$\qquad$ Answers

Score: _key_/120

## CHEM 302

Organic Chemistry I
Exam I
7-October-2009

1) Write complete, correct IUPAC names for the following compounds:
a)

(3S), (4S)-2,3,4-trimethylhexane
c)

trans-4-ethyl-1-tert-butylcyclohexane
b)

(2R)-2-bromo-3,3,-dimethylbutane
d)


E-4-fluoro-3-methyl-4-octene
(can also name: trans-1-(1,1-dimethylethyl)-4-ethylcyclohexane)
e)


E-4-tert-butyl-3-isopropyl-5-methyl-3-octene
2) Write structures for the following names:
a) 1-bromo-2-methylpentane
b) cis-1-bromo-2-chlorocyclopropane

(no stereochemistry was specified, so this picture is sufficient.)
c) (2S, 3S)-2-bromo-3-methylpentane
d) (E)-3-Bromo-1-fluoro-2-methylpropene


e) (E)-5-Methyl-4-(1-methylbutyl)-4-hepten-2-yne

(I sent an email about a typo in this problem)
3) Being able to name complex side-chains is an important part of organic chemistry, as the structures below demonstrate. Give IUPAC (i.e. proper) names for all the alkyl groups marked by dashed lines in the structures of these biologically important molecules below. Identify each group as a primary, secondary, or tertiary alkyl substituent.
a)


## Vitamin D

The attachment is secondary (carbon of attached group is itself attached to two other carbons) and would be named: 5,6-dimethyl-2-heptyl.
b)


Cholesterol
The attachment here is (again) secondary for the same reasons, and the group is named: 6-methyl-2-heptyl.
c)


Valine
Secondary
2-propyl
(isopropyl)

d)

Leucine

Primary
2-methyl-1-propyl (isobutyl)
e)

Isoleucine

Secondary 2-butyl
4) Assuming that as alkyl groups get larger, the torsional strain they induce increases (i.e. two ethyl induce more strain than an ethyl and a methyl, which induce more strain than two methyls), draw a qualitative energy diagram for 3,4dimethylhexane, viewed down the $\mathbf{C} 3, \mathbf{C} 4$ bond. Please use the structure given below. (Later, we will discuss why I chose this structure.)


Probably the best way to approach this problem is to draw the conformers, and then try to put them in some sort of order. Here are the conformers:

1

2

3



Now here is a relative energy ordering. We need to realize that: $\mathbf{2}$ and $\mathbf{6}$ are the same, as are $\mathbf{3}$ and $\mathbf{5}$. It seems to me that $\mathbf{1}$ is the highest energy, and that $\mathbf{4}$ is the lowest energy. $\mathbf{2}$ and $\mathbf{6}$, being staggered are going to be of lower energy than $\mathbf{3}$ and $\mathbf{5}$, which are eclipsed. So we have: $\mathbf{4 < 2 ( = 6 ) < 3 ( = 5 ) < 1}$

5) How would you differentiate between the two compounds in each of the following pairs by ${ }^{13} \mathrm{C}$-NMR spectroscopy?

a)

4 different signals
8 different signals
b)


3 different signals
and


2 different signals


4 different signals
8 different signals.
6) In the text, Prof. Jones developed the molecular orbitals (MOs) for $\mathbf{H}_{\mathbf{2}}$. Let's expand on that diagram and use it to generate the MOs for linear $\mathrm{H}_{3}(\mathrm{H}-\mathrm{H}-\mathrm{H})$. [This molecule may not exist, but the method of development is still valid!) This diagram may be more easily generated if one inserts the third hydrogen between the other two (i.e. $\mathrm{H}-\boldsymbol{H}-\mathrm{H}$ where the $H$ is the inserted one.) Beware of orthogonal interactions, and place these orbitals in terms of increasing energy. Be clear in your drawing!

Here is a simple MO diagram for $\mathrm{H}_{2}+\mathrm{H} ; \mathrm{H}_{2}$ on the left, H on the right, hypothetical $\mathrm{H}_{3}$ in the middle.

$$
\mathrm{H}-\mathrm{H} \quad \mathrm{H}-\mathrm{H}-\mathrm{H}
$$

H


The lowest and highest orbitals are formed from the addition and subtraction of the H -atom orbital and the $\mathrm{H}_{2}$ bonding orbital (the lower energy one). The middle orbitals is (essentially) the unchanged $\mathrm{H}_{2}$ anti-bonding orbital. Here's the logic. There are only three atomic orbitals entering the mixing scheme, so there can only be/need to be only three molecular orbitals. If we let the H -atom orbital interact with the antibonding $\mathrm{H}_{2}$ orbital, no matter how we do the mixing, we get one "bonding" (i.e. favorable) interaction and one "antibonding" (unfavorable) interaction. Since that would give us four orbitals and we only need three, we can take a liner combination of these two and get the orbital shown. (There is also a symmetry-based argument which beyond what this class is aimed at covering.)

