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Chem 220 -Organic Chemistry

Problem Set 6

Solution Set

Chapter 7, Structure and Synthesis of Alkenes

Due: Monday, October 18, 2010

Notice: For those of you who are using the 6th edition of the textbook, you can learn about olefin metathesis by clicking here.

1. Read Degree (Elements) of Unsaturation. How many degrees of unsaturation are present in $C_{16}H_{13}ClN_2O$? Draw two structures, one cyclic, the other acyclic, that have the number of degrees of unsaturation you determined and that is necessarily in agreement with the formula.
We begin with $C_{16}H_{13}ClN_2O$.

Dropping O gives $C_{16}H_{13}ClN_2$.

Drop Cl, add one H: $C_{16}H_{14}N_2$

Each N is worth CH; therefore, $C_{18}H_{16}$

The most saturated C_{18} hydrocarbon is $C_{18}H_{38}$. (38-16)/2 = 11 degrees of unsaturation.

If you like formulas, let's derive one from what was done above.

The number of hydrogens in the most saturated hydrocarbon must be 2C + 2 less the number hydrogens, halogens and nitrogen equivalents all divided by 2. Since the number of carbons in the most saturated hydrocarbon is increased when nitrogen is replaced by CH, one has D.U. = {[2(C+N)+2]-(H+X+N)}/2. This equation can be reduced to D.U. = C-((H+X-N)/2)+1. For the case at hand, D.U. = 16-(12/2)+1 = 11.

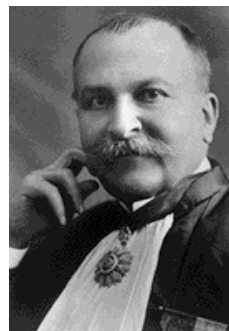*Two structures are below. The cyclic structure happens to be valium (About its inventor, Leo Sternbach).*
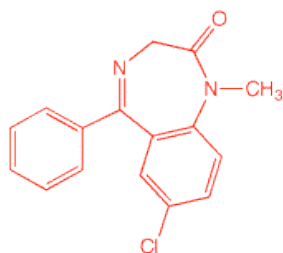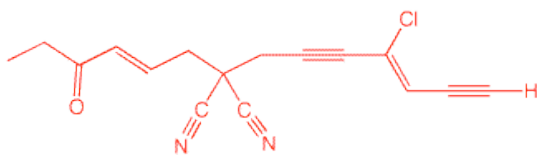
Paul Sabatier
1912 Co-Nobel
Prize in Chemistry
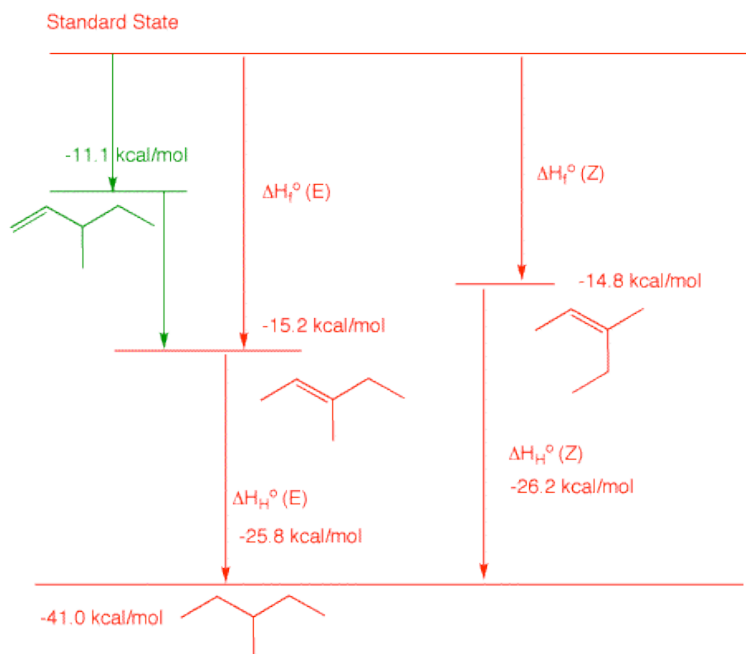Hydrogenation by
Metal Catalysis

