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Chem 220 -Organic Chemistry

Problem Set 6, Solution Set

Chapter 7, Structure and Synthesis of Alkenes

Due: Monday, October 19, 2009

1. Read Degree (Elements) of Unsaturation. How many degrees of unsaturation are present in $C_{10}H_{12}BrClN_2OS$? 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.
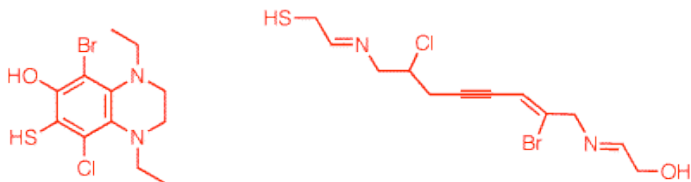
$C_{10}H_{12}BrClN_2OS$; drop O and S,
$C_{10}H_{12}BrClN_2$; drop Br and Cl; add two H's,
$C_{10}H_{14}N_2$; drop two N's; add two C's and two H's
$C_{12}H_{16}$; compare with the most saturated C_{12} alkane,
$C_{12}H_{26}$,
(26-16)/2 = 5 degrees of unsaturation.

Paul Sabatier
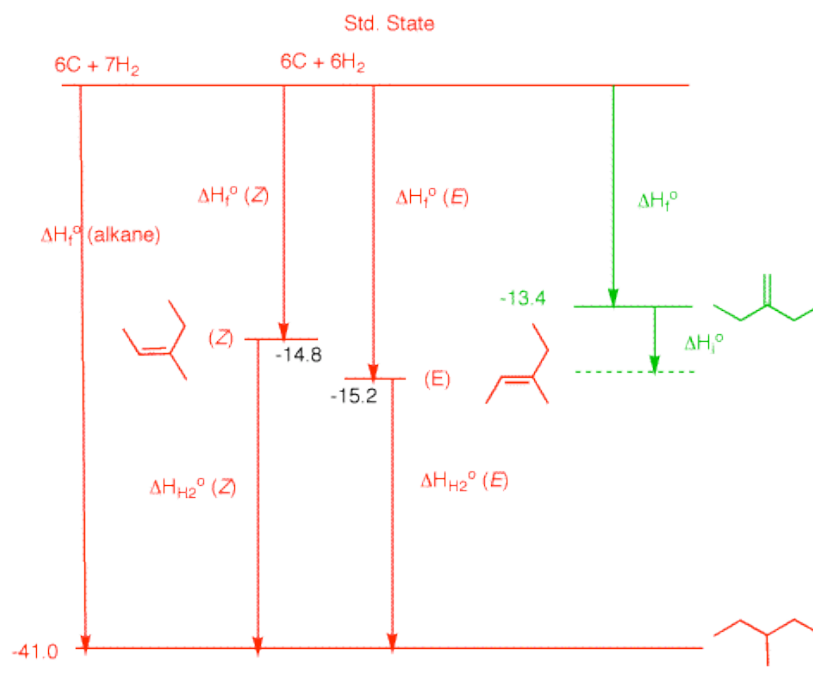1912 Co-Nobel Prize in Chemistry
Hydrogenation by Metal Catalysis

2. a) **Estimate** the heat of hydrogenation of 3-ethyl-2-pentene using the heat of formation table. Show work.

Since the heat of hydrogenation of all unstrained, equally substituted double bonds is about the same and the compound in question does not appear, use 2-methy-2-butene as a model. Its ΔH_f^o = -10 kcal/mol. Its product of hydrogenation is 2-methylbutane: ΔH_f^o = -36.7 kcal/mol. The difference of -26.7 kcal/mol is the estimated heat of hydrogenation.

b) *Calculate the heat of hydrogenation of (E)-and (Z)-3-methyl-2-pentene. Show work.*

From the Table:

(E)-3-methyl-2-pentene: ΔH_f^o = -15.2 kcal/mol

(Z)-3-methyl-2-pentene: ΔH_f^o = -14.8 kcal/mol

3-methylpentane: ΔH_f^o = -41.0 kcal/mol

Heat of hydrogenation of (E)-3-methyl-2-pentene: -41.0 - (-15.2) = -25.2 kcal/mol.

Heat of hydrogenation of (Z)-3-methyl-2-pentene: -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?

Diagram is on the right (red only). The (E)-isomer is more stable/ It has the lower heat of formation. From the diagram ΔH_f^o (E) + ΔH_{H2}^o (E) = ΔH_f^o (Z) + ΔH_{H2}^o (Z). Transposing, ΔH_f^o (E) - ΔH_f^o (Z) = ΔH_{H2}^o (Z) - ΔH_{H2}^o (E); -15.2 - (-14.8) = -26.2 - (-25.2) = -1.0 kcal/mol. This difference is also the heat of isomerization, ΔH_i^o.

d) There is only one disubstituted alkene isomer 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 disubstituted alkene to the (E)-isomer? Show work. Add the disubstituted alkene to your diagram in 2c and illustrate the heat of isomerization.

