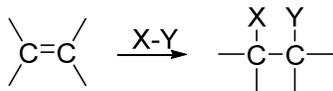# Loudon Ch. 5 Review: Alkene Reactions
Jacquie Richardson, CU Boulder – Last updated 10/4/2019

This entire chapter consists of more reactions of alkenes. Most of them are along the lines of the addition reactions that we saw in Ch. 4:
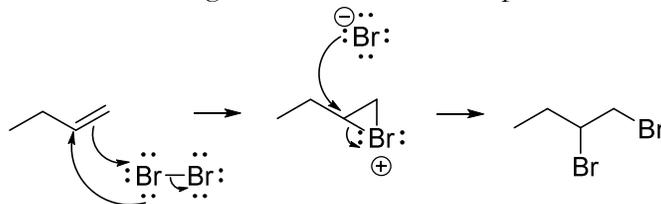

Dihalogenation

In this reaction, X & Y are both halogens. This works best for Cl_2 or Br_2 – F_2 and I_2 don't work as well. Since Br_2 is a liquid, it's easier to do the reaction with than Cl_2, which is a gas. Here are a couple of examples of the overall reaction:


The products of this reaction are called **vicinal dihalides**, since the two halogens are vicinal (in the vicinity of each other, or on neighboring carbons). The mechanism for this reaction starts out looking a little like HX addition, but there's a difference. With HX addition, we showed the alkene attacking a proton, creating a carbocation. We could show an equivalent step here, with the alkene attacking a halogen, but if we did, the lone pair on the halogen would immediately attack the carbocation. This is because a halogen with a positive charge is more stable than a carbon with a positive charge, since at least the halogen has a full octet.

Not a real part
of mechanism!
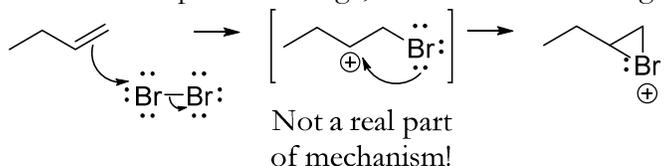
Instead, rather than occurring as two separate mechanistic steps, these three arrows occur all at once – the alkene attacks the halogen atom, the halogen drops the other halogen atom and simultaneously back-attacks onto the more substituted carbon of the alkene. This immediately makes a three-membered **halonium ring** (bromonium, in this case), which can then be attacked by the second halogen atom in the next step.

Note that we showed the second halogen atom attacking the more substituted carbon – this has to do with charge distribution on the molecule. We can show a couple of alternative forms. If we break the ring we can show the positive charge on the bromine (the best option), or on the more substituted C (bad), or on the less substituted carbon (even worse). This means we can distribute a little of the positive charge out to the more substituted carbon, so any attack will happen there.
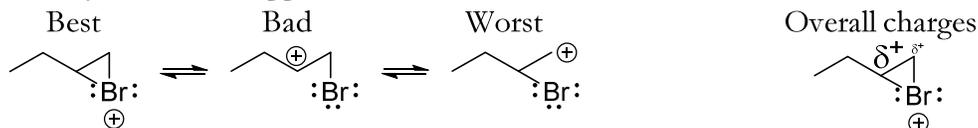
Best	Bad	Worst	Overall charges

Halohydrin Formation

Once the halonium ring forms, other nucleophiles can react with it as well if they're added to the reaction. Water is one example. This creates a halohydrin – something with a halogen and a hydroxyl group (OH) on adjacent carbons.

The first step of the mechanism is the same, but once the ring forms, water comes in and attacks it. However, since water was neutral before the attack, it is now positive. This charge needs to be removed to get a stable, neutral product, but sending electrons directly at the oxygen won't help – it's already got a full octet. Instead, it needs to be deprotonated. Just like for acid-catalyzed hydration, you can show this being performed by another water molecule, or just happening on its own.
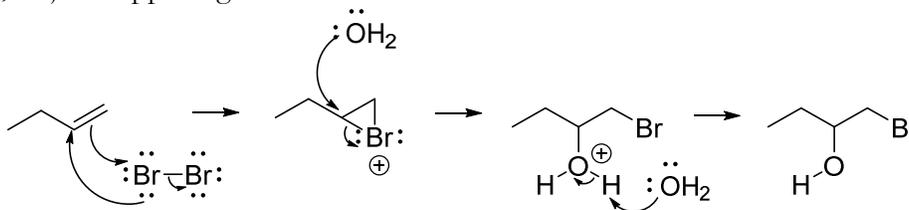
Note that just like in dehalogenation, the attack on the bromonium ring occurs at the more substituted carbon.