Cyclic

Acyclic

2. a) Determine the heat of formation of 3-methyl-1-pentene by using the <u>heat of formation</u> tables to determine typical heats of hydrogenation for monosubstituted alkenes. Show work. *The hydrogenation product of 3-methyl-1-pentene is 3-methylpentane, ΔH_f^o = -41.0 kcal/mol. Looking at the ΔH_f^o of typical 1-alkenes, one can see: 1-butene (ΔH_f^o = 0 kcal/mol), 1-pentene (ΔH_f^o = -5.0 kcal/mol) and 1-hexene (ΔH_f^o = 10.2 kcal/mol). Notice each one differs by ~5 kcal/mol. Their respective alkanes are: n-butane (ΔH_f^o = -30.0 kcal/mol), n-pentane (ΔH_f^o = -35.1 kcal/mol) and 1-hexene (ΔH_f^o = -39.9 kcal/mol). The heats of hydrogenation of each of these is,respectively, the difference in the heats of formation: -30.0 kcal/mol, -30.1 -30.0 kcal/mol and -30.0 kcal/mol-29.7 -30.0 kcal/mol. The average is -29.9 kcal/mol. Therefore, the ΔH_f^o of 3-methyl-1-pentene is x = -41.0 -(-29.9) = -11.1 kcal/mol. The reported ΔH_f^o of 2-methyl-1-butene is -6.1 kcal/mol. Add a methylene to this structure (-5.0 kcal/mol) and you obtain ΔH_f^o = -11.1 kcal/mol for 3-methyl-1-pentene.*

b) Calculate the heat of hydrogenation of (E)-and (Z)-3-methyl-2-pentene. Show work. *From the Heats of Formation Table, (E)-3-methyl-2-pentene is ΔH_f^o = -15.2 kcal/mol and (Z)-3-methyl-2-pentene is ΔH_f^o = -14.8 kcal/mol. The heat of formation of 3-methylpentane is ΔH_f^o = -41.0 kcal/mol. The heat of formation of the (E)-isomer is -41.0 - (-15.2) = -25.8 kcal/mol. The heat of formation of the (Z)-isomer is -41.0 - (-14.8) = -26.2 kcal/mol.*

c) Use a diagram to illustrate that the difference in the heat of hydrogenation of the two geometrical isomers in 2b is equal to the difference in their heats of formation. Which isomer is more stable based upon the heats of formation? Why?

From the diagram on the right, $\Delta H_f^o(E) + H_H^o(E) = \Delta H_f^o(Z) + H_H^o(Z)$. Therefore, $\Delta H_f^o(E) - H_f^o(Z) = \Delta H_H^o(Z) - H_H^o(E)$. The (E)-isomer is more stable. more negative heat of formation; lower heat of hydrogenation.

d) There is only one monosubstituted alkene having the carbon skeleton of the (E)- and (Z)- isomers in 2b. What is its structure? Assuming that $\Delta G^o = \Delta H^o$, which of the three isomeric alkenes would dominate in an equilibrium mixture? How much heat is liberated in the isomerization of the monosubstituted alkene to the (E)-isomer? Show work. Add the monosubstituted alkene to your diagram in 2c and illustrate the heat of isomerization. *The isomer is 3-methyl-1-pentene, the answer to part a). The (E)-isomer would dominate in an equilibrium mixture because it is the most stable. The heat of*

Standard State

-11.1 kcal/mol

ΔH_f^o (E)

ΔH_f^o (Z)

-14.8 kcal/mol

-15.2 kcal/mol

ΔH_H^o (E)

