

Chapter 4. Ouellette, 2/e. Chemistry X402.

Ch 4. Alkenes and alkynes.

Read Ch 4 for class 3.

Homework. See homework section below, which includes a flexible written assignment.

Skip: Sections 5, 12-14. An overview of these sections is later in the handout.

Advanced:

- In general, we will emphasize alkenes over alkynes. For the most part, they are quite “similar”, and alkenes are much more common, both in the lab and in Nature.

You are responsible for

- the basic nomenclature of alkynes;
- the general idea that they usually behave similarly to alkenes;
- the basic geometry of alkynes.

But most details specific to alkynes, such as the special reduction (hydrogenation) reactions for alkynes (p 114) are “advanced”.

- The orbital explanation for the bonding in unsaturated compounds is introduced in Sect 1.8. This is not critical for understanding the content of Ch 4, but really is important if you are going on. A good goal is to make sense of Fig 1.6, and understand how the π bond of an alkene restricts free rotation, thus leading to cis-trans isomerism. More about this in Computer resources.

⇒ A **practice quiz** for Alkenes is at the web site.

Reminders...

- Please sign up for the class e-mail list; see handout or web page for information.
- Ch 3 homework is due in class 3.
- Test 1 is week 4; it will (probably) cover Ch 3-4. I will hand out a sample test in class 2.

Essay. Not assigned. Also note the (non-assigned) essay in Ch 10 (p 286). This is on retinal, the vision pigment. Part of its action involves a cis-trans isomerism at a C=C double bond. Both of these essays are on biochemical issues.

Notes

Sections 4.2-4 discuss naming the geometric isomers of alkenes. Both the cis-trans system and E,Z system are described. Which should you use? Both are common. Cis-trans is “traditional”, but E,Z is official IUPAC and more versatile. Further, learning the priority rules for the E,Z system will help you in Ch 6; the same priority rules are the basis of the R,S system for

naming chiral isomers. It is good to learn both cis-trans and E,Z, so you can recognize them. If you are naming a compound, you can use either, unless the question specifies -- or unless one does not work. For practice, you might try using both. But when you find cis-trans ambiguous, stick with E,Z.

I have posted a web page introducing the E,Z system for naming alkene isomers. It includes more examples, mainly in response to student comments about things that were not entirely clear from Ouellette. Ouellette tells the basic E,Z story fine, but you may find this a useful elaboration.

Sect 4.7 discusses oxidation of alkenes. All of the other reactions of alkenes that we discuss are addition reactions. These oxidation reactions seem to be a type of exception, but actually they are additions, too. The oxidation reactions shown are quite complex, involving multiple steps. In each case, step 1 is an addition across the double bond; see Computer Resources, below, for an example. The purpose of this comment is to help you unify the material; you are not responsible for the mechanistic details of the oxidations. See Marx (2003) below, for more about ozonolysis.

Sect 4.8 & 9, Markovnikov's rule. Note that the M rule was originally an empirical observation, without explanation. Even as such, it is useful; we can predict the products of a reaction, even if we do not understand why. Sect 9 then discusses the reaction in more detail, and that deeper understanding reveals the reason for the M rule. You are responsible for this discussion of reaction mechanism. (This is the only reaction mechanism you are responsible for in this course.)

Sect 4.11, polymers. There are two broad classes of polymers. One class, introduced here, is addition polymers. These can be thought of, formally, as the addition of one alkene across the double bond of another alkene. The adding alkene is of the form A-B, as with all adding reagents. "A" is the H attached to a double bond. (I'll draw this out in class.) The second class of polymers, condensation polymers, will be introduced in Ch 12, with the underlying basic condensation reaction. The distinction between the two classes will be clearer after both have been introduced.

As a generality, condensation polymers are much more important in biology than are addition polymers. However, addition polymers include many of the common "plastics" (Table 4.2).

Reaction summary. Don't be intimidated by how long it seems. Remember that we are emphasizing alkenes over alkynes, and that we skipped the sections on synthesis. But even if you consider the entire list, look for ways to organize it. For example, how many of his 13 items could all be listed under one main heading, addition reactions? Also note that the synthesis reactions (which you are not responsible for at this point) are essentially the reverse of some of the addition reactions. Showing such reactions in pairs, where both the forward and reverse reactions are important, is another good way to organize reactions.

