## HOMEWORK PROBLEMS: ALKENE REACTIONS

1. Does the addition of HBr to the following alkene give syn addition, anti addition or a mixture of both? Briefly explain your answer using the structure of the intermediate formed in this addition. How/why is this different from addition of $\mathrm{Br}_{2} ? \mathrm{H}_{2}$ ?

2. Rank the following compounds from most reactive (1) to least reactive (4) towards $\mathrm{O}_{3}$. Also rank their reactivity towards $\mathrm{BH}_{3}$. Briefly explain your answers.
P1
3. In the addition of electrophiles to alkenes, most electrophiles will add to the most reactive alkene first (most electron rich alkene). The two exceptions to this generalization are $\mathrm{H}_{2}$ and $\mathrm{BH}_{3}$. Provide the products when the following alkene reacts with the two reagents shown below. Be sure to draw correct stereochemistry where necessary and explain why the electrophile added to the position you indicated.

4. Preparation of Alkenes. The main way to prepare an alkene is to perform an elimination reaction of an alcohol (via carbocation) or an alkyl halide. For the two reactions shown below draw all possible products and then circle the one that is favored under thermodynamic conditions. We will see mechanisms for these reactions in a later chapter.


5. A compound with molecular formula $\mathrm{C}_{13} \mathrm{H}_{19} \mathrm{Cl}_{2} \mathrm{NO}_{2}$ reacts with 2 equivalents of $\mathrm{H}_{2}$ upon hydrogenation, how many rings are present in this compound? Upon ozonolysis, one equivalent of $\mathrm{CO}_{2}$ is produced. Draw a structure that fits this data.
6. Which reagents give anti addition to alkenes? What do they all have in common? Which reagents give syn addition? What do they all have in common?
7. Mechanisms. Provide a complete mechanism for each of the following reactions.



8. Reactions. Give the structure of the major organic product(s) expected from each of the following reactions. If necessary, indicate product stereochemistry.












9. Supply the missing reagent, reactant, or product. If more than one product can formed, give all possible products, and indicate which would be the major product. Be sure to indicate the stereochemistry and regiochemistry of the products where appropriate. The last three are particularly challenging.
a.

b.

c.

d.

e.


f.


g.

h.

i.
j.


$$
\xrightarrow{\mathrm{Br}_{2}}
$$

$\xrightarrow{\mathrm{H}_{2}, \mathrm{Pd} / \mathrm{C}}$
k.

1.

m.

10. Give the missing products, reactants, or reagents for the following reactions.
a.

b.

c.

d.


e.

f.

g.

h.

$\xrightarrow[\text { 2) } \mathrm{NaBH}_{4}]{\text { 1) } \mathrm{Hg}(\mathrm{OAc})_{2}, \mathrm{H}_{2} \mathrm{O}}$
i.

j.
k.


1.

m.

n.

o.

p.

11. Using mechanistic arrows, draw a detailed mechanism for the following reactions.
a.

b.

12. Draw a reasonable mechanism to explain the outcome of the following reaction. Be sure that your mechanism explains the observed stereochemistry.



13. Given the results from the oxymercuration reaction below, predict the products from treating the same alkene with $\mathrm{Br}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$. Draw a mechanism that explains the regiochemistry and stereochemistry of the product.




$\xrightarrow{\mathrm{Br}_{2}, \mathrm{H}_{2} \mathrm{O}}$
??
14. Give the stereochemical relationship of the products formed (i.e. enantiomers, diastereomers, etc) in the reactions below. Recall that the method we use is to look at the products from both top and bottom face attacks and then to determine the stereochemical relationship between them.
a.
b.




15. Provide a synthetic sequence to go from the given starting material to the desired product. Show all reagents and synthetic (not reaction) intermediates. All these syntheses can be accomplished in two or three steps.
a.

b.



c.


d.

e.

f.

g.

h.

16. Propose syntheses to accomplish the following transformations. Each transformation can be done in two or three steps.
a.

b.

c.

(can't avoid the mixture of these two compounds)
17. Treatment of compound $\mathbf{A}\left(\mathrm{C}_{6} \mathrm{H}_{14} \mathrm{O}\right)$ with $\mathrm{H}_{2} \mathrm{SO}_{4}$ gave two alkene products, with $\mathbf{B}$ as the major product. Catalytic hydrogenation of $\mathbf{B}$ gave 2-methyl-pentane as the only product. Hydroboration (1. $\left.\mathrm{BH}_{3}-\mathrm{THF} ; 2 . \mathrm{H}_{2} \mathrm{O}_{2}, \mathrm{NaOH}\right)$ of $\mathbf{B}$ gave a single compound, alcohol C. Ozonolysis of $\mathbf{B}$ gave a ketone and an aldehyde (no formaldehyde): compounds $\mathbf{D}$ and $\mathbf{E}$. Show the structures of all the compounds: $\mathbf{A}, \mathbf{B}$, $\mathbf{C}, \mathbf{D}$, and $\mathbf{E}$.