Haloether Formation

This is another reaction that starts by forming a halonium ring and then attacks it with a different nucleophile – an alcohol, in this case. This creates a haloether - something with a halogen and an alkoxy group (OR) on adjacent carbons. The product is an ether – you can view the entire starting molecule as one of two R groups that make up the ether molecule.

Both can be written as R-O-R, so both are ethers.

The mechanism is the same as for halohydrin formation, but we only have one choice of which H to remove in the last step (R doesn't detach so easily).
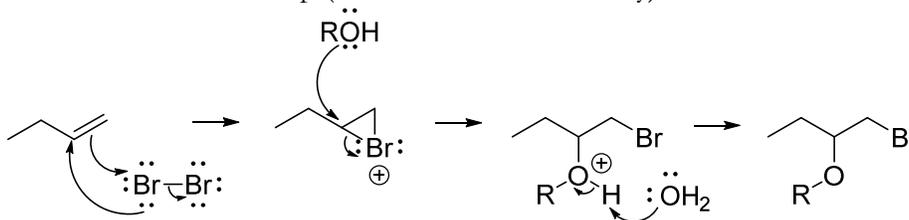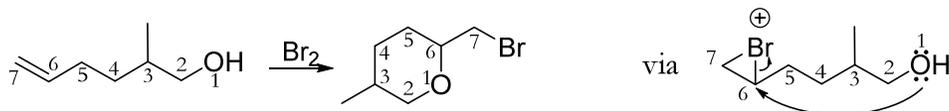

Intramolecular Reactions

This reaction is one case we'll see where we're connecting two different alkyl groups (one with an OH, and one with an alkene). There's no reason these two groups can't be on the same molecule. **Intramolecular reactions like this will make a new ring**.

It's easiest to keep track by numbering the atoms. The new bond formed is between oxygen #1, and carbon #6, which makes a six-membered ring. Meanwhile, carbon #7 is outside of the ring, but it ends up with the bromine. Make sure to keep track of groups attached to any other carbons – for example, the methyl group on carbon #3.

This reaction is helped by the **proximity effect** – it's easier for two functional groups to react when they're already tethered together as part of the same molecule, because they're a lot more likely to run into each other than two separate molecules are.
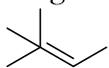
Oxymercuration-Reduction

This is another reaction that adds an H and an OH, like acid-catalyzed hydration, but it does it in a way that avoids the risk of carbocation rearrangements. Here is a case where this would be very useful: say you need to synthesize the following alcohol. The carbon that ends up carrying the OH group must have been part of an alkene to begin with, so there are hypothetically two places where the alkene could have been. But one of these is impossible because it creates an octet violation on carbon. The other option initially looks like it could work, but once we start going through the mechanism, it turns out not to – the carbocation would rearrange, giving a different product.
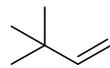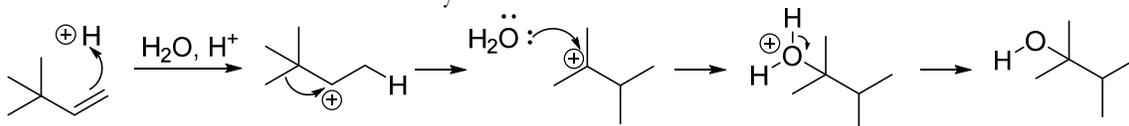
Need to make:

Could begin with:

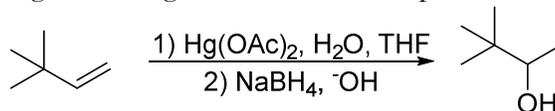or
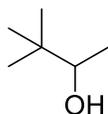
Octet violation!
Doesn't work