I encourage you to make your own reaction summaries, either by going through the chapter yourself or by reorganizing his. Reaction summaries that include

material from more than one chapter may be useful, too. Show them to me, and I will offer comments, and maybe even share some of them with the class.

Homework

If you would like written feedback on some of these... Anything you turn in at class 3 will be returned in class 4 -- which is test night. If you would like it back sooner, give me a SASE when you turn it in, and I will try to get it in the mail within a day or so. You can also ask me questions during the week, by the class e-mail list, private e-mail, or phone. You can mail me things during the week; if I get it by class-day mail, I will bring it to the next class.

As usual, I encourage you to do the Explorations with Models. If nothing else, do #1 even if you do it simply on paper.

Suggested problems: #1-44, 53-54. As you do these, remember to emphasize alkenes over alkynes. But doing the practice with both is probably good. #45-52 are on "advanced" topics.

As a written assignment, choose one of each type (i.e., one from each section). Remember, the main value of turning in homework is the feedback, not impressing me with how many you did. It is to your advantage to turn in some sampling, so I can look over your work generally, and also to turn in those that bother you. Unfortunately, feedback is slow with a once-a-week class, so be sure to turn work in early enough that you get it back before a test.

Errata

p 114, eqn at bottom of page. In structure shown for 5-decyne, the double bond should be a triple bond.

p 136, #39. Answer given in back of book for compound a is garbled. Answer in Study Guide is fine. That answer is:

"Compound a gives a single product because the carbon atoms of the double bond contain different numbers of alkyl groups. Thus the Markovnikov addition product results."

p 136, #46b. =CH₃ should be =CH₂.

Overview of skipped sections

Some notes, for those who want to explore these sections on their own...

- Sect 5 is on the acidity of C-H bonds in hydrocarbons. For our purposes, at least at this point, these bonds are not acidic. Those who want more can read this. If you have heard the term carbide, such as in the context of the chemical calcium carbide, CaC₂... that "carbide" is the di-anion from ethyne (acetylene). We will see an example of enhanced acidity of certain C-H bonds (near an O) in Section 10-10.

- Sect 12 is on reactions that make alkenes. We will skip this for now, but will discuss it in Ch 8 Sect 6 (reactions of alcohols). If you do read this, note that the reactions to make alkenes are formally the reverse of the reactions of alkenes.
- Sect 13 is on dienes. The most interesting issue is the special behavior when double and single bonds alternate (“conjugated” double bonds). Be sure you have the basics of (mono)alkene addition reactions before going into this.
- Sect 14 is on a major and interesting class of biochemicals, called terpenes, that can be thought of as resulting from addition reactions of isoprene (p 128). Note that most of the terpenes are further modified after the simple addition. Rubber (p 484) is a natural polymer made by adding together thousands of isoprene units. Rubber is usually not classified as a terpene, but one might think of it as a terpene polymer. The biological process for these addition reactions is much more complex.

Ch 17 is a more advanced chapter on polymers; we will not cover it. It includes synthetic rubbers, made by chemical polymerization of isoprene or similar dienes.

Further reading (See Old Articles page at web site for more.)

R H Crabtree, Chemistry: Switched-on nickel. *Science* 291:56, 1/5/01. News. Discusses recent work to try to develop a better method for separating alkenes in general from alkanes. The physical properties generally do not allow any useful separation. What is proposed here is a method based on binding of alkenes to nickel complexes, with the reversibility of the binding being controlled by electrochemistry.

N Suzuki et al, Isolation and structural characterization of 1-zirconacyclopent-3-yne, five-membered cyclic alkynes. *Science* 295:660, 1/25/02. The 180° bond angle for a triple bond is incompatible with the geometric constraints of small rings. Here, with some interesting tricks, they make a cyclopentyne-type compound.

C S Zuker, Neurobiology: A cool ion channel. *Nature* 416:27, 3/7/02. News. Menthol is a terpene (Sect 4.14), and is commonly associated with “cool”. Why? It interacts with a receptor that responds to both coldness and to the chemical menthol. Previous work had shown that the receptor for capsaicin, the “hot” of peppers, responds to high temperature as well as to certain chemicals. (Also: *Science* 295:2228, 3/22/02. News.)

