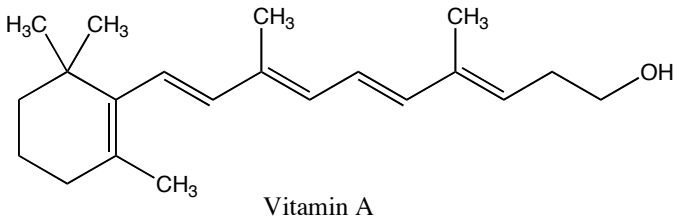
Answers to Problem Set #3

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.



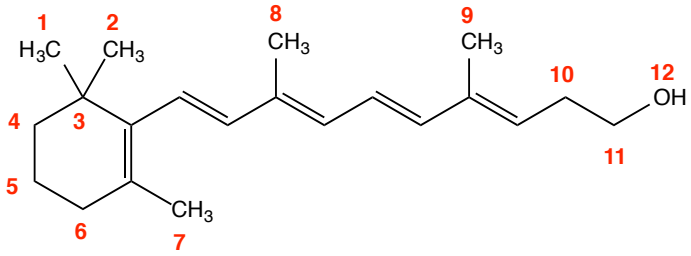
Vitamin A

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

one ring and 5 double bonds = six degrees of unsaturation

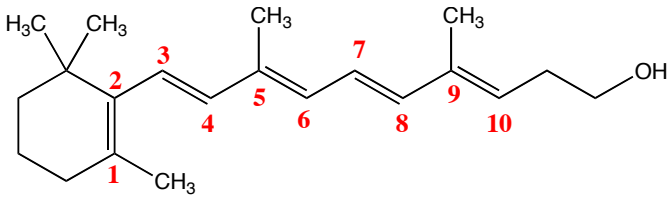
b) How many atoms are sp^3-hybridized?

12 total: 11 carbon atoms and one oxygen atom



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

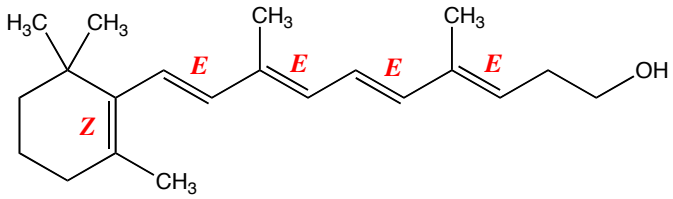
10 total: all carbon atoms



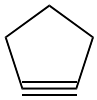
d) How many atoms are sp-hybridized?

none

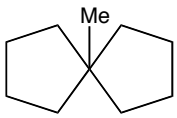
e) Label each double bond in vitamin A as (*E*), (*Z*), or "not applicable."



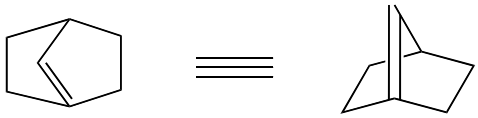
Question 2. For each compound below, briefly describe why the structure is unstable or cannot exist.

a) 

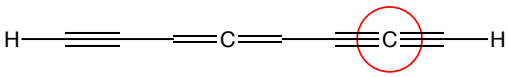
Triple bonds are only stable in rings of 8 carbons or greater

b) 

The central carbon atom has 5 bonds (impossible)

c) 

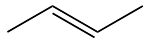
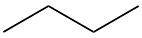
This structure diobeys Bredt's Rule

d) 

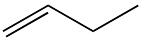
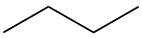
The circled carbon has 6 bonds (impossible)

Question 3. Use the data from equations 1-3 to answer the questions below.

ΔH (kcal/mol)

(1)  (H_2 gas, Pt catalyst)  –27

(*E*)-2-butene

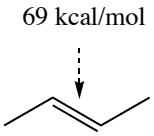
(2)  (H_2 gas, Pt catalyst)  –30

1-butene

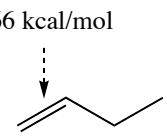
(3)  (H_2 gas, Pt catalyst)  –36

cyclobutene

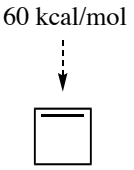
a) Estimate the bond dissociation energy of each double bond in the starting materials above (BDEs: H–H = 104 kcal/mol; C–H = 100 kcal/mol).



