Chapter 4 – Introduction to Alkenes. Structure & Reactivity

Introduction

Chapters 4 and 5 both deal with alkenes and can be viewed as a single extended chapter. Chapter 4 introduces several basic features of alkenes, the functional group corresponding to a carbon-carbon double bond. Chapter 5 continues this discussion by focusing on chemical transformations of alkenes. The division of topics between chapters 4 and 5 is not precise, however, and this provides me with an opportunity to make an important point: material introduced in an early chapter will often be the platform for a discussion in a later chapter. You need to regard all of the chapters that will be covered this semester (and next) as parts of a single, interconnected whole. If you should happen to lose track of, or skip, material in one chapter, you will find yourself having to deal with all kinds of loose ends in subsequent chapters.

Checklist

When you have finished studying Chapter 4, you should be able to:

1. Describe the covalent bonding in (and around) an alkene
   a. Identify sp^2 hybridized atoms
      i) Draw orbital cartoons of sp^2 hybrid orbitals showing their directionality and nodal surfaces
   b. Identify atomic (hybrid) orbitals on neighboring atoms that can engage in *sigma* overlap
   c. Identify atomic orbitals on neighboring atoms that can engage in *pi* overlap
   d. Draw an orbital interaction diagram showing
      i) relevant atomic (hybrid) orbitals, their occupancies, and relative energies
      ii) bonding and antibonding orbitals, their occupancies and relative energies
   e. Draw orbital cartoons of bonding and antibonding orbitals.
      i) Locate nodal surfaces on your cartoons
   f. Correlate atom hybridization, orbital overlap, bond length, and bond strength
2. Name and draw alkenes and cycloalkenes
   a. Name and draw *Z* and *E* stereoisomers
   b. Name and draw *cis* and *trans* and stereoisomers
3. Use a molecular or structural formula to calculate a molecule's *unsaturation number*
4. Predict the physical properties of alkenes
   a. Predict boiling point and water solubility by comparison with the analogous alkane
   b. Predict relative dipole moments of *Z* and *E* stereoisomers and the analogous alkane
5. Use *heats of formation*
   a. To calculate the *standard enthalpy change* for a chemical reaction
   b. To compare the stabilities of alkene isomers and stereoisomers
6. Starting with two structural formulas, use substituent effects and van der Waals repulsions to estimate the relative *stabilities* of alkene isomers and stereoisomers
7. Use chemical equations to identify *addition* reactions
8. Plan and predict the outcomes of the following chemical reactons:[1]
   a. Addition of hydrogen halides to alkenes
   b. Acid-catalyzed addition of water to alkenes (*hydration*)
   c. Addition of hydrogen to alkenes (*catalytic hydrogenation*)
9. Describe and interpret phenomena associated with the chemical reactions listed in items #8ab
   a. by drawing *detailed mechanisms*, complete with curved arrows and alternative resonance structures (when called for)
   b. by drawing *reaction energy diagrams*
   c. by referring to reaction *rate laws*
      i) and *rate-determining steps*
      ii) and the *principle of microscopic reversibility*
   d. by referring to the structure and energy of key *transition states*
   e. by referring to the structure and energy of key *intermediates*, particular *carbocations*
      i) and by referring to the *Hammond postulate*
      ii) by invoking well-precedented *carbocation rearrangements*, such as *hydride shifts* and *alkyl shifts*
   f. by anticipating *regioselectivity* and *carbocation rearrangements*
   g. by applying *Markovnikov's rule*

[1] This is the complete list of new reactions in chapter 4.

Top 13 Problems for Chapter 4

All of these problems are drawn from the *Additional Problems* located at the end of the chapter 4.

The top 13 for chapter 4 are **41, 44, 47, 50, 54, 56, 57, 58, 60, 63, 65, 66, 67**.

Supplement

This chapter introduces many important *types* of topics: drawing chemical reactions, drawing reaction mechanisms, functional group transformations, the construction and interpretation of reaction energy diagrams, and several related concepts: transition states, barriers, reaction intermediates, and so on. It also describes several *specific examples that you are expected to learn*. Therefore, this supplement is a bit longer than most.

Three Study Tips: Draw. Draw. Draw.

