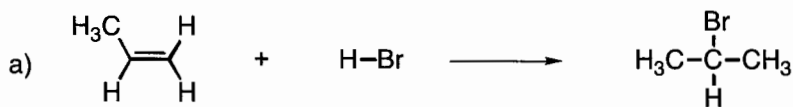


+ 4 sets of diastereomers

d) Label the relationships between the stereoisomers.

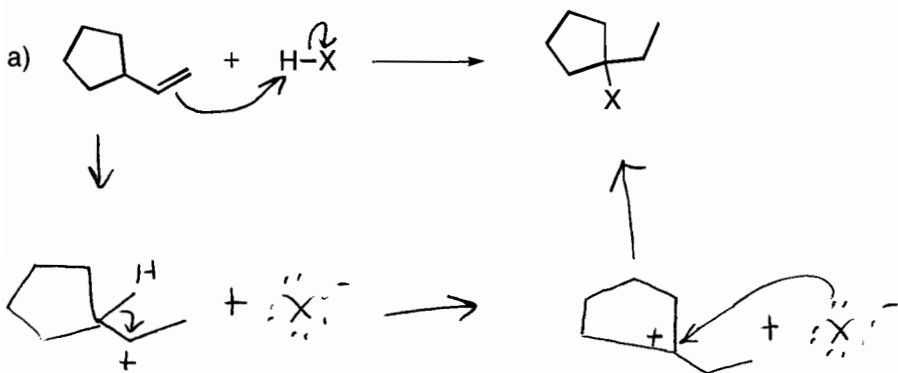
e) The products are (circle one): optically active or optically inactive

9. Reaction **b** proceeds  $2.5 \times 10^8$  times faster than reaction **a**. Explain with mechanisms and reaction coordinate diagrams.

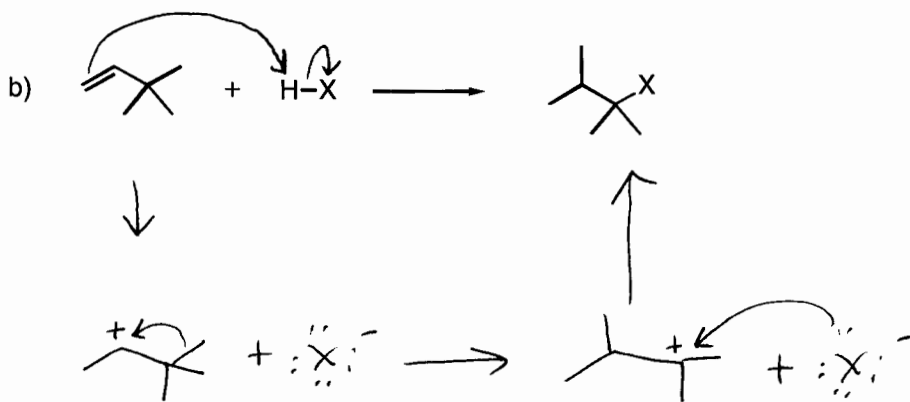


The intermediate of reaction **b** is resonance stabilized, + lower in energy than the intermediate of reaction **a**. Formation of the intermediate is an endothermic process. Thus, the structure of the  $TS^\ddagger$  resembles the structure of the intermediate. Because the intermediate of **b** is lower in energy than **a**, the transition state of **b** is also lower in energy. Therefore, reaction **b** has a smaller  $\Delta G^\ddagger$  + occurs faster.