H J Choi et al, The origin of the anomalous superconducting properties of MgB₂. *Nature* 418:758, 8/15/02. (+ News, p 733.) Nothing organic here. Superconductivity is the flow of electricity without resistance. A major recent story is the discovery that the simple and inexpensive inorganic compound magnesium diboride, MgB₂, shows superconductivity at temperatures as high as 39 K. But why is still under study. Fig 1 of this paper shows the bonding in MgB₂ -- and shows both σ and π bonds. The analysis shows how both types of bonds contribute to the superconducting properties.

A Otto et al, Natural product terpenoids in Eocene and Miocene conifer fossils. *Science* 297:1543, 8/30/02. Analysis of hydrocarbons, including terpenes, in fossils helps to characterize them. Paleochemosystematics, if you want a big word.

L Khriachtchev et al, A gate to organokrypton chemistry: HKrCCH. JACS 125:6876, 6/11/03. An alkyne -- with a Kr attached. This is the first neutral organic chemical containing Kr, and they think it may be useful in synthetic work.

J Marx, Medicine: Ozone may be secret ingredient in plaques' inflammatory stew. Science 302:965, 11/7/03. News. Sect 7 discusses the ozonolysis of double bonds. Recent work has suggested that ozonolysis of cholesterol in your arteries may be physiologically relevant to plaque production. The claim itself has been much challenged (e.g., A J Kettle & C C Winterbourn, Do neutrophils produce ozone? An appraisal of current evidence. BioFactors 24:41-45, 2005); I'm inclined to say that it has not been resolved. More about the chemistry of this claim in the practice quiz for Ch 13 (the Ch on lipids).

R West, Chemistry: Japan bats a triple. Science 305:1724, 9/17/04. π bonds are uncommon with larger atoms; this news story introduces the first stable compound with a Si-Si triple bond. Interestingly, the bond angles at the triple bond are substantially less than 180° .

R Seshadri et al, Genome sequence of the PCE-dechlorinating bacterium Dehalococcoides ethenogenes. Science 307:105, 1/7/05. PCE = tetrachloroethene (also called perchloroethene, where the "per" means that all H have been replaced by the indicated atom). The bacterium studied here has an unusual ability to completely metabolize highly chlorinated compounds. The genome sequence suggests that the organism contains genes for 17 dehalogenases, presumably for various substrates. Such work might ultimately lead to a process for bioremediation of highly chlorinated compounds, but caution: it is a long way from a research report on such an activity to a useful process.

N E Holt et al, Carotenoid cation formation and the regulation of photosynthetic light harvesting. Science 307:433, 1/21/05. The problem is how the photosynthetic apparatus dissipates excess energy. The answer has to do with energy transfer among various molecules in the photosynthetic membranes, including carotenoids (molecules similar to β -carotene or vitamin A). From UC Berkeley and Lawrence Berkeley Lab (in part). For a news story about this in the UCB paper, see the web site.

L Cardellini, Chemistry, creativity, collaboration, and C_{60} : An interview with Harold W Kroto. J Chem Educ 82:751, 5/05. The story behind the discovery of a new form of carbon, the soccer ball-shaped buckminsterfullerene, or "buckyball". Kroto shared the 1996 Nobel prize in chemistry with Curl and Smalley for the discovery of C_{60} . Also see Computer resources, below.

G Y Liu et al, Staphylococcus aureus golden pigment impairs neutrophil killing and promotes virulence through its antioxidant activity. J Experimental Medicine 202(2):209-215, 7/18/05. The "aureus" of the bug's name refers to its characteristic color, which is due to carotenoids. More virulent strains have more pigment. Why? Here they show that the pigment carotenoids, known to be anti-oxidants, help to overcome body defenses that involve oxidations. They also suggest, then, that a novel target for an antibiotic would be to inhibit carotenoid synthesis.

M Enserink, Plant science: New gene boosts plant's defenses against pests. Science 309:1976, 9/23/05. News. Discusses recent work in which plant resistance to a pest was improved by a

genetic modification affecting terpene synthesis. Interestingly, the modification worked best if targeted to the mitochondria.

M Haruta, Catalysis: Gold rush. *Nature* 437:1098, 10/20/05. News story about the development of conditions where nanocrystalline gold catalyzes the oxidation of an alkene to the epoxide (cyclic ether; Ch 9), using “cheap and clean” molecular oxygen as the oxidant. If this can be developed as a practical process, it is more environmentally friendly than current procedures.

