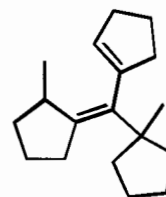
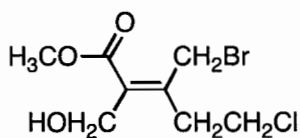
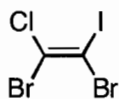


Problem Set #3

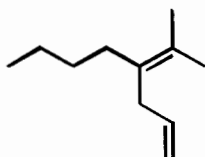
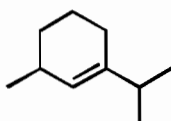
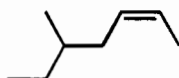
Due: March 3, 4:00 pm

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

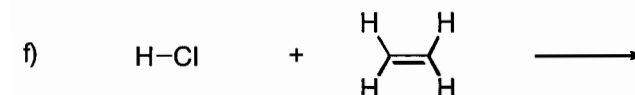
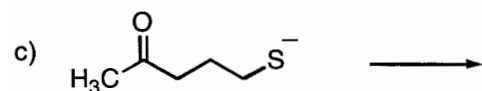
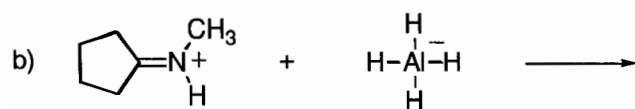
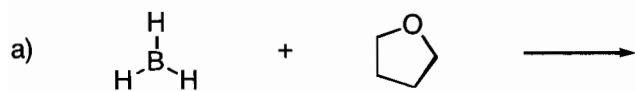
2. Assign *E-Z* configuration to each alkene.



3. Name the following alkenes.



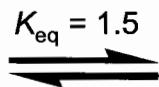
4. For each of the following reactions, label the type of nucleophile: lone pair (n), pi bond (π), sigma bond (σ), and the type of electrophile: empty atomic orbital (a), polarized pi bond (π^*), polarized sigma bond (σ^*). Draw in all lone pairs and use curved arrows to show how the nucleophile attacks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

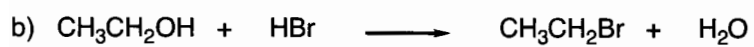


b) Write the equilibrium equation.

$$K_{\text{eq}} =$$

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

6. Calculate ΔH for each of the following reactions. (See the table at the end of this problem set).



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

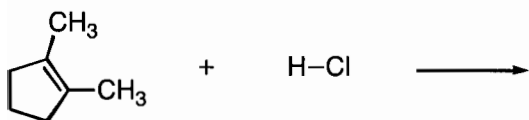
e) The reaction is: exergonic endergonic

f) ΔG is: positive negative

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

8. Consider the following reaction.

a) Show the product (ignore stereochemistry).



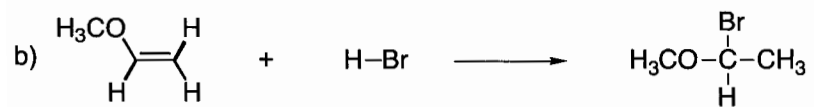
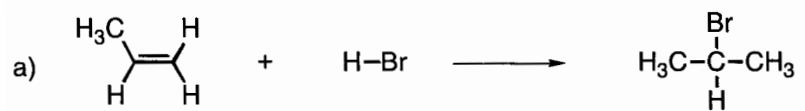
b) How many stereoisomers will form during this reaction?

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

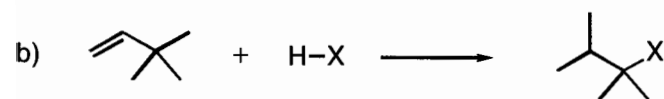
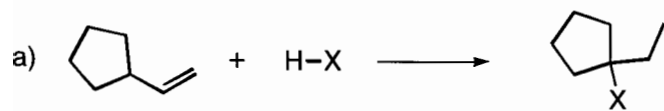
d) Label the relationships between the stereoisomers.

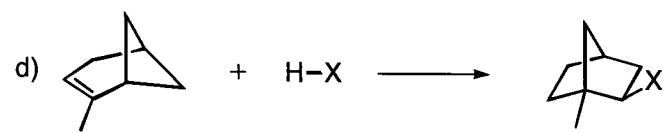
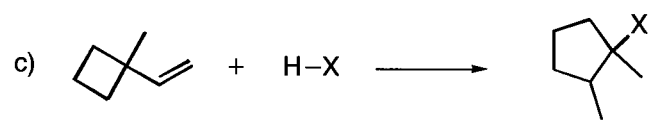
e) The products are (circle one): optically active or optically inactive

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



10. Show the mechanism for each reaction.





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

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

Bond Dissociation Energies ^{a,b} —Single Bonds: Diatomic Molecules					
Bond	Energy	Bond	Energy	Bond	Energy
H—H	104.2 [436.0]	F—Cl	61 [255]	H—F	135.8 ^c [568]
D—D	106.0 [444.5]	F—Br	60 [251]	H—Cl	103.0 ^c [431]
F—F	38 [159]	F—I	58 [243]	H—Br	87.5 ^c [366]
Cl—Cl	58 [243]	Cl—Br	52 [218]	H—I	71.3 ^c [298]
Br—Br	46.0 [192]	Cl—I	50 [209]		
I—I	36.1 [151]				

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

Table 2.8 (Continued)

Bond	Energy	Bond	Energy
		H ₂ N—CH ₂ CH ₃	78 [326]
		H ₂ N—C ₆ H ₅	91 [381]
		H ₂ N—COCH ₃	~96 [401]
CH ₃ —CF ₃	100 [418]	O ₂ N—NO ₂	13.6 [57]
CH ₃ —CHCH ₂	92 [385]	O ₂ N—COCH ₃	97 [406]
CH ₃ —C ₆ H ₅	93 [389]		
CH ₃ —CCH	117 [490]		
CH ₃ —CH ₂ C ₆ H ₅	72 [301]		
CH ₃ —CH ₂ CHCH ₂	72 [301]		

Multiple Bonds

Bond	Energy	Bond	Energy
O=O	119 [498]	CF ₂ =CF ₂	76.3 [319]
O=CO	128 [536]	CH ₂ =NH	~154 [644]
O=CH ₂	175 [732]	C≡O	257 [1075]
O=NH	115 [481]	N≡N	226 [946]
HN=NH	~109 [456]	N≡CH	224 [937]
CH ₂ =CH ₂	163 [682]	HC≡CH	230 [962]

Representative Average Bond Energies^d—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]	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]

^aFrom 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.

^bIn kcal mol⁻¹. Numbers in brackets are values in kJ mol⁻¹.

^cBenson, S. W. *J. Chem. Educ.* **1965**, *42*, 502. Reprinted by permission of the Division of Chemical Education.

^dFrom 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 ΔH_f° '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 ΔH and -103.8 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. ΔH_f° when that gas pressure and are in calories to other ten

2. In order arbitrary values obtained

In simple ΔH_f° of the bond affect important cellular enthalpic