-25.8 kcal/mol

ΔH_H^o (Z)

-26.2 kcal/mol

-41.0 kcal/mol
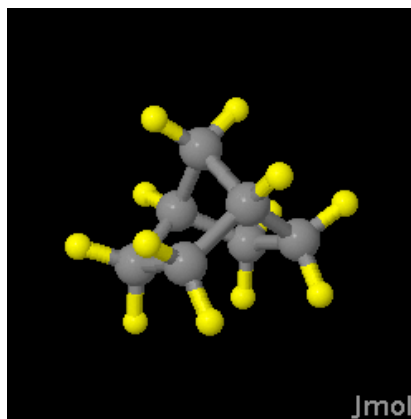
isomerization equals -15.2 - (-11.1) = -4.1 kcal/mol.

3. a) Using the standard values for the relative reactivity of 1º, 2º and 3º C-H bonds toward free radical chlorination, determine the relative amount of the four possible monochlorides formed from the chlorination of [2.2.1]-bicycloheptane.

norbornane   1-exo   2-endo   3-bridgehead   4
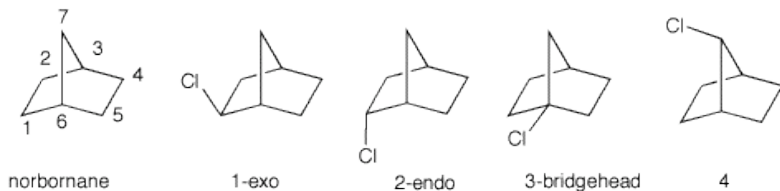
Positions 1, 2, 4 and 5 are all the same type of CH_2 [8 x 4.5 = 36]. They lead to the same radical. Position 7 is a unique CH_2 [2 x 4.5 = 9]. Positions 3 and 6 are bridgehead hydrogens [2 x 5.5 = 11]. Dividing each of these products by the sum (56) gives the relative amounts: 16%, 64% and 20%, respectively.

b) The experimental result is: **1**, 72%; **2**, 25%; 4, 3%; **3**, 0%. Why is no bridgehead isomer formed even though tertiary C-H bonds are highly reactive? *The radical from the the bridgehead hydrogen cannot become planar.*

c) There are two types of secondary radicals formed. What is their relative reactivity? [**Hints:** Measure the C_2-C_1-C_6 and the C_3-C_7-C_6 bond angles in norborane on the right in which the radical is formed on the central carbon. How do these values compare with cyclopentane? The chlorination of cyclobutane is slower than the chlorination of cyclopentane.] *97/3 = 32.3, which is the sum of exo + endo divided by 3% for **4**. This selectivity is eight times greater than 36/6 = 4 calculated in part a). Since the C-C-C bond angle in cyclopentane is 104º and in cyclobutane it is 88º and cyclobutane is slower to chlorinate, perhaps this is part of the problem. Measuring the angles in norbornane, the C_2-C_1-C_6 is 103º and the C_3-C_7-C_6 bond angle is 93.5º.*

d) At what point in the radical chain are the endo and exo isomers formed? Why does the exo isomer dominate? Explain and illustrate. *The radical formed at C_1, C_2, C_4 or C_5 in the first propagation step, reacts with chlorine in the second propagation step proximate to C_7, leading to the exo isomer, or distal to C_7, leading to the endo isomer. Imagine a plane through carbons 6-1-2-3. A reaction is less hindered proximate to the the smaller methano- bridge (C_7) than to the ethano- bridge (C_4-5). This is why the exo isomer dominates.*

e) Are the four monochlorides optically active, racemic, or achiral? *Exo and endo are racemic; the other two are achiral.*

Jmol

How to manipulate Jmol structures.