10. Show the mechanism for each reaction.

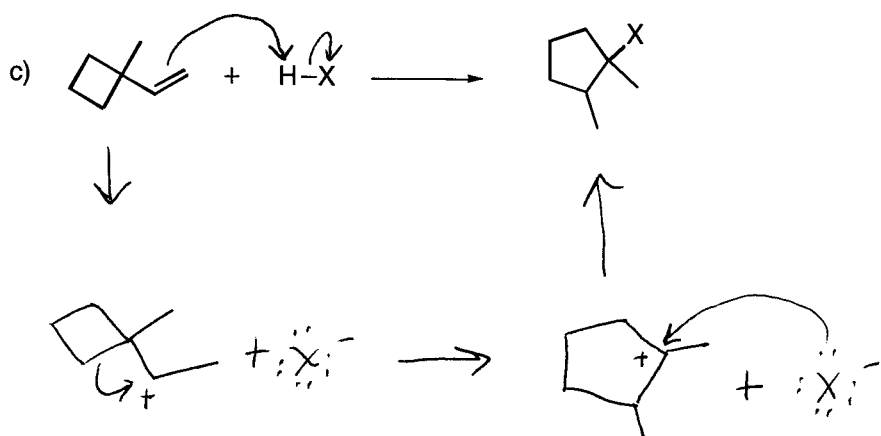


hydride shift:  $2^\circ$  to  $3^\circ$  carbocation

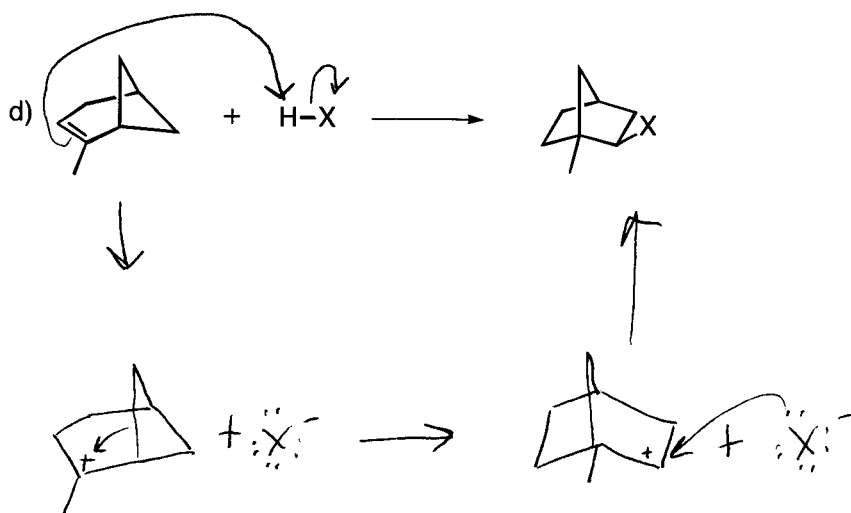


methyl shift:  $2^\circ$  to  $3^\circ$  carbocation





ring expansion 4 (strained) to 5 carbon ring



4 (strained) to 5 carbon ring expansion

From: Mechanism + Theory in Organic Chemistry 3rd ed  
 Thomas H. Lowry & Kathleen S. Richardson  
 1987, Harper Collins Publishers

**Table 2.8** BOND DISSOCIATION ENERGIES AND AVERAGE BOND ENERGIES FOR VARIOUS TYPES OF BONDS

Bond Dissociation Energies<sup>a,b</sup>—Single Bonds: Diatomic Molecules

| Bond  | Energy        | Bond  | Energy   | Bond | Energy                   |
|-------|---------------|-------|----------|------|--------------------------|
| H—H   | 104.2 [436.0] | F—Cl  | 61 [255] | H—F  | 135.8 <sup>c</sup> [568] |
| D—D   | 106.0 [444.5] | F—Br  | 60 [251] | H—Cl | 103.0 <sup>c</sup> [431] |
| F—F   | 38 [159]      | F—I   | 58 [243] | H—Br | 87.5 <sup>c</sup> [366]  |
| Cl—Cl | 58 [243]      | Cl—Br | 52 [218] | H—I  | 71.3 <sup>c</sup> [298]  |
| Br—Br | 46.0 [192]    | Cl—I  | 50 [209] |      |                          |
| I—I   | 36.1 [151]    |       |          |      |                          |