Looks like it
could work

But when we go through the mechanism, this
doesn't work either with acid-cat. hydration:

Fortunately, the new reaction we are covering, oxymercuration-demercuration, would work just fine without a rearrangement to get us to the desired product.

$$\text{1) Hg(OAc)}_2, \text{H}_2\text{O, THF}$$
$$\text{2) NaBH}_4, \text{ }^-\text{OH}$$

This is the first reaction we've seen where the reagents need to be brought in as two separate steps. This is written as step 1), then step 2). It's very important to separate these out – if you added all the reagents from both steps at once, they'd just react with each other and not with the alkene. There are a couple new abbreviations in this set of reagents: THF is a moderately polar solvent that is good at dissolving both the polar compounds (H_2O) and nonpolar compounds (alkene) used in this reaction. It doesn't participate chemically, however. The acetoxy group or OAc is a convenient leaving group on mercury (Hg).
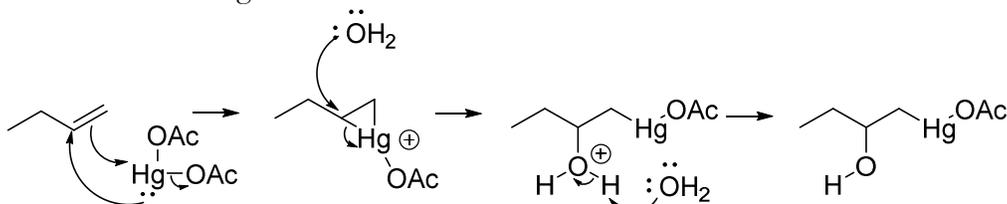
3

THF or tetrahydrofuran
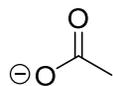
$^-$OAc group - shown here with a negative charge

The first part of this mechanism looks a lot like halonium ring formation – the alkene attacks the mercury atom, which drops an acetoxy group and simultaneously back-attacks onto the alkene to form a new ring.
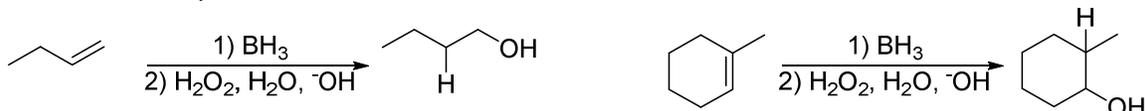

The second step ends up replacing the HgOAc group with an H. The mechanism for this is a little beyond the scope of what we've covered so far since it involves transition metal chemistry, so you don't need to know it.
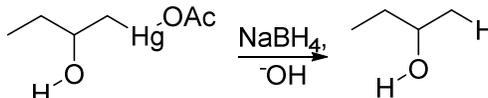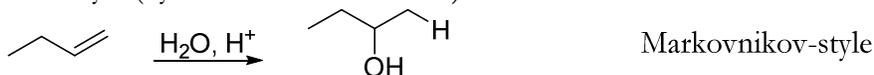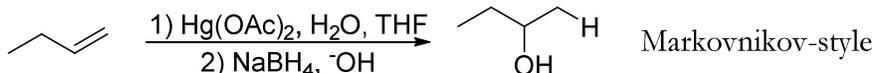

Hydroboration-Oxidation
This is another reaction that adds H and OH to the carbons of the alkene, but it does it anti-Markovnikov style.


As a reminder, Markovnikov-style adds an H to the less-substituted carbon and a non-H to the more substituted carbon, while anti-Markovnikov does the opposite. We've seen two examples of reactions that add H & OH Markovnikov-style (acid-catalyzed hydration and oxymercuration-reduction), and now we're seeing a new one that adds H & OH anti-Markovnikov-style (hydroboration-oxidation.)