Larger Version

4. The major product **B** from free radical monobromination of alkane **A** (C_6H_{14}) readily reacts with water to form **C**, $C_6H_{14}O$. Treatment of bromide **B** with KOH in ethanol produces two, and only

two, compounds, **D** and **E**. Compound **D** liberates 1.6 kcal/mol more heat upon hydrogenation to **A** than does **E**. What are the structures **A-E**? What is the heat of isomerization of **D** to **E**? Illustrate and explain. [**Hint:** What are the structures possible for **A**?]

*There are five possible structures, **1-5**, for the acyclic, saturated alkane **A**. Since bromide **B** reacts readily with water (S_N1) to form alcohol **C**, structures **1** and **5** are eliminated. Structure **3** is also eliminated because E2 elimination of 3-bromo-3-methylpentane could give three alkenes: 2-ethyl-1-butene and (E)- and (Z)-3-methyl-2-pentene. That leaves **6** and **7** from **2** and **8** and **9** from **4** for the structures of **D** and **E**. Lookup the heats of formation of **4**, **8** and **9** in the the [Heats of Formation Tables](#). From these data, one calculates the difference in the heat of hydrogenation as 1.1 kcal/mol, which isn't the value 1.6 kcal/mol. Alternatively, Table 7-1 in Wade gives the difference as 1.4 kcal/mol. (there is some discrepancy here.) Neither **6** nor **7** appear in the heats of formation table but we can look at lower homologs and calculate the heats of formation using the 5.0 kcal/mol/CH_2. Thus, 2-methyl-1-butene (ΔH_f^o = -8.4 kcal/mol) gives ΔH_f^o = -13.4 kcal/mol for **7** while 2-methyl-2-butene (ΔH_f^o = -10.0*
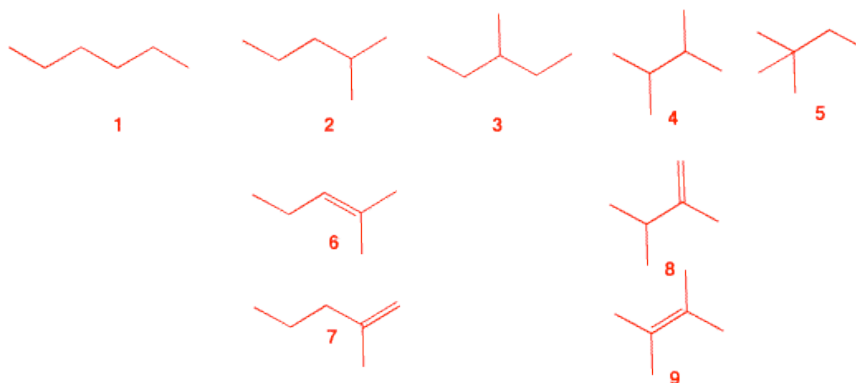
*kcal/mol) affords ΔH$_f^o$
= -15.0 kcal/mol for **6**.
The difference is 1.6
kcal/mol. [There is
actually no need to
include the 5 kcal/mol
correction because the
difference would be the
same.] Using Table 7-1
in Wade, a value of 1.6
kcal/mol is obtained.
So, **A** = 2-
methylpentane; **B** = 2-
bromo-2-
methylpentane; **C** = 2-
methyl-2-pentanol; **D**
= 2-methyl-1-pentene
(**7**); **E** = 2-methyl-2-
pentene (**6**). **D**, with a
less negative heat of
formation than **E**,
liberates more heat on
hydrogenation.*

5. In 1968 Wiberg and Fenoglio determined the heat of combustion of
cyclopropene: -485.0 kcal/mol. Determine the heat of hydrogenation of
cyclopropene to cyclopropane. Explain and illustrate with a diagram. What is
needed is the heat of formation of both cyclopropene and cyclopropane. *The
alkene's heat of formation is calculated as +66.2 kcal/mol in the usual way.
See left side of diagram on the right. The heat of formation of cyclopropane
comes from the Heats of Formation Tables. The difference in heats of
formation is the heat of hydrogenation: -53.5 kcal/mol. In the chart below the
heats of formation of simple cycloalkenes and cycloalkanes are listed. The
heats of hydrogenation are computed. Cyclopropene's double bond is really
distorted (bond angles). Note that the heat of hydrogenation of cyclohexene
is no different from the heat of hydrogenation of (Z)-2-butene.*