Polyatomic Molecules

| Bond   | Energy     | Bond   | Energy     |
|--|------------|--|------------|
| H—CH <sub>3</sub>                                | 104 [435]  | CH <sub>3</sub> CH <sub>2</sub> —CHCH <sub>2</sub>             | 89 [372]   |
| H—CH <sub>2</sub> CH <sub>3</sub>                | 98 [410]   | CH <sub>3</sub> CH <sub>2</sub> —C <sub>6</sub> H <sub>5</sub> | 90 [377]   |
| H—CHCH <sub>2</sub>                              | 103 [431]  | CH <sub>2</sub> CH—CHCH <sub>2</sub>                           | 100 [418]  |
| H—C <sub>6</sub> H <sub>5</sub>                  | 103 [431]  | HCC—CCH  | 150 [628]  |
| H—CCH  | ~125 [523] | C <sub>6</sub> H <sub>5</sub> —C <sub>6</sub> H <sub>5</sub>   | 100 [418]  |
| H—CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>  | 85 [356]   | CH <sub>2</sub> CH—C <sub>6</sub> H <sub>5</sub>               | 99 [414]   |
| H—CH <sub>2</sub> CHCH <sub>2</sub>              | 85 [356]   |  |            |
| H—CH <sub>2</sub> OH                             | 93 [389]   | CH <sub>3</sub> —COCH <sub>3</sub>                             | 82 [343]   |
| H—CF <sub>3</sub>                                | 104 [435]  | CH <sub>3</sub> CH <sub>2</sub> —COCH <sub>3</sub>             | 79 [331]   |
| H—CCl  | 96 [401]   | CH <sub>3</sub> —CN  | 122 [510]  |
| H—COCH <sub>3</sub>                              | 87.5 [366] | CH <sub>2</sub> CH—COCH <sub>3</sub>                           | 89 [372]   |
| H—CN   | 130 [543]  | CH <sub>2</sub> CH—CN  | 128 [536]  |
|  |            | CH <sub>3</sub> CO—COCH <sub>3</sub>                           | 83 [347]   |
| F—CH <sub>3</sub>                                | 108 [451]  | NC—CN  | 144 [602]  |
| Cl—CH <sub>3</sub>                               | 83.5 [349] | CF <sub>3</sub> —CF <sub>3</sub>                               | 97 [406]   |
| Br—CH <sub>3</sub>                               | 70 [293]   | H—OH   | 119 [498]  |
| I—CH <sub>3</sub>                                | 56 [234]   | H—O <sub>2</sub> H   | 90 [377]   |
| F—CH <sub>2</sub> CH <sub>3</sub>                | 106 [443]  | H—SH   | 90 [377]   |
| Cl—CH <sub>2</sub> CH <sub>3</sub>               | 81.5 [341] | H—OCH <sub>3</sub>   | 102 [427]  |
| Br—CH <sub>2</sub> CH <sub>3</sub>               | 69 [289]   | H—OC <sub>6</sub> H <sub>5</sub>                               | 85 [356]   |
| I—CH <sub>2</sub> CH <sub>3</sub>                | 53.5 [224] | H—O <sub>2</sub> CCH <sub>3</sub>                              | 112 [469]  |
| Cl—CHCH <sub>2</sub>                             | 84 [351]   |  |            |
| F—C <sub>6</sub> H <sub>5</sub>                  | 116 [485]  | HO—CH <sub>3</sub>   | 91.5 [383] |
| Br—C <sub>6</sub> H <sub>5</sub>                 | 72 [301]   | HO—CH <sub>2</sub> CH <sub>3</sub>                             | 91.5 [383] |
| I—C <sub>6</sub> H <sub>5</sub>                  | 65 [272]   | HO—C <sub>6</sub> H <sub>5</sub>                               | 103 [431]  |
| F—CF <sub>3</sub>                                | 129 [540]  | HO—COCH <sub>3</sub>   | 109 [456]  |
| Cl—CF <sub>3</sub>                               | 85 [356]   |  |            |
| Br—CF <sub>3</sub>                               | 70 [293]   | CH <sub>3</sub> O—CH <sub>3</sub>                              | 80 [335]   |
| I—CF <sub>3</sub>                                | 54 [226]   | CH <sub>3</sub> O—CH <sub>2</sub> CH <sub>3</sub>              | 80 [335]   |
| F—CCl <sub>3</sub>                               | 106 [444]  | CH <sub>3</sub> O—CHCH <sub>2</sub>                            | 87 [366]   |
| Cl—CCl <sub>3</sub>                              | 73 [305]   | CH <sub>3</sub> O—C <sub>6</sub> H <sub>5</sub>                | 91 [381]   |
| Br—CCl <sub>3</sub>                              | 54 [226]   | CH <sub>3</sub> O—COCH <sub>3</sub>                            | 97 [406]   |
| F—COCH <sub>3</sub>                              | 119 [79]   |  |            |
| Cl—COCH <sub>3</sub>                             | 83.5 [349] | HO—OH  | 51 [213]   |
| I—COCH <sub>3</sub>                              | 52.5 [220] | HO—Br  | 57 [238]   |
|  |            | CH <sub>3</sub> O—OCH <sub>3</sub>                             | 36 [151]   |
| CH <sub>3</sub> —CH <sub>3</sub>                 | 88 [368]   |  |            |
| CH <sub>3</sub> —CH <sub>2</sub> CH <sub>3</sub> | 85 [356]   | H <sub>2</sub> N—H   | 103 [431]  |
| CH <sub>3</sub> —CH <sub>2</sub> OH              | 83 [347]   | H <sub>2</sub> N—CH <sub>3</sub>                               | 79 [331]   |

Table 2.8 (Continued)