There is only one disubstituted isomer: 2-ethyl-1-butene (green section of diagram). Since it is disubstituted, it is less stable than the trisubstituted isomers: ΔH_f^o = -13.4 kcal/mol (Table). The ΔH_i^o = 15.2 - (-13.4) = -1.8 kcal/mol.
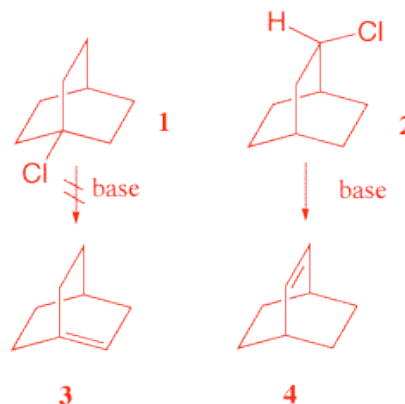
3. a) [2.2.2]-Bicyclooctane forms how many monochloro constitutional isomers upon free radical chlorination? What are their structures? *Structures are 1 and 2 (above). There are only two bridgehead, tertiary hydrogens and 12 secondary hydrogens. Chloroalkane 1 is achiral; secondary chloride 2 will be a racemate. If H and Cl are switched, the enantiomer of 2 would arise.*

b) In what ratio are they expected to be formed? Show work. *tertiary: 2 x 5.5 (reactivity) = 11; 11/(11 + 54) = 0.17 = 17% secondary: 12 x 4.5 = 54 = 54/(11 + 54) = 0.83 = 83 %*

c) Are they optically active, racemic, or achiral? *See 3a.*

d) How many different alkenes are formed from the monochloro compounds upon treatment with a strong base? Explain and illustrate. *Chloride 2 forms only one alkene: 4. Elimination of 2 toward the bridgehead gives a strained alkene 2, which does not have a planar double bond. In other words, there is poor overlap between the bridehead C-H bond and the C-Cl bond. For the same reasons, 3 cannot form from 1.*

4. Compound **A** ($C_5H_{11}Br$) reacts readily with water to form **B**, $C_5H_{12}O$. Exposure of compound **A** to aq. NaOH gives only **C** (major) and **D** (minor). Hydrogenation of **C** liberates 26.8 ± 0.1 kcal/mol heat while **D** liberates 28.4 ± 0.1 kcal/mol of heat during hydrogenation. Both **C** and **D** form **E** upon hydrogenation. What are the structures **A-E**? Explain. *Compounds A and B have 0 degrees of unsaturation. They are both acyclic and devoid of unsaturation. Compound reacts readily with water (S_N1) to form **B**, an alcohol, requires compound A to be tertiary bromide. With only five carbons available, there is only one possible structure for A: 2-bromo-2-methylbutane. Compound **B** is then 2-methyl-2-butanol. Compounds **C** and **D** are the products of E_2 elimination. Since hydroxide is a small base, the major produc **C** must be the trisubstituted alkene 2-methyl-2-butene and **D** is the alkene 2-methyl-1-butene. For the heats of hydrogenation: (text, Table 7-1), **C**: -26.9 kcal/mol; **D**: -28.5 kcal/mol. (ΔH_f^o table [calc'd.]) **C**: -26.7 kcal/mol ; **D**: -28.3 kcal/mol. The values are consistent.*
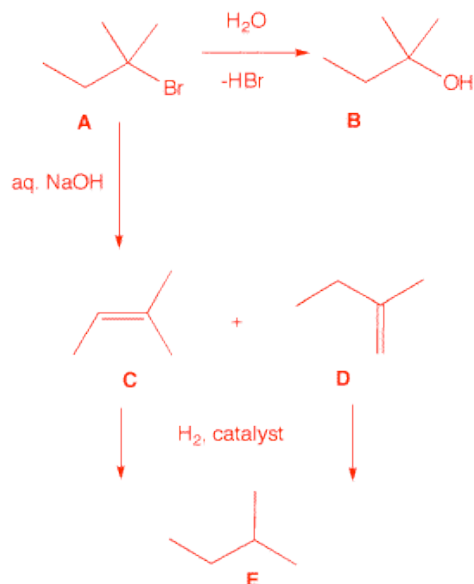
5. a) Determine the heat of hydrogenation of cyclohexene from the heat of formation tables. b) How does this value compare with the heat of hydrogenation of an unstrained cis-disubstituted double bond? c) Given the heat of hydrogenation of cyclopentene (chapter 7) determine the heat of formation of cyclopentene. d) BONUS: Why is the heat of hydrogenation less for cyclopentene than that for cyclohexene? Show all work.

