Answers to Problem Set #3

Question 1. The chemical structure for vitamin A, a highly unsaturated hydrocarbon (with one oxygen atom) is shown below. Use this structure to answer the following questions.

![Vitamin A structure](image)

a) How many degrees of unsaturation are there in vitamin A?

*one ring and 5 double bonds = six degrees of unsaturation*

b) How many atoms are sp$^3$-hybridized?

*12 total: 11 carbon atoms and one oxygen atom*

c) How many atoms are sp$^2$-hybridized?

*10 total: all carbon atoms*

d) How many atoms are sp-hybridized?

*none*
e) Label each double bond in vitamin A as (E), (Z), or "not applicable."

\[
\begin{align*}
&\text{H}_3\text{C} & & \text{CH}_3 & & \text{E} & & \text{CH}_3 & & \text{E} & & \text{OH} \\
&\text{Z} & & \text{E} & & \text{E} & & \text{CH}_3 & & \text{E} & & \text{E} \\
&\text{CH}_3 & & \text{E} & & \text{E} & & \text{E} & & \text{E} & & \text{E}
\end{align*}
\]

Question 2. For each compound below, briefly describe why the structure is unstable or cannot exist.

a) \[
\text{Triple bonds are only stable in rings of 8 carbons or greater}
\]

b) \[
The central carbon atom has 5 bonds (impossible)
\]

c) \[
This structure obeys Bretl's Rule
\]

d) \[
The circled carbon has 6 bonds (impossible)
\]
Question 3. Use the data from equations 1-3 to answer the questions below.

\[ \Delta H \text{ (kcal/mol)} \]

\begin{align*}
\text{(1)} & \quad \text{(E)-2-butene} & \quad \text{H}_2 \text{ gas} & \quad \text{Pt catalyst} & \quad \text{1-butene} & \quad -27 \\
\text{(2)} & \quad 1\text{-butene} & \quad \text{H}_2 \text{ gas} & \quad \text{Pt catalyst} & \quad -30 \\
\text{(3)} & \quad \text{cyclobutene} & \quad \text{H}_2 \text{ gas} & \quad \text{Pt catalyst} & \quad -36
\end{align*}

a) Estimate the bond dissociation energy of each double bond in the starting materials above (BDEs: \( \text{H–H} = 104 \text{ kcal/mol}; \text{C–H} = 100 \text{ kcal/mol} \)).

\[ \begin{array}{c}
(\text{E)-2-butene}) \\
69 \text{ kcal/mol}
\end{array} \quad \begin{array}{c}
(\text{1-butene}) \\
66 \text{ kcal/mol}
\end{array} \quad \begin{array}{c}
(\text{cyclobutene}) \\
60 \text{ kcal/mol}
\end{array} \]

b) What is the cause of the 6 kcal/mol difference in energy between the C–C double bond in 1-butene and cyclobutene?

In a 4-membered ring, bond angles are forced to be near 90°. Since \( \text{sp}^2 \)-hybridized carbon prefers 120° bond angles, this deviation will increase the energy of the system and weaken the \( \pi \)-bond (this deviation from ideal bond angles is called angle strain). Angle strain is not a problem in acyclic systems such as 1-butene. In addition, \( \text{sp}^3 \)-hybridized carbon has a little less angle strain in a 4-membered ring than \( \text{sp}^2 \)-carbon because the deviation from the ideal angles (109.5° for \( \text{sp}^3 \)) is smaller.
c) How many signals for carbon are there in the NMR spectrum of 1-butene? Of \((E)-2\)-butene? How many hydrogen atom signals are observed for each of these compounds?
d)

4 carbon signals

5 hydrogen signals

2 carbon signals

2 hydrogen signals
Question 4. For the following pairs of compounds, circle the molecule that is more stable.

a) Increased olefin substitution

b) This structure disobeys Bredt's Rule

c) Increased olefin substitution

d) This structure has increased angle strain - see Question 3, part c.
Question 5. How would you tell the following pairs of compounds apart by $^{13}$C NMR spectroscopy?

a) 

3 signals

b) 

4 signals

8 signals

c) 

4 signals

8 signals