  Markovnikov-style

  Markovnikov-style
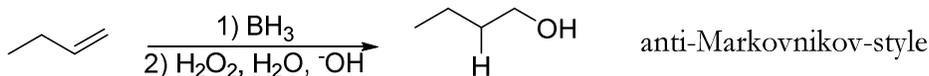
  anti-Markovnikov-style

Like the name implies, this reaction involves doing hydroboration first (adding an H and a boron, B), followed by oxidation (replacing B with OH). The first step, hydroboration, uses borane (BH_3) or some reagent that generates borane. This can be B_2H_6, or BH_3·THF, or BH_3·diglyme – these all break down to produce BH_3. The first step involves the alkene attacking the empty p orbital on boron, but if this were the only thing that happened, a

4

carbocation would be generated. Then a hydride would shift over to the carbon to stabilize it.
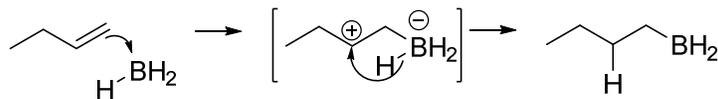
Not a real part
of mechanism!

Kind of like we saw with the dehalogenation mechanism, though, the carbocation is prevented from ever forming because these two steps happen at the same time. This is a **concerted** addition – the H and BH_2 add simultaneously.


There is still some δ^+ buildup on carbon during the reaction, which is why it occurs at the more substituted carbon and why the H adds there. So the same overall rules are still being followed – carbocations are more stable when they're more substituted – but this reaction adds H as a hydride (H^-) instead of a proton (H^+), so that's why the regioselectivity is different. Just like in a Markonikov-style reaction like HX addition, the more nucleophilic atom is still adding to the more substituted carbon, though.

This reaction can actually happen with each H on a B atom, so each molecule of BH_3 can potentially react with three alkenes to make a trialkyl borane (as opposed to a monoalkyl borane or dialkyl borane). Whether this happens depends on the molar ratios of alkene and borane that are used – if there's excess borane, each borane will probably only get one alkyl group, but if there's excess alkene, each borane will get more alkyl groups.

Monoalkylborane   Dialkylborane   Trialkylborane
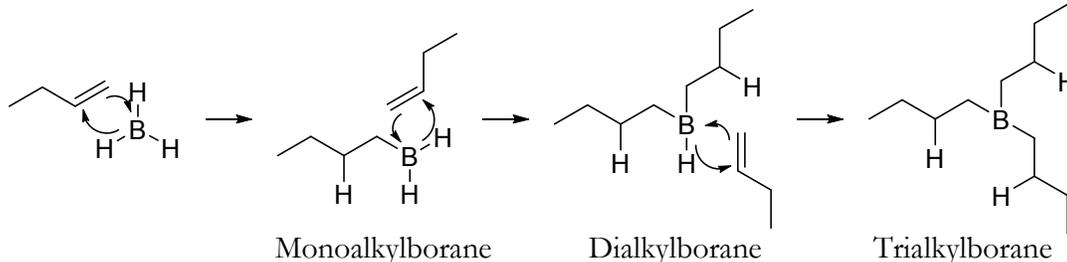
Next, the oxidation step happens and replaces B with an OH group. You don't need to know the mechanism for this step.
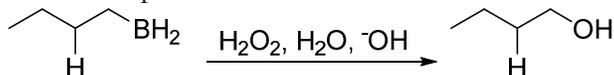
Ozonolysis

This is the only reaction in this chapter that doesn't follow the general trend of converting the alkene to a single bond and adding two new groups. Instead, it breaks the double bond entirely and adds two new double bonds to oxygen atoms. The final outcome depends on what reagents are used for the second step. If you use DMS (dimethyl sulfide, or CH_3SCH_3), then no further changes are made.
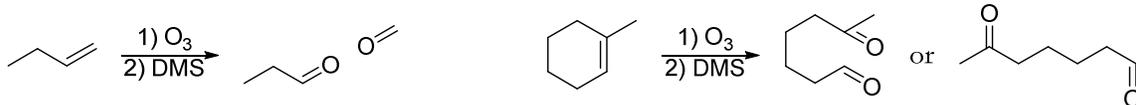
However, if you use H_2O and H_2O_2 (H_2O_2 is actually optional but it does speed up the reaction), then you make one further change: you replace any H atoms that are right next to a C=O with an OH group instead, but you can only do this once per carbonyl (C=O group).
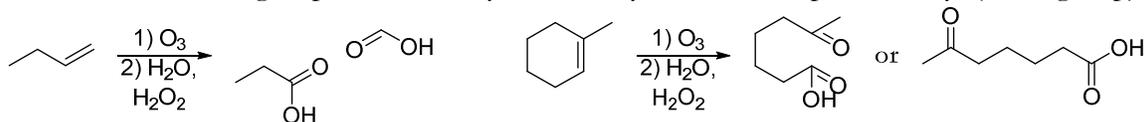