D-K Ro et al, Production of the antimalarial drug precursor artemisinic acid in engineered yeast. *Nature* 440:940, 4/13/06. One class of anti-malarial drugs is based on artemisinin, a terpene derivative isolated from wormwood. Natural sources of this drug are not adequate to meet needs. This article discusses work on synthesis of artemisinin-like molecules, using genetically engineered microbes. Some steps use enzymes whose genes have been transferred from the wormwood to the yeast being used here. One step illustrates the P450 monooxygenase reaction (Ouellette, p 127). The work is from a UC Berkeley group. Web links related to this project are at my web site. Also see Service (2008).

R F Service, Chemistry: Catalyst combo offers new route for turning waste products into fuel. *Science* 312:175, 4/14/06. News. Discusses work to make liquid fuels from low molecular weight alkanes. It makes use of two catalytic systems, one for dehydrogenating the alkanes to alkenes, and the second for alkene metathesis: “stitching together” the alkenes (see Computer Resources). It is far from practical yet, but is offered here as an example of the kinds of work going on in organic chemistry to develop new processes.

J M Hayes, Geochemistry: The pathway of carbon in nature. *Science* 312:1605, 6/16/06. News. Studying the organic compounds present in ancient rocks provides a clue to the biology of the time. But the nature of the clue is poorly understood, because the compounds undergo extensive changes over geological time. In the work discussed here, a pathway for reduction of double bonds by sulfur compounds, such as H₂S, is shown.

P-P Ilich et al, Polar addition to C=C group: Why is anti-Markovnikov hydroboration-oxidation of alkenes not “anti-”? *J Chem Educ* 83:1681, 11/06. A discussion of various ways to add things to alkenes. Somewhat advanced and confusing. However, if you understand why Markovnikov addition works and you are going on in organic chem, this can be useful.

J A Santiago-Blay & J B Lambert, Amber’s botanical origins revealed. *Amer Sci* 95:150, 3/07. Amber is formed from plant resins, which consist of terpenoid compounds. This article is an overview of what amber is, how it is formed, and how it is tested to identify its plant source. It is written for the general audience.

F Studt et al, Identification of non-precious metal alloy catalysts for selective hydrogenation of acetylene. *Science* 320:1320, 6/6/08. For some purposes it is important that ethylene (ethene) be quite free of acetylene (ethyne). This is accomplished by selectively hydrogenating the acetylene. This paper discusses the development of inexpensive catalysts to do this step. They started with theoretical calculations, and were able to show why the current noble metal catalysts were effective. Further calculations allowed them to predict that certain other metals might work; experimental work confirmed their predictions.

J Zhang et al, Surface-modified carbon nanotubes catalyze oxidative dehydrogenation of n-butane. *Science* 322:73, 10/3/08. This paper discusses how alkenes are made from alkanes. Unfortunately, common catalysts -- based on transition metals -- are not ideal; they tend to promote oxidation beyond the desired alkenes. Here they report a new catalyst, based on carbon nanotubes (CNT). A key finding is that treatment of the CNT with phosphorus suppresses oxidation beyond the alkene. Thus their metal-free catalyst is effective at specifically producing 1,3-butadiene from butane. The butadiene is a major industrial chemical, used to make synthetic rubber.

R F Service, Biofuels: Eyeing oil, synthetic biologists mine microbes for black gold. *Science* 322:522, 10/24/08. The paper above by Ro et al (2006) discusses how microbes are being genetically engineered to make an anti-malarial drug. In fact, they think they could make use of the same basic biosynthetic capabilities to produce "gasoline" (liquid transportation fuel). Other groups are exploring other alternatives for getting microbes to make gasoline. The big challenge is economics. They made great strides to get the price of the drug down to about a dollar per gram; that is a good price for a drug, but would translate to gasoline at about \$500 per gallon. This news story discusses some of the approaches and the challenges.

P D Hustad, Frontiers in olefin polymerization: Reinventing the world's most common synthetic polymers. *Science* 325:704, 8/7/09. Perspective. We introduce addition polymers, including the common plastics, in this Ch. In fact, there is much complexity to the story, which Ouellette introduces in Ch 17. The properties of a polymer depend on detailed structural issues, and these depend on the specific catalyst used in the synthesis (e.g., Sect 17.8). Here, Hustad, from Dow Chemical, explores developments in how polyolefins are made. He provides a good view of the roles of academia and industry in such developments.