I can't overstate this: DRAW. Why should you draw? Because:

- drawing uses a different part of the brain than reading, seeing, or listening; getting more parts of your brain involved in learning strengthens your learning; the authors of a widely used textbook may have put it best when they said organic chemistry needs to be learned through one's "fingertips";
- drawing is a problem-solving tool in its own right; although *simple* problems, i.e., the kind that can be completely visualized and solved in your head, don't require drawing, simple problems will be the *exception*, not the rule;
- drawing is how you communicate your answers on exams; the ability to make complete and accurate drawings quickly is essential and only comes through practice;
- no matter how much you *understand* about how to make a drawing, it is the actual ability to draw that counts and this requires practice.

So here are three tips that will help you get the drawing practice you need:

#1 – Carry a pencil and some scratch paper everywhere you go (and use them). If you don't have pencil and paper handy, use a chalkboard.

#2 – Draw everything. OK, don't draw *everything*, but force yourself to draw more than you think is necessary or even helpful. The more you draw, the easier it gets. The more you draw, the better your drawings will be. The more you draw, the more helpful drawing will be to you. If a figure in your book shows a mechanism, *copy* it. If you see another transformation that probably occurs by the same mechanism, try drawing the mechanism again for the new molecule. Draw lone pairs and formal charges. Draw curved arrows. Draw conformations and energy diagrams. Draw *everything you can*, until drawing becomes so easy that you no longer notice the effort it takes. Then, *and only then,* you can think about cutting back.

#3 – Be your own coach. Notice what is easy, what is difficult, and adjust your practice accordingly. Learn to spot your own weaknesses and convert them into strengths.

Chemical Transformations – Plan, Predict, Describe

This chapter introduces a topic that will occupy us for the rest of the year: *functional group transformations*. Alkene reactions are a good place to start because alkenes are easy to spot (just look for C=C) and most alkene reactions are *additions* (Ch. 4.6).

When chemists think about a functional group transformation, they naturally think about three questions:

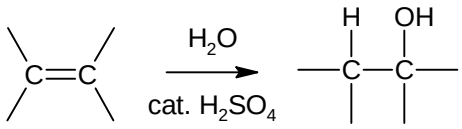
- **Planning** – What must I do to obtain a particular compound (A-C-C-B)? What reactant (C=C) should I start with? What reagents are needed?
- **Predicting** – If I combine a molecule and a reagent, what will happen? What product will be obtained?
- **Describing** – Describing includes many things. Is a transformation favorable? Exothermic? Does it occur quickly? Is there any ambiguity regarding the product that will obtained, e.g., is the reaction regioselective (Ch. 4.7A) or can a key intermediate rearrange before forming the product (Ch. 4.7B)? How do we explain these observations? Is there a step-by-step mechanism that is consistent with these observations?

The first two questions – planning, predicting – apply to *all* of the chemical transformations covered in this course. You need to learn three things: the functional group that you must begin with (the *reactant*), the *reagents* that transform this group, and the functional group that you end with

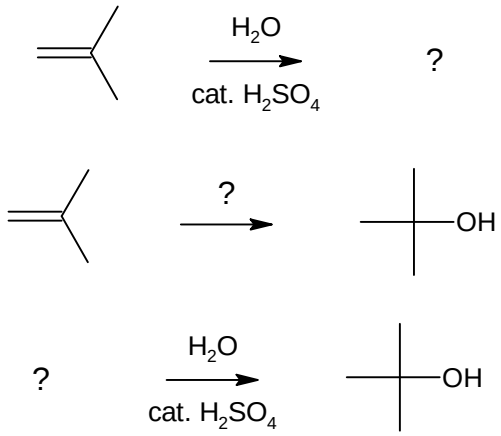
(the *product*). For example, the acid-catalyzed hydration of alkenes can be viewed as:

- Reactant: alkene, C=C
- Reagents: H_2O + catalyst (often H_2SO_4)
- Product: alcohol, H–C–C–OH

Another way to summarize this is with a chemical equation that contains all three key items:



A very simple kind of question that checks a student's understanding of this material is to leave out one item and ask the student to fill in the blank, e.g.,



The top question asks for a prediction, what will happen? The middle and bottom questions ask for planning, what is needed to make this work? The answer to any of these questions is simply the missing piece.