We won't cover the mechanism for ozonolysis.

Free-Radical HBr addition

Like regular HX addition, this reaction adds an H and a Br, but it does it anti-Markovnikov-style if you add a radical initiator with the general structure of ROOR (a diakyl peroxide). It only works for Br – none of the other halogens will do this, just due to the way that bond formation energies work out during this reaction.

The mechanism for this is quite different from other ones we've seen so far. This is because it involves **free radicals** – structures with a single unpaired electron. This means that the arrows we'll show are fishhook arrows, showing the movements of single electrons. Radicals are often created by **homolytic** bond breakage, where a bond is broken and each atom from that bond gets one electron. This is common for bonds between two electronegative atoms. All of the bond-breaking we've seen before is by **heterolytic** bond breakage, where one atom gets two electrons form a bond and the other gets none.

$$H\overset{\frown}{-}OH \longrightarrow H\oplus \quad \ominus OH \qquad \text{Heterolytic bond breaking}$$

$$RO\overset{\frown}{-}\overset{\frown}{O}R \longrightarrow RO\cdot \quad \cdot OR \quad \text{Homolytic bond breaking}$$

The steps for this reaction (and all free-radical reactions) are broken down into 3 categories:

1. **Initiation**: This is when the radicals are created that will go on to perform the reaction. Many, but not all, initiation steps involve starting with 0 radicals and ending up with 2. For this particular reaction, the initiation steps start with ROOR splitting into two RO· radicals. These can then take an H from HBr. This step involves RO· contributing only one electron to form a new bond, so the other electron has to come from the H-Br bond. The leftover electron from this bond then falls back onto Br to make a new Br· radical.

$$RO\overset{\frown}{-}\overset{\frown}{O}R \longrightarrow RO\cdot \quad \cdot OR$$

$$RO\cdot \overset{\frown}{} H\overset{\frown}{-}Br \longrightarrow RO-H \quad \cdot Br$$

2. **Propagation**: This is the reaction with the actual organic molecule that creates the major product. Each propagation step starts and ends with one radical. Furthermore, the same radical that exists at the start of propagation – the Br· in this case – has to be recreated at the end of the propagation steps.
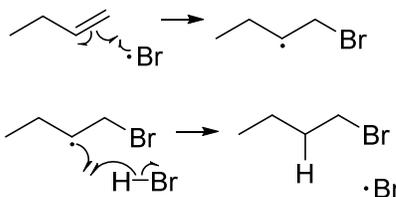
During this step the Br· could have added to either carbon – why did it add to the less substituted? It has to do with carbon radical stability. Just like carbocations, carbon radicals are most stable when they are most substituted.

More subs. C·   Less subs. C·
More stable   Less stable
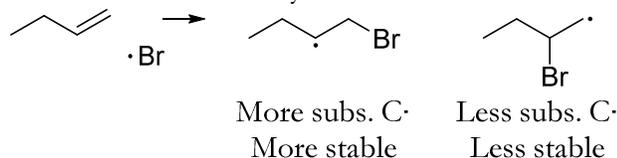
In fact, radicals are also sp^2 hybridized and have trigonal planar geometry, just like carbocations. The only difference between them is that radicals will not rearrange to become more substituted the way that carbocations will.

3. **Termination**: This is when any two radicals combine to form a bond. This can happen between any radicals that exist at any point in the reaction. Some examples are shown below for this reaction.