a) ΔH_f^o (cyclohexane) - ΔH_f^o (cyclohexene) = ΔH_{H2}^o ; -29.5 - (-1.2) = -28.3 kcal/mol for the heat of hydrogenation.

b) An unstrained cis double bond model would be the hydrogenation of (Z)-2-butene. ΔH_f^o (butane) - ΔH_f^o ((Z)-2-butene) = ΔH_{H2}^o ; -30.0 - (-1.7) = -28.3 kcal/mol. both values are the same. Since cyclohexane, butane and (Z)-2-butene are unstrained, cyclohexene is unstrained.

c) The ΔH_f^o (cyclopentane) from the heats of formation table is -18.3 kcal/mol. The ΔH_{H2}^o is -26.6 kcal/mol (text, 7-7D). Now ΔH_f^o (cyclopentene) = ΔH_f^o (cyclopentane) - ΔH_{H2}^o; -18.3 - (-26.6) = +8.3 kcal/mol for ΔH_f^o (cyclopentene).

BONUS: The diagram on the right contains the data (in red) for 5a and 5b. Since cyclohexane and cyclohexene are unstrained, the difference for the heat of hydrogenation of cyclopentene vs. cyclohexene must lie with either strain in cyclopentane and/or cyclopentene. One approach is to have a vitual, strain-free

cyclopentane (ΔH_f^o = -24.5 kcal/mol) and cyclopentene (ΔH_f^o = +3.8 kcal/mol) (in blue). The heats of formation of these two can be determined by adding +5 kcal/mol to the heats of formation of cyclohexane and cyclohexene. Recall that the difference in the heat of formation of n-pentane and n-hexane is ~5 kcal/mol. Note that the heat of hydrogenation of this strain-free cyclopentene is the same as the heat of hydrogenation of cyclohexene. Thus, virtual cyclopentene lies 4.5 kcal/mol below real cyclopentene and virtual cyclopentane lies 6.2 kcal/mol below real cyclopentane (magenta in diagram). This analysis suggests that there is relatively more strain in cyclopentane than in cyclopentene. The difference between 6.2 and 4.5 kcal/mol is the same as the difference in the heats of hydrogenation.

-4.5

+3.8

+8.3

Std. State

+5.0

-1.2

-26.6

-28.3

-28.3

-18.3

-6.2

-24.5

-11.2

+5.0

-29.5

strain-free cyclopentane
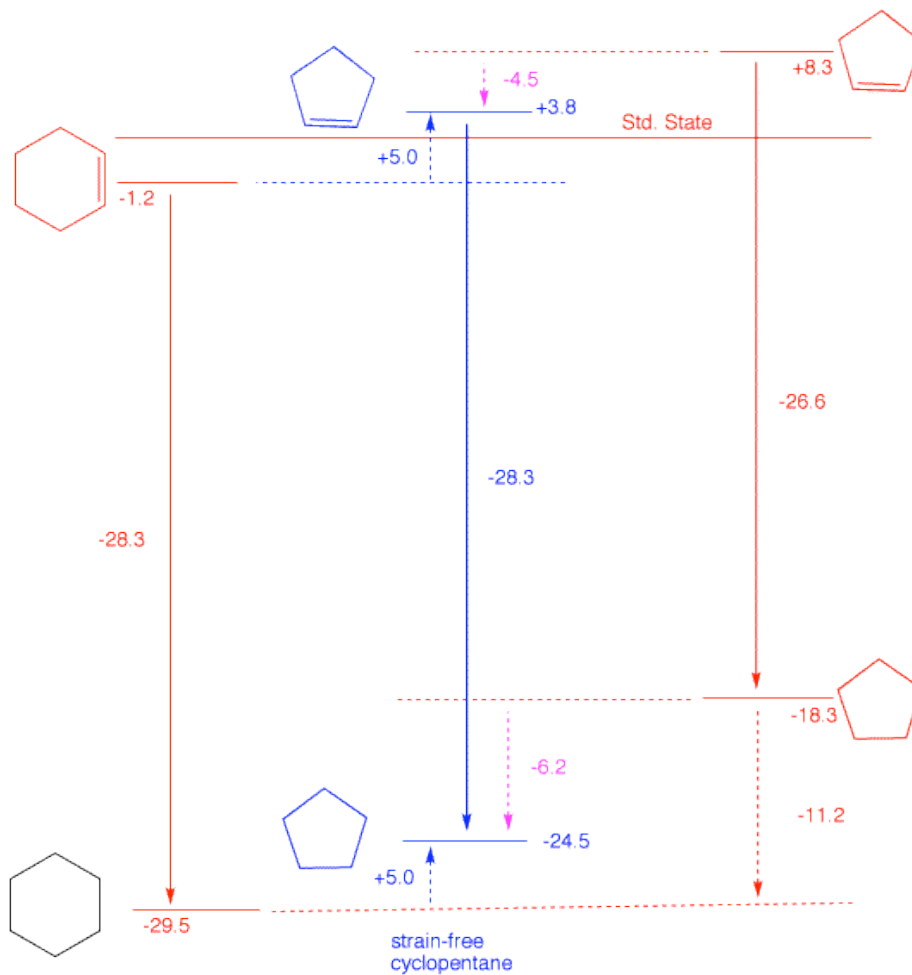
6. Two stereoisomers, **A** and **B**, absorb one equivalent of hydrogen upon catalytic hydrogenation to form cyclooctane. Compound **A**, which is capable of resolution, liberates 34.5 kcal/mol of heat while **B** liberates 24.3 kcal/mol of heat.