In some sense, functional group transformations are the "vocabulary" of organic chemistry. If you think of organic chemistry as a foreign language, you know that mastering the vocabulary is fundamental, but not an end in itself. You must master a language's vocabulary so that you can begin to tell stories, to make sentences and paragraphs.

To press this analogy one step further: you also know that a foreign vocabulary must be in your head to be useful. If you have to reach for a dictionary to translate every word, you don't really know anything at all. The vocabulary must be memorized. Flash cards are one useful way to do this and the Study Guide/Solutions Manual contains some helpful examples (see Fig. SG5.1, p. 73, and the text that accompanies it).

I haven't said much about the third question: "describe". How to describe a transformation, and even what needs to be described, is fairly nebulous. The most complete description is one in which we can 1) draw a step-by-step mechanism for the reaction, and 2) say something about the structure and energy of each key species (transition states, reactive intermediates, competing products) that might appear during the reaction. However, a full description of this sort is not always helpful to beginning students. Therefore, your book provides extensive descriptions of some reactions, e.g., addition of hydrogen halides, and very limited descriptions of others, e.g., catalytic hydrogenation, and the amount you need to learn should be adjusted accordingly.

Learning and Drawing Mechanisms

Every mechanism is a hypothesis. A mechanism can never be proven (to "prove" a mechanism, one would have to observe every molecule that undergoes a reaction and all of the changes it undergoes), but experimental measurements can disprove a mechanism. So why is it important to draw mechanisms?

When we hear the word "hypothesis", we often find ourselves thinking "tentative, unreliable, anybody's guess," but this perspective is not helpful. Not all hypotheses are created equal. I can posit "the Moon is held in the sky by a big invisible bird", but my hypothesis has never been tested. The scientific explanation for the Moon's behavior (the Moon is attracted to the Earth by gravity, but is moving so fast that it never falls on us) may seem rather odd (what is "gravity"? I don't see the Moon moving!), but it has withstood countless tests. Not only that, the scientific explanation is consistent with many other experimental observations. Of course, these things don't prove the scientific hypothesis, but we certainly shouldn't regard this hypothesis as "unreliable" or "anybody's guess".

A similar statement can be made about many of the mechanism drawings in your book. They have withstood many tests and they provide a consistent view of many chemical reactions, not just one or two. Therefore, while we can't literally say a mechanism is "true", we can usually know that learning a mechanism will provide insight into a great deal of chemistry.

Most organic reactions require several steps and a complete step-by-step drawing of the mechanism should include the following:

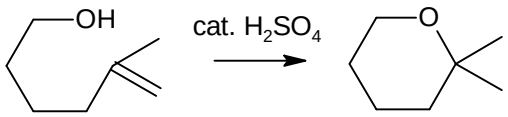
- each step of the reaction
  - What is a *mechanistic step*? A step corresponds to the crossing of a single reaction barrier, i.e., passage through a single transition state.
  - Physically, a step might correspond to *one* energetic collision (bimolecular step) or *one* energetic vibration (unimolecular step).
  - Steps should be separated by reaction arrows: →.
- curved arrows
- complete structural details around *reacting* atoms and bonds
  - Essential structural details include: formal charges, lone pairs, *neighboring* atoms and bonds.
  - Do not use skeletal formulas for the *reacting* atoms. Avoid using skeletal formulas for the *reacting* bonds.

A mechanism problem is an opportunity to tell a story. How did compound A turn into compound B? As with the telling of any story, leaving stuff out or introducing unexplained changes makes your story hard to follow. You must tell your story with *great care* in order to be understood.

Many mechanism problems are also puzzles. They give you a seemingly surprising transformation and ask you to explain how it came about. It is important to remember that you are being asked to construct a hypothesis and this hypothesis will be more plausible if it looks like other hypotheses (mechanisms) that chemists already accept. To put it another way, a puzzle problem asks you to take *what you already know* about mechanisms and apply it to a new situation. You will never be asked to invent new chemistry to solve a (textbook) puzzle, so if you feel that you are drawing something you've never seen or drawn before (so-called "novel" chemistry), you are almost certainly headed in the wrong direction. Go back and look for something more familiar that can explain the observations.

