Loudon Ch. 4 Review: Alkene Structure & Reactivity

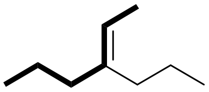
Jacquie Richardson, CU Boulder – Last updated 9/2/2020

In this chapter we're looking at alkenes – compounds with carbon-carbon double bonds.

Alkene Nomenclature

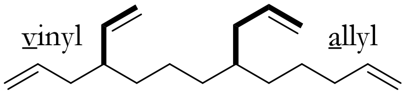
All the rules from alkane naming still apply, but they're all overridden by a few new rules that apply when double bonds show up.

1. **Determine the longest/principal/parent chain.** This is the chain with the most double bonds in it, even if this is shorter than a longer chain with fewer alkenes. Here is an example of the parent chain not being the longest chain anymore. If there are multiple chains that are tied for most double bonds, then choose the longest chain from among them.

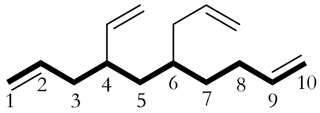


Parent chain is 6 carbons, not 7 (longest chain).

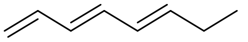
2. **Name each group coming off the parent chain.** Same as before, but there are a couple of new alkene-containing substituents that we'll see here: vinyl and allyl. These get alphabetized and listed the same as any other alkyl branch group.



3. **Number the carbons of the parent chain.** Start numbering at the end closest to the first double bond, or, if both ends are equally close to the first double bond, choose the end that gives the lower number at the first point of difference for all double bonds. If the locations of the double bonds are the same no matter which end you count from, then you can start using the alkane rules to determine it.

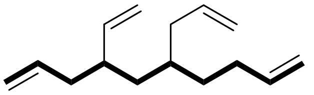


4. **Name the compound as "location #"-"substituent""parent".** Drop "ane" from the end of the parent name and add "ene" if there's one double bond, "adiene" if there's two, "atriene" if there's three, etc. To describe the location of double bonds, put the numbers of the first carbon of each double bond either before the parent chain name, or in the middle of the parent chain name before the new ending.



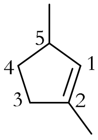
1,3,5-octatriene or octa-1,3,5-triene

Describe the location of substituents the same as before.

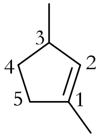


6-allyl-4-vinyl-1,9-decadiene
or
6-allyl-4-vinyldeca-1,9-diene

5. **Sometimes the parent is a ring, instead of a chain.** For naming rings, you still want to minimize the location of the double bond, so all cycloalkenes will have a double bond between carbons 1 and 2 of the ring (so if there's only one double bond, this location identifier can be dropped.) But that still leaves ambiguities about naming which can be resolved by the old alkane rules about minimizing branch locations.

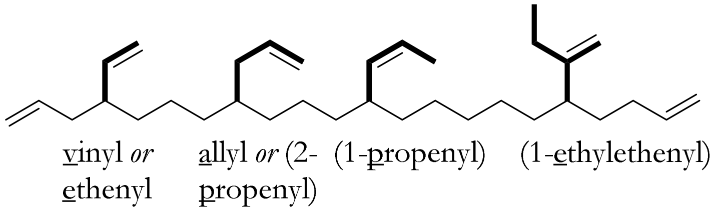


Branches at 2 & 5
Worse choice



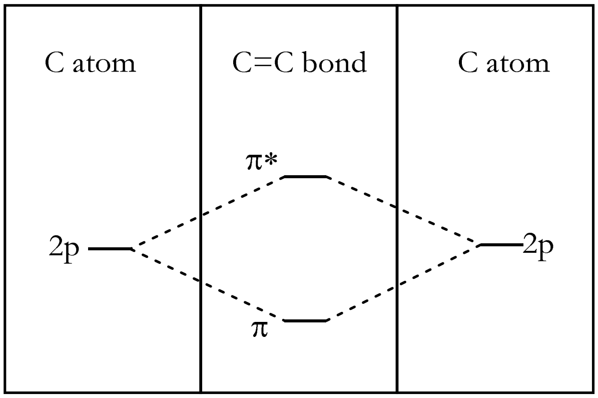
Branches at 1 & 3
Better choice
1,3-dimethylcyclopentene

6. **In some cases, we will see substituents-of-substituents.** This is similar to alkyl substituents – the point of attachment to the parent is always carbon #1 of the group, but the ending changes to "enyl" rather than "yl", and you will need to include information about the location of the double bond within the group. Once there are any numbers inside the substituent name, you have to put the whole thing in parentheses.