Heats of Formation of Cycloalkenes, Alkanes and Heats of Hydrogenation (kcal/mol)

	Cycloalkene	Cycloalkane	Hydrogenation	
C3	-66.2	12.7	-53.5	
C4	37.5	6.6	-30.9	
C5	8.5	-18.3	-26.8	
C6	-1.2	-29.5	-28.3	
(Z)-2-butene	-1.7	-30	-28.3	
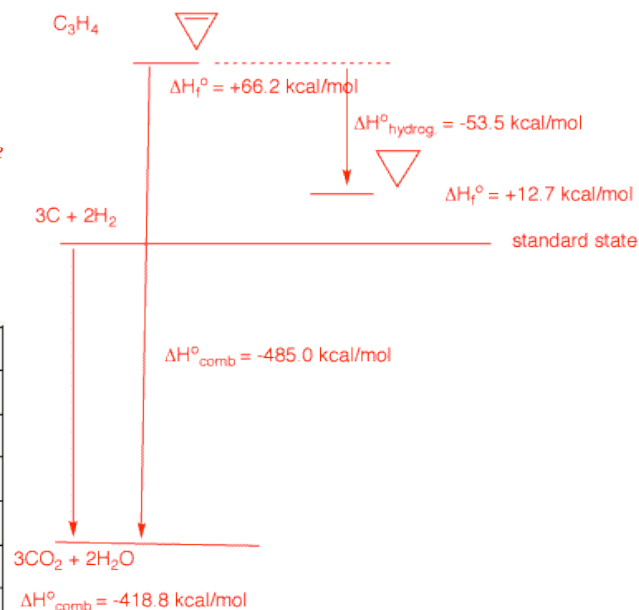
6. Two stereoisomers, **A** and **B**, absorb one
equivalent of hydrogen upon catalytic
hydrogenation to form cyclooctane. Compound

A, which is capable of resolution, liberates 34.5 kcal/mol of heat while **B** liberates 24.3 kcal/mol of heat.

a) What are the structures of **A** and **B** ? *Since A and B both absorb only one equivalent of hydrogen to form cyclooctane, they must be cis- and trans-cyclooctene. trans-Cyclooctene is more strained than cis-cyclooctene because a chain of six methylene groups is the minimum length to span a double bond that is trans. It gives off more heat on hydrogenation. Therefore, A is trans; B is cis.*

b) What are the heats of formation of **A** and **B** ? *The heat of formation of cyclooctane is from Heats of Formation Tables. The heats of hydrogenation are given. The differences gives the respective heats of formation.*

c) What is the difference in strain energy between **A** and **B** ? *The difference between the heats of formation: 10.2 kcal/mol.*

d) What is the difference in the heat of combustion between **A** and **B**? *From the diagram on the right it is obvious than the difference in the heats of combustion is the same as the difference in the strain energy of the two.*

e) Why is **A** capable of resolution? The non-superimposable mirror images of trans-cyclooctene do not interconvert. *It is difficult for the the vinyl hydrogens to pass through the ring to racemize. Link to Jmol structures here.*

$\Delta H_f^\circ = 4.8$ kcal/mol

C_8H_{14}

$\Delta H^\circ_{hydrog} = -34.5$ kcal/mol

Std. State

$\Delta H_f^\circ = -5.4$ kcal/mol

C_8H_{14}

$\Delta H^\circ_{hydrog} = -24.3$ kcal/mol

$\Delta H_f^\circ = -29.7$ kcal/mol

ΔH°_{comb} trans ΔH°_{comb} cis

$8CO_2 + 7H_2O$