Some common drawing mistakes:

- Combining different reactions in a single step. This is sometimes motivated by a desire to "save space". It always reflects a failure to appreciate the significance of each step in the drawing. Combining steps defeats the purpose of a mechanism, namely, it keeps us from seeing each transformation that a molecule must undergo to get from reactant to product. Each step, each intermediate, deserves its moment of glory.
- Three-molecule collisions. This mistake usually appears with the previous one. If you think A, B, and C all collide in one step to make D, think again. Probably A and B collide to make Z, and then a bit later, Z collides with C to make D.
- Assuming water is the solvent. Most organics are insoluble in water so water is rarely used as a solvent (even when it is a reagent).
- Assuming the reactants and reagents must be separate molecules. For example, alcohols (ROH) can add to alkenes (C=C) in an acid-catalyzed reaction. If a molecule contains both a hydroxyl (OH) group and an alkene (C=C), these groups may combine in an *intra*molecular reaction, e.g.,



- Drawing HO^- as the base for a reaction carried out under neutral or acidic (or acid-catalyzed) conditions. If a solution is neutral, or acidic, the concentration of HO^- must be *extremely low*. Therefore, its participation is almost impossible. It is much more likely that a neutral molecule acts as a base (solvent? a second reactant molecule?).
- Drawing H_3O^+ as the acid for a reaction carried out under neutral or basic conditions. The participation of H_3O^+ under these conditions is almost impossible (see previous paragraph). Here, too, a neutral molecule probably acts as an acid.
- Keep in mind that a strong acid such as H_3O^+ and a strong base such as HO^- are incompatible reagents. If both were present, they would neutralize each other long before any other interesting chemistry, e.g., addition to an alkene, might occur.

The best way to learn to draw a mechanism is to *draw*, but not just any drawing will do. An *accurate* drawing is called for. Therefore, it is best to get started by *copying* the drawings in your book. You can do this in a couple of ways:

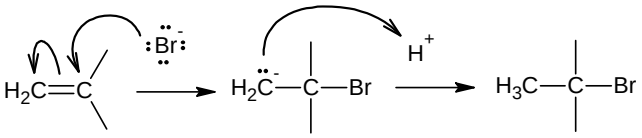
- Copy a mechanism that it is in the book. For example, copy the drawings in eqns. 4.19 and 4.20

(p. 150). Can you see how each of *your* drawings leads to a different carbocation?

- Copy and then add "missing" pieces to a mechanism in the book. For example, eqn. 4.28 (p. 156) shows two mechanisms *without* curved arrows. Copy the entire mechanism and add a convincing set of arrows.

When you copy a mechanism, don't just copy the symbols. Also copy the *information* contained in these symbols. This information is packaged in many ways:

- Each reaction belongs to a *family*. Give its name. For example, in eqn. 4.28 (p. 156), there is a:
  - Proton transfer (acid-base reaction)
  - Methyl shift (rearrangement reaction)
  - Lewis acid-base reaction
- Pay attention to *electrons* and the atoms that hold them.
  - Where does each electron pair start?
  - Where does it end up?
  - How does its energy change? (Does a bond become a lone pair? Does a lone pair become a bond? Does a sigma bond become a pi bond?)
- Pay attention to the *sequence* of reactions. The following mechanism for HBr addition to an alkene uses *exactly the same* reactions as the orthodox mechanism, but in reverse sequence. This leads to many differences. How many can you find?

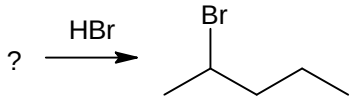


- Pay attention to the *roles* of the reactants.
  - Make a habit of finding the nucleophile, electrophile, and leaving group (if there is one).
  - If a particular kind of reaction requires special roles, then find these role players. Which molecule is an acid? A base? A Lewis acid or base? A carbocation?
  - If a role can be characterized energetically, make this characterization. Is an acid strong or weak? Is a base strong or weak? Is a carbocation primary, secondary, or tertiary?
- When you "pay attention", don't just "think" the information. Say it out loud. Write it down.