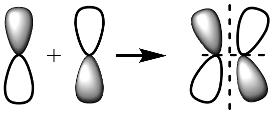


Alkenes & Orbital Geometry

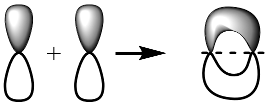
We already saw in Ch. 1 that π bonds are based on side-on overlap of leftover p orbitals.



π* orbital comes from destructive (different-color) interference: (note extra node)



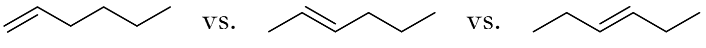
π orbital comes from constructive (same-color) interference:



There are a couple of consequences of this side-on overlap that forms the π bond. For one thing, p orbitals have to be in the same plane to overlap, so the C=C double bond is not freely rotating the way a σ bond would be. For another, π bonds are more easily broken than σ bonds since side-on overlap is not as strong as head-on overlap. This is why we showed π bonds breaking during the formation of new resonance states in Ch. 3.

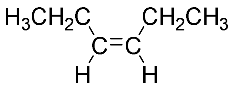
Alkene Stereoisomers

Not only are constitutional isomers possible, based on the location of the double bond:



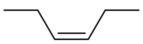
1-hexene 2-hexene 3-hexene

…but also the double bond itself is locked into one of two possible positions, because it's not freely rotating. When each double-bonded carbon has one H and one non-H, these two options are called *cis* and *trans*. This descriptor goes in front of the overall compound name, in italics.

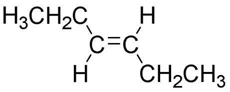


$$\begin{array}{ccc} H_3CH_2C & & CH_2CH_3 \\ & C{=}C & \\ H & & H \end{array}$$

or

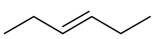


vs.



$$\begin{array}{ccc} H_3CH_2C & & H \\ & C{=}C & \\ H & & CH_2CH_3 \end{array}$$

or



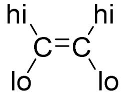
Both non-H groups are pointing same direction: *cis*-3-hexene

Both non-H groups are pointing opposite directions: *trans*-3-hexene

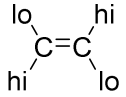
The two versions of this molecule have identical connectivity but different spatial arrangement, which makes them **stereoisomers** (specifically, *cis-trans* stereoisomers). If you swap the two groups connected to one of the double-bonded Cs, you'll interconvert between the two stereoisomers. This means that each double-bonded C is a **stereocenter**. We'll see other examples of stereocenters and stereoisomers later.

What if each double-bonded C does not have one H and one non-H? In this case, we need to use different descriptors: *E* and *Z* (from the German words *entgegen*, or opposite, and *zusammen*, or together). First we assign priority to each pair of groups on each double-bonded carbon: of the pair, one gets high priority and one gets low priority. If both high priority groups are pointing the same direction, it's *Z* because "zey are on zee zame zide." If the high priority groups are pointing opposite directions, it's E. This means that *cis* is a subset of *Z*, and trans is a subset of *E*.

Both hi groups are pointing same direction:
***Z* alkene**



Both hi groups are pointing opposite directions:
***E* alkene**

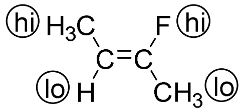


To assign priority, we'll use Cahn-Ingold-Prelog priority rules, or CIP rules. These are:

1. Move 1 step out at a time from the central atom and compare until you reach the first point of difference.
2. Higher atomic number takes priority over lower atomic number. If atomic number is the same but atomic weight is different, then higher atomic weight takes priority over lower atomic weight.
3. Double or triple bonds are treated as bonds to multiple copies of that atom.

Here are some examples. In this case, we move one atom out from the double bond and compare C vs. H on the left, and F. vs. C on the right. The high priority groups are on the same side so this first alkene is *Z*.

Compare C vs. H: C wins

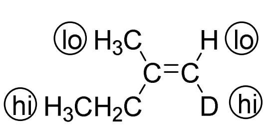


Compare F vs. C: F wins

***Z* alkene**

In the second example, we compare C vs. C on the left side, which is tied. We have to move one step further out and compare all the atoms attached to this C. The three atoms on the top left carbon are (H, H, H), compared to (C,H,H) on the bottom carbon. If we list these in descending order of priority and compare between groups, we run into a point of difference after the first comparison (C vs. H), so the bottom group wins after the second step. On the right side of this molecule, we compare D vs. H. D stands for deuterium, an isotope of hydrogen with one proton and one neutron, and an atomic weight of about 2. So it takes priority over H. With both high priority groups on the same side, this alkene is also *Z*.