P J Ziemann, Atmospheric chemistry: Thwarting the seeds of clouds. *Nature* 461:353, 9/17/09. News. Isoprene is the basis of the terpenes; plants emit both. Although we may often think of terpenes as nice odors, they also represent a substantial air pollution problem. Fast growing trees, such as those farmed for commercial use, are particularly strong emitters of these pollutants. These compounds have environmental effects through multiple physical and chemical processes, including oxidation and aerosol formation. The new work suggests that the C-5 isoprene and the C-10 monoterpenes may have different effects. This adds further complexity to the story. It is an interesting and complex story of both biology and chemistry.

S Allmann & I T Baldwin, Insects betray themselves in nature to predators by rapid isomerization of green leaf volatiles. *Science* 329:1075, 8/27/10. "Damage caused by a caterpillar releases compounds that are transformed by the pest's saliva into a predator attractant." Plants use volatile compounds for communication. Here they show that an herbivore attacking a plant may cause the volatiles to be modified -- at the double bonds -- in a way that attracts carnivorous predators, which will protect the plant. Ah, the complexity of chemical ecology!

Computer resources (See web page for details and links.)

Dr. T Newton at Univ of Southern Maine has an animation showing how a double bond is

formed in terms of orbitals. It shows how two p orbitals, one from each bonding C, overlap sideways. This sideways overlap of elongated orbitals is called π (pi) bonding. It provides an easy way to explain why free rotation is not possible around a double bond. [“Regular” bonding is called σ (sigma) bonding.] In effect, this is an animated version of the right hand side of Fig 1.6.

As noted earlier, the oxidation reactions in Sect 4.7 do not appear to be additions, given their overall description. However, the first step really is an alkene addition. This page shows the details of the ozonolysis reaction, and shows the primary addition step; look at the malozonide. The page is part of a more comprehensive organic chem site at the Univ Calgary.

The Macrogalleria site on polymers, at the University of Southern Mississippi: “A cyberwonderland of polymer fun”. It is a major educational resource on polymers, and is very readable over a wide range of topics.

World’s first ‘green’ linear polyethylene launched. Press release from the Royal Society of Chemistry about a Brazilian company making ethylene (ethene) -- and then polyethylene -- from bio-ethanol. We note in class that both directions of the simple interconversion between ethanol and ethylene are industrially useful, with the balance typically depending on the price of oil. Brazil has particularly favorable economics of making ethanol, from sugarcane. Now they have extended this: sugarcane \rightarrow ethanol by fermentation \rightarrow ethylene by chemical dehydration \rightarrow polyethylene, as usual.

The 2000 Nobel Prize in Chemistry was awarded to three scientists (including Alan Heeger at UC Santa Barbara) for the discovery of electrically conductive polymers. The polymers are polyacetylenes. You can think of polyacetylene the same way as polyethylene: the polymer is made by addition; the polymer itself has alternating single and double bonds. The Nobel site article includes an animation of the charge transfer along a polymer molecule, and between a polymer molecule and the dopant.

The 2005 Nobel Prize in Chemistry was awarded to three scientists for the development of alkene metathesis. The idea is to combine smaller alkenes into larger ones, by a process that formally looks something like double replacement (i.e., a rearrangement). See Service (2006).

For more about farnesol (p 128, bottom), to the tune of Jingle Bells.

Self-healing polymers. Biological materials incur damage or decay over time; biological processes restore them. But ordinary chemical materials? Now there is work to design a polymeric material with self-repair capability.

Recycling information. Among other things, check the “Reuse and Recycling Guide.” From Contra Costa County; includes links to recycling agencies in some other local areas. [An article about the merits of burning vs burying plastics, Piasecki et al (1998), is on the Old Articles web page.]

I have a Glossary entry for saturated and unsaturated. It deals with a possible confusion about whether the term unsaturated refers to presence of double bonds or to the hydrogen count.

A kit that lets you make your own C₆₀ “buckyballs” is available at the web site, on the Download page. The kit may be suitable for ages 8+. Also see Cardellini (2005), above.

Also mentioned above: E-Z system for naming alkene isomers; practice quiz.

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