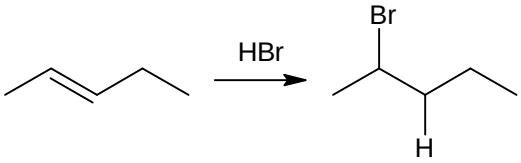
Remember, mechanism drawings are more complicated than any other drawings you will make in this course. They are a story in drawings. We only resort to them when we have to (for example, the fill-in-the-blank problems in the previous section should not be solved by drawing mechanisms), but they reflect how organic chemists think and this is what you are trying to learn.

A Few More Words about Synthetic Planning

The most common mistake is to follow a plausible method for generating answers, generate one answer, and *stop thinking*. For example, what starting material might be suitable for the following transformation?



If you recall that "H" and "Br" usually add to *adjacent* C, you might notice that the central C in the product is bonded to two H, and then draw the following:



This isn't bad, but it ignores the fact that HBr can add to an alkene in *two* ways and you need to consider whether HBr addition will be *regioselective*. The alkene shown above probably won't react selectively so two products should be expected. A better plan would be to start with an alkene that will react regioselectively, but you won't figure this out if you fall into the trap of thinkin, "I've got an answer. I'm done."

The best synthetic plan is one that relies on chemical reactions that are favorable, reasonably fast, and *have no competing side reactions*.

Energy Barriers, $\Delta G^{o\ddagger}$, and Rate Constants, *k*

Your book talks about the relationship between reaction *rates* and energy barriers (Ch. 4.8B and eqns. 4.32, 4.33), but it doesn't say anything about rate constants. Let's explore this point a bit further.

The rate of a chemical reaction depends in some way on the concentrations of the reacting species. For example, if A + B → C in a one-step reaction, the reaction rate can be increased by raising the concentration (moles per volume) of either A or B because this will make collisions between A and B more frequent. This relationship can be expressed mathematically,

$$\text{rate} = k[A][B]$$

The proportionality constant that connects rate and concentration is called the *rate constant, k*. This constant reflects the intrinsic difficulty of the reaction. To see this, imagine [A] = [B] = 1 *M*. The reaction rate under these conditions will be equal to the rate constant.

The other quantity that represents the intrinsic difficulty of the reaction is the energy barrier, $\Delta G^{o\ddagger}$. The reaction rate and energy barrier have an *inverse* relationship: the larger the barrier, the smaller the reaction rate. Moreover, the relationship is exponential. Small changes in the barrier lead to large changes in the rate.

Your book makes the point (Ch. 4.8B) that at room temperature, if the *barriers* of two competing reactions differ by 5.7 kJ/mol, the *rates* will differ by a factor of 10. Since rates and rate constants are proportional, we can now say that the *rate constants will differ by a factor of 10* as well.

When you look at a reaction energy diagram like that in Fig. 4.14, you should be able to assess the energy barrier for each step in both the forward and reverse directions. You should also be able to estimate the relative size of the *rate constants* in each direction. The largest rate constant will be associated with the smallest barrier and *vice versa* (but remember that this relationship is *exponential*; small changes in barrier lead to LARGE changes in rate and rate constant).

The maximum magnitude of a rate constant is limited by physical constraints.[2] If a reaction is bimolecular, the maximum rate corresponds to a situation where *every collision* produces a reaction (this is called a *diffusion-controlled* reaction). The rate constant for a diffusion-controlled process is about 10^{10} M s^{-1}. If a reaction is unimolecular, the maximum rate corresponds to a situation where *every vibration* produces a reaction. The rate constant in this situation is about 10^{13} s^{-1}. Hardly any reactions approach these rates, however, and most rate constants are less than one (10^0).

One reaction that proceeds very quickly is a *favorable proton transfer*, e.g., HCl + NaOH → H_2O + Na^+ + Cl^-. The barriers for these reactions are always quite small and the rate constants are always very large. When you draw a mechanism, expect *favorable* proton transfers to occur more rapidly than any other process save a change in conformation. When you draw an energy diagram for such a mechanism, make the barrier for this reaction very small.

Favorable Lewis acid-base reactions can also be very fast. If you look at the reaction energy diagram in Fig. 4.14 (p. 163), you will see that the carbocation and bromide ion can react in two ways: a favorable proton transfer that leads back to the reactants and a favorable Lewis acid-base reaction that leads to the product. The energy barriers for both reactions are quite small (and the rate constants would be correspondingly large).