Compare C vs. C: tie after 1 step
Compare (H,H,H) vs. (C,H,H): (C,H,H) wins after 2nd step



Compare H vs. D: D wins

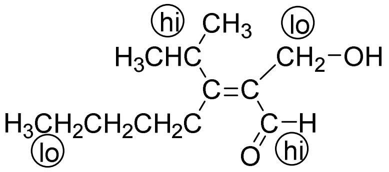
***Z* alkene**

In this third example, we also have to move out more than one step before we can assign priorities on the left side.

Loudon Ch. 4 Review: Alkene Structure & Reactivity

Jacquie Richardson, CU Boulder – Last updated 9/2/2020

Compare C vs. C: tie after 1 step
Compare (C,C,H) vs. (C,H,H):
(C,C,H) wins after 2nd step



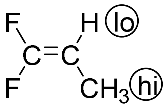
Compare C vs. C: tie after 1 step
Compare (O,H,H) vs. (O,O,H):
(O,O,H) wins after 2nd step

***E* alkene**

It's important to note that even though the bottom left group has more carbons overall, it still loses to something with fewer carbons because the top left group has more bonds to C at the first point of difference. On the right side, it's C vs. C for the first step. For the second step we compare (O,O,H) because there are two bonds to the oxygen, vs. (O,H,H) because there is only one bond to the oxygen. The top left group wins.

If either carbon has both of its groups the same, then there are no stereoisomers possible and it's neither *E* nor *Z*.

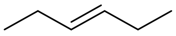
Compare F
vs. F:
same group



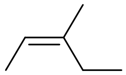
Compare
H vs. C:
C wins

Neither *E* nor *Z*

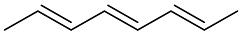
Once *E* or *Z* has been determined, it can go in parentheses at the start of the overall name. If there are multiple double bonds present that need *E*/*Z* descriptors, then you can put the number of the double bond before each descriptor, and separate them all with commas.



(*E*)-3-hexene or
trans-3-hexene



(*Z*)-3-methyl-2-pentene



(2*E*, 4*E*, 6*E*)-2,4,6-octatriene

Relative Alkene Stability

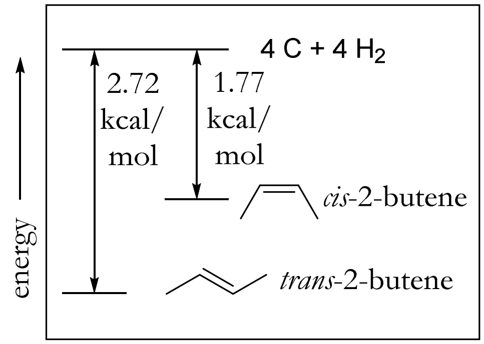
Stability is based on heat of formation or ΔH_f, the energy (or more specifically, enthalpy) released when a molecule is (hypothetically) assembled from its constituent elements in their default state. For some atoms, like hydrogen, this may mean diatomic rather than single-atom molecules.

$$4\ C + 4\ H_2 + \Delta H_f \longrightarrow C_4H_8$$

For most molecules ΔH_f is negative, meaning that energy is released when the molecule is assembled (in other words, it's an exothermic process). For a few quite unstable molecules, ΔH_f is positive, meaning that energy needs to be absorbed when the molecule is assembled (in other words, it's an endothermic process). You can compare ΔH_f between two molecules of the same formula to compare relative stability. For example, *trans*-2-butene releases 2.72 kcal/mol of energy when it forms, compared to only 1.77 kcal/mol for *cis*-2-butene. This means that the *trans* form is about 1 kcal/mol more stable.

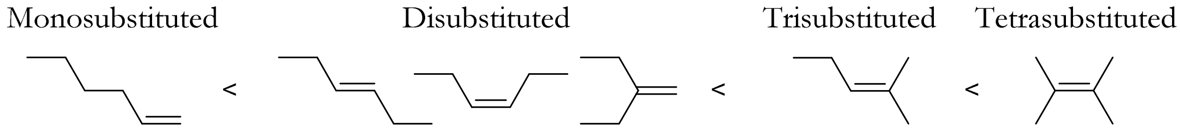
Loudon Ch. 4 Review: Alkene Structure & Reactivity

Jacquie Richardson, CU Boulder – Last updated 9/2/2020



There are three factors that affect ΔH_f for alkenes:

1. Overall number of atoms: generally, more atoms in the molecule means more heat is released, if the structure is about the same.
2. The more R groups are attached to the alkene carbons, the more stable the alkene is.