| Bond  | Energy      | Bond   | Energy      |           |           |          |          |           |
|---|-------------|--|-------------|-----------|-----------|----------|----------|-----------|
|   |             | H <sub>2</sub> N—CH <sub>2</sub> CH <sub>3</sub> | 78 [326]    |           |           |          |          |           |
|   |             | H <sub>2</sub> N—C <sub>6</sub> H <sub>5</sub>   | 91 [381]    |           |           |          |          |           |
|   |             | H <sub>2</sub> N—COCH <sub>3</sub>               | ~96 [401]   |           |           |          |          |           |
| CH <sub>3</sub> —CF <sub>3</sub>                                | 100 [418]   | O <sub>2</sub> N—NO <sub>2</sub>                 | 13.6 [57]   |           |           |          |          |           |
| CH <sub>3</sub> —CHCH <sub>2</sub>                              | 92 [385]    | O <sub>2</sub> N—COCH <sub>3</sub>               | 97 [406]    |           |           |          |          |           |
| CH <sub>3</sub> —C <sub>6</sub> H <sub>5</sub>                  | 93 [389]    |  |             |           |           |          |          |           |
| CH <sub>3</sub> —CCH  | 117 [490]   |  |             |           |           |          |          |           |
| CH <sub>3</sub> —CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>  | 72 [301]    |  |             |           |           |          |          |           |
| CH <sub>3</sub> —CH <sub>2</sub> CHCH <sub>2</sub>              | 72 [301]    |  |             |           |           |          |          |           |
| Multiple Bonds  |             |  |             |           |           |          |          |           |
| Bond  | Energy      | Bond   | Energy      |           |           |          |          |           |
| O=O   | 119 [498]   | CF <sub>2</sub> =CF <sub>2</sub>                 | 76.3 [319]  |           |           |          |          |           |
| O=CO  | 128 [536]   | CH <sub>2</sub> =NH                              | ~154 [644]  |           |           |          |          |           |
| O=CH <sub>2</sub>   | 175 [732]   | C≡O  | 257 [1075]  |           |           |          |          |           |
| O=NH  | 115 [481]   | N≡N  | 226 [946]   |           |           |          |          |           |
| HN=NH   | ~109 [456]  | N≡CH   | 224 [937]   |           |           |          |          |           |
| CH <sub>2</sub> =CH <sub>2</sub>                                | 163 [682]   | HC≡CH  | 230 [962]   |           |           |          |          |           |
| Representative Average Bond Energies <sup>d</sup> —Single Bonds |             |  |             |           |           |          |          |           |
|   | C           | N  | O           | F         | Cl        | Br       | I        | Si        |
| H   | 100 [418]   | 93 [389]   | 110 [460]   | 136 [569] | 103 [431] | 88 [368] | 71 [297] | 72 [301]  |
| C   | 81 [339]    | 69 [289]   | 84 [351]    | 105 [439] | 79 [331]  | 67 [280] | 57 [238] | 69 [289]  |
| N   |             | 38 [159]   | 43 [180]    | 65 [272]  | 48 [201]  |          |          |           |
| O   |             |  | 33 [138]    | 50 [209]  | 50 [209]  | 53 [222] | 57 [238] | 103 [430] |
| F   |             |  |             |           | 60 [251]  | 60 [251] | 67 [280] | 141 [586] |
| Cl  |             |  |             |           |           | 53 [222] | 50 [209] | 96 [402]  |
| Br  |             |  |             |           |           |          | 43 [180] | 69 [289]  |
| I   |             |  |             |           |           |          |          | 50 [209]  |
| Si  |             |  |             |           |           |          |          | 45 [188]  |
| Multiple Bonds  |             |  |             |           |           |          |          |           |
| Elements  | Single bond | Double bond                                      | Triple bond |           |           |          |          |           |
| O—O   | 33 [138]    | 96 [402]   |             |           |           |          |          |           |
| N—N   | 38 [159]    | 100 [418]  | 226 [946]   |           |           |          |          |           |
| C—C   | 81 [339]    | 148 [619]  | 194 [812]   |           |           |          |          |           |
| C—O   | 84 [351]    | 172 [720]  |             |           |           |          |          |           |
| C—N   | 69 [289]    | 148 [619]  | 213 [891]   |           |           |          |          |           |

<sup>a</sup>From Gordon, A. J.; Ford, R. A. "The Chemists Companion"; Wiley: New York, 1972. Reprinted by permission of John Wiley & Sons. Copyright 1972 John Wiley & Sons, Inc.

<sup>b</sup>In kcal mol<sup>-1</sup>. Numbers in brackets are values in kJ mol<sup>-1</sup>.

<sup>c</sup>Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502. Reprinted by permission of the Division of Chemical Education.

<sup>d</sup>From Waser, J.; Trueblood, K. N.; Knobler, C. M. "Chem One"; McGraw-Hill: New York, 1976. Adapted by permission of McGraw-Hill.

of Benson's gas phase, almost always even better

Benson's  $\Delta H_f^\circ$ 's of the ligands. For in the group notation the first and the experiment for a new contributions from (-42.17 kJ (-84.35 kJ [ $\Delta H_f^\circ = -4 -20.16 -4$  mental  $\Delta H$  and -103.1 condensed-phase hydrogen bonds are not added

Tables 9.1 for adding a carbon-carbon since all carbon refers to a carbon refers to an element X; and the abbreviation

### Guide to the

1.  $\Delta H_f^\circ$  when that gas pressure and are in calories to other ten

2. In our arbitrary values obtained

In simple  $\Delta H_f^\circ$  of the bond affect important cellular enthalpic