(*E*)-2-butene

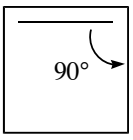


1-butene



cyclobutene

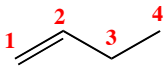
b) What is the cause of the 6 kcal/mol difference in energy between the C–C double bond in 1-butene and cyclobutene?



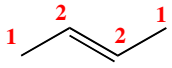
In a 4-membered ring, bond angles are forced to be near 90°. Since sp^2-hybridized carbon prefers 120° bond angles, this deviation will increase the energy of the system and weaken the π-bond (this deviation from ideal bond angles is called angle strain). Angle strain is not a problem in acyclic systems such as 1-butene. In addition, sp^3-hybridized carbon has a little less angle strain in a 4-membered ring than sp^2-carbon because the deviation from the ideal angles (109.5° for 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?

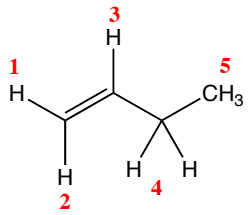
d)



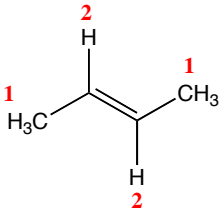
4 carbon signals



2 carbon signals

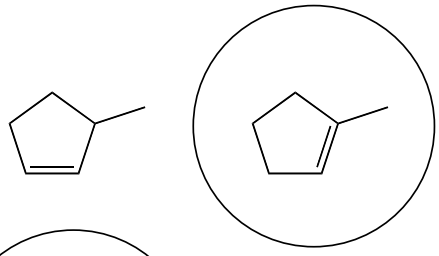


5 hydrogen signals

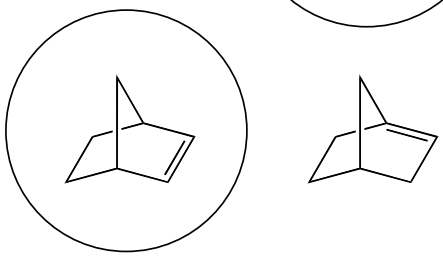


2 hydrogen signals

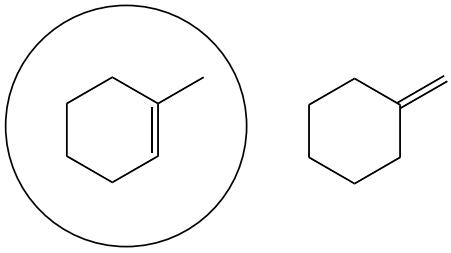
Question 4. For the following pairs of compounds, circle the molecule that is **more stable**.

a) 

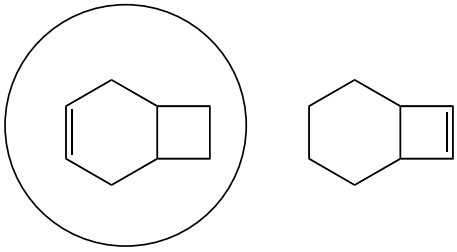
Increased olefin substitution

b) 

This structure disobeys Bredt's Rule

c) 

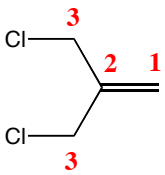
Increased olefin substitution

d) 

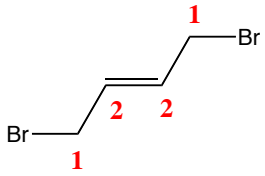
This structure has increased angle strain - see Question 3, part c.

Question 5. How would you tell the following pairs of compounds apart by ^{13}C NMR spectroscopy?

a)

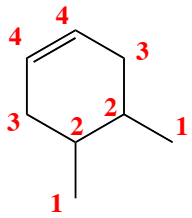


3 signals

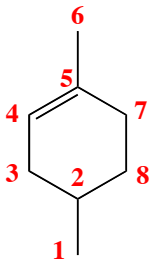


2 signals

b)

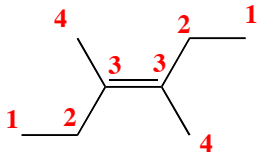


4 signals

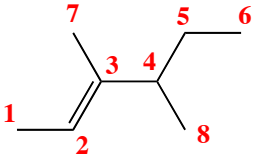


8 signals

c)



4 signals



8 signals