Substituent Effects, Hyperconjugation, and Carbocations

This chapter introduces two kinds of alkyl group effects, one involving alkenes and the other involving carbocations. Before you think too much about these effects, try for a moment to recall another alkyl group effect that you have studied. Can you think of any?

We have considered the chemical effects of alkyl groups once before in connection with pK_a values (Ch. 3). In that context, we found that alkyl groups did not affect these values in any important way. For example, HOH and all kinds of ROH had about the same pK_a values. A similar

[2] Quantum mechanical "tunneling" provides a physical alternative to standard collisions and vibrations, and rate constants can be larger when tunneling is important.

non-effect was observed on the pK_a values of HCO_2H versus RCO_2H, and NH_4^+ versus RNH_3^+. If alkyl groups (de)stabilize an acid to any degree, they appear to have about the same effect on its conjugate base.

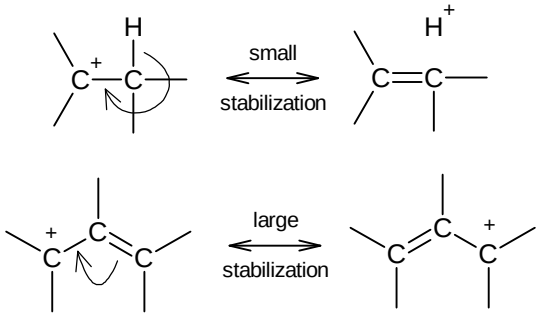
The non-effect of alkyl groups on pK_a values is useful to remember because an acid and its conjugate base have different ionization states. This suggests that alkyl groups interact about the same way with neutral and charged functional groups.

The data in this chapter present a different picture of alkyl group effects. Replacing an alkene hydrogen with an alkyl group stabilizes the alkene by about 7 kJ/mol. Alkenes are neutral and electron-rich, so these data suggest that alkyl groups are electron-withdrawing groups.

Other data, however, show that replacing a carbocation hydrogen with an alkyl group stabilizes the cation by about 70 kJ/mol, a much larger effect. Carbocations are positively charged and electron-poor, so these data suggest that alkyl groups are electron-donating.

These conflicting views, alkyl groups are electron-withdrawing/donating, are not easily reconciled. It may be that different mechanisms are responsible for the stabilizing effect of alkyl groups on alkenes and carbocations.

Although your book does not mention it (yet), other kinds of groups have much larger effects on carbocation energy. When these groups are present, the effects of alkyl groups become much less important. For example, a single *vinyl* group ($-CH=CH_2$) stabilizes a carbocation about as much as *two* alkyl groups, and a single *phenyl* group ($-C_6H_5$) provides even more stabilization.



Why is a vinyl group so much better than an alkyl group at stabilizing a carbocation? An answer can be developed through a comparison of resonance structures. *Hyperconjugation* (top) delocalizes *sigma* electrons in one structure, converting them into *pi* electrons in the second structure. Pi electrons are not as stable as sigma electrons, so the structures do not contribute equally to the resonance hybrid. *Conjugation* (bottom), on other hand, delocalizes *pi* electrons and preserves them as pi electrons. The delocalized electrons have about the same energy in both resonance structures so the structures *contribute about equally* to the resonance hybrid. This situation produces much greater resonance stabilization.

Another explanation can be developed using MO models. The Study Guide/Solutions Manual describes an MO model of hyperconjugation in section 4.3 (p. 50-51). The orbital interaction diagrams that are shown in Fig. SG4.1 and below (upper) show that hyperconjugation stabilizes the electrons occupying the CH sigma BMO. You can easily construct an analogous diagram for a conjugated system by replacing the CH sigma BMO with a CC *pi* BMO (below, lower). The pi BMO has a higher energy than the sigma BMO, so the energy gap between it and the empty C *2p* orbital is smaller. Also, the pi MO overlaps more effectively with the empty C *2p* orbital. These two factors, a smaller energy gap and better total overlap, make $E_{stabilization}$ larger in the conjugated system.

Orbital interaction diagrams for hyperconjugation (top) and conjugation (bottom) in carbocations