Br⌒⌒OR → Br—OR
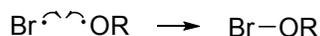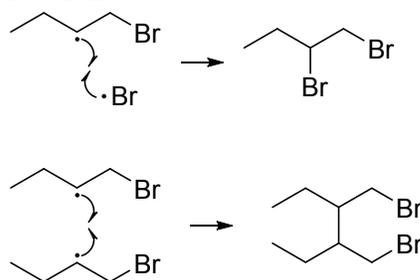
For all radical reactions, the major product is formed during the propagation steps, and any minor products are formed during the termination steps. Only a few molecules exist as radicals at any given time – they are formed, then they react with an alkene to eventually create a new radical, which reacts with another alkene. These radicals can cycle through the propagation steps hundreds or thousands of times, converting alkene to product. Eventually though, a radical will run into another radical, and they will kill each other off by going through termination.

Another option that will sometimes be used as an initiator is AIBN, which forms radicals by a different process. This is favored because it forms a very strong N-N triple bond.

NC—⟨ ⟩—CN   NC—⟨ ⟩—CN
    N=N   N≡N

Polymerization

This is more a category of reactions – anything that links together a lot of molecules into a long chains. There are several polymerization reactions that can be done to alkenes, but we'll look at free-radical alkene polymerization. Like before, it uses an initiator, but this one

happens to create R· instead of RO· radicals. These can then go on to attack an alkene, which can attack another alkene, which can attack another alkene. This creates a very long chain, or a polymer.
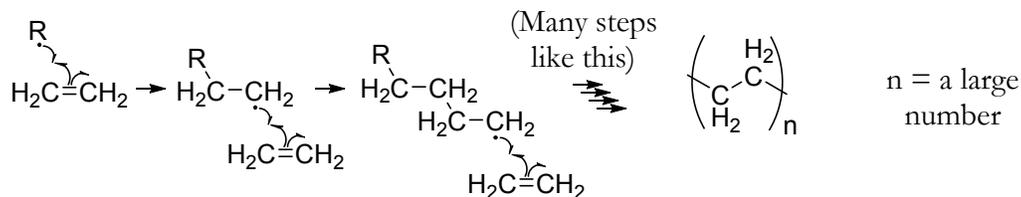
This example starts with ethene or ethylene (its old non-IUPAC name), so its polymer is called polyethylene. This makes up many plastic items as either HDPE (high-density polyethylene) or LDPE (low-density polyethylene). Another example is polystyrene, which is made from styrene.

Ethylene	Polyethylene	Styrene	Polystyrene
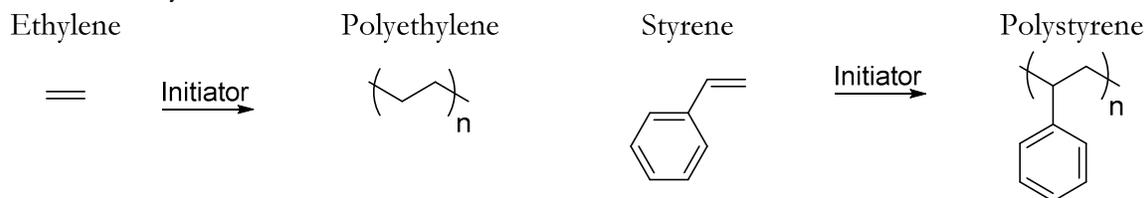
Summary of Alkene Reactions

We've covered a lot of alkene reactions, but they can be broken down into categories that will be very useful later on, when we start putting together multiple reactions in a synthesis sequence. Polymerization isn't included here because it tends to make very large molecules that are not terribly useful for synthesis.

1. Reactions that add 2 non-H groups: dihalogenation, halohydrin formation, haloether formation
2. Reactions that add 1 non-H and 1 H:
    a. Markovnikov-style: hydrogen halide (HX) addition, acid-catalyzed hydration, oxymercuration-reduction
    b. Anti-Markovnikov-style: hydroboration-oxidation, free-radical HBr addition
3. Reactions that add 2 H: hydrogenation
4. Reactions that break C=C bond entirely: ozonolysis