a) What are the structures of **A** and **B** ? *A and B must be stereoisomers of cyclooctene. Both absorb one equivalent of hydrogen. Trans-cyclooctene, which is capable of resolution, is more strained than cis-cyclooctene. Trans-cyclooctene (A) will liberate more heat upon hydrogenation. Cis-cyclooctene*

is B.

b) What are the heats of formation of **A** and **B** ?

ΔH_f^o (trans-cyclooctene) = ΔH_f^o (cyclooctane) - ΔH_{H2}^o; -29.7 - (-34.5) = +4.8 kcal/mol for ΔH_f^o (trans-cyclooctene).

ΔH_f^o (cis-cyclooctene) = ΔH_f^o (cyclooctane) - ΔH_{H2}^o; -29.7 - (24.3) = -5.4 kcal/mol for ΔH_f^o (cis-cyclooctene).

c) What is the difference in strain energy between **A** and **B** ?

Δ(Strain Energy) = H_f^o (trans-cyclooctene) - ΔH_f^o (cis-cyclooctene); +4.8 - (-5.4) = +10.2 kcal/mol.

d) What is the difference in the heat of combustion between **A** and **B**?

The same as the difference in strain energy. Both isomers go to $8CO_2$ and $8H_2O$.

e) Why is **A** capable of resolution?

It is racemic mixture of chiral enantiomers that have a high barrier to interconversion.

7. Comment critically on the following proposed synthesis of the now banned gasoline additive, methyl tertiary-butyl ether (MTBE). If you believe the reaction will be successful, provide the type of mechanism that is operable and illustrate it with the curved arrow formalism. If you feel that the reaction will not be successful, state the expected product of the reaction and the mechanism by which it is formed. Illustrate with curved arrows. If no reaction takes place, state so and explain why not.
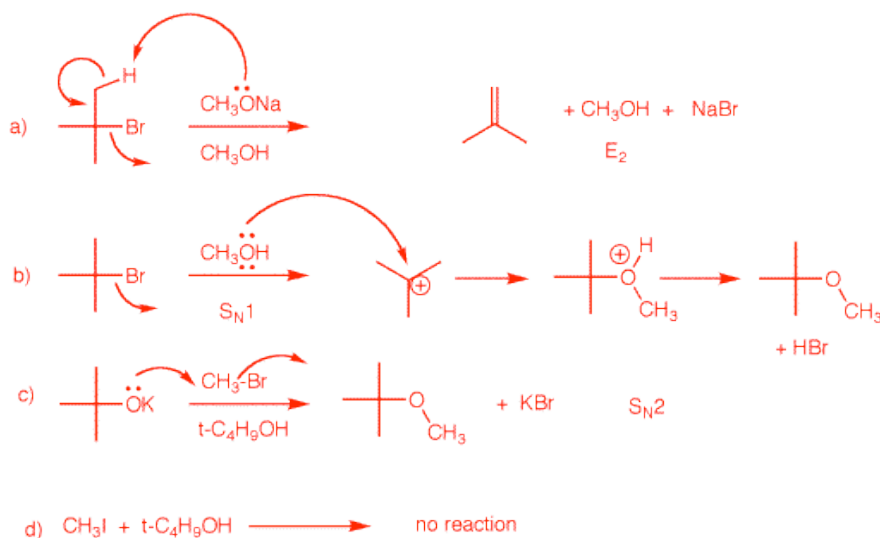
a) Tertiary halides in the presence of strong base undergo E_2 elimination, not substitution.

b) Tertiary halides in the presence of hydroxylic solvents (poor nucleophiles) undergo ionization to a cation that is captured by the solvent. S_N1 reaction.

c) No elimination possible with methyl bromide. S_N2 displacement with t-butoxide. Williamson ether synthesis.

d) No reaction. t-BuOH is a poor nucleophile. Methyl bromide does not undergo S_N1 reactions. No β-hydrogens for elimination.