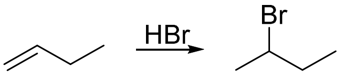
Monosubstituted alkenes are the least stable and tetrasubstituted alkenes are the most stable. This is because there are more bonds between sp^2 and sp^3 hybridized carbons, and these bonds are shorter and stronger than sp^3-sp^3 carbons, due to having more s-character (33% s vs 25% s).

3. Cis is slightly less stable than trans, due to steric between groups on the same face. If you drew a Newman projection of a cis alkene, you would see alkyl groups eclipsing each other, which is less stable than alkyl groups eclipsing hydrogens.

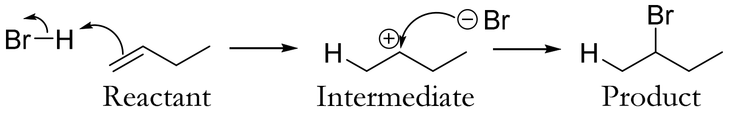
How to Show Reactions

This is the first set of full-on organic reactions that we'll see. There are a couple of different ways of writing reactions, depending on what level of detail is needed.

Overall reaction: Just show reactants and products. Usually only the "important" organic reactant is shown before the arrow, and other reagents are written above or below the arrow (above vs. below doesn't matter). It's usually implied that all reagents on the arrow are present in stoichiometric excess (more moles of these reagents are present than are needed to perform the reaction), unless stated otherwise, or unless they're catalysts.



Mechanism: Show the movement of electrons ("arrow pushing") that allows the reactants to be converted into the products. This might take more than one step.



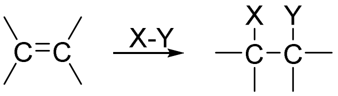
Loudon Ch. 4 Review: Alkene Structure & Reactivity

Jacquie Richardson, CU Boulder – Last updated 9/2/2020

Any structures that occur in between the reactants and products are called intermediates. Often, intermediates will be high-energy structures with unfilled octets, charged atoms or both. Reactants and products will usually not have unfilled octets or charges (but sometimes they will!). If you're asked to show the products of a reaction on an exam, you are not required to show the mechanism, but it might be helpful for figuring out what the products are in some cases. Note that mechanistic steps are often reversible/in equilibrium, but we generally don't show equilibrium arrows. Normally we only show the steps that lead directly from starting material to product – a "productive mechanistic pathway" – even if there are other steps that could occur.

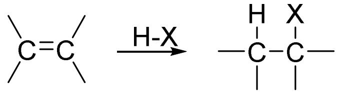
Alkene Addition Reactions

Most of the reactions we'll see in Ch. 4 and 5 are addition reactions to alkenes: they convert the double bond to a single bond, and in the process add a new group to each carbon of the double bond. X and Y might come in from the same molecule, or they might originally be part of different molecules. The exact details vary enormously among the alkene reactions we'll cover, but this is still the general pattern for most of them.



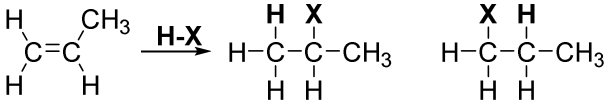
Hydrogen Halide Addition.

This is the first reaction we'll cover. The overall reaction forms an alkyl halide.



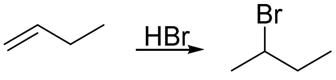
X = F, Cl, Br, or I

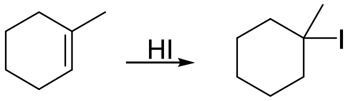
But what if the two carbons of the double bond are not the same? Which one gets H and which gets X? It turns out that the carbon with more R groups attached to it – the more substituted carbon – gets the X most of the time. This gives the major product. There will still be a minority of molecules where the H and X added the other way around.

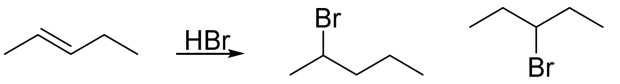


Major product Minor product

This is one example of **Markovnikov's rule**. Most reactions that add one H and one non-H follow Markovnikov's rule by adding the non-H to the more substituted carbon, so they are described as Markovnikov-style. (We'll see a few reactions that break this rule – these are described as anti-Markovnikov.) This is one example of **regioselectivity** or **regiochemistry** – a reaction where multiple different sites could theoretically react the same way, but only one is favored by a given reaction. A side note: If both carbons are equally substituted then there will usually be close to a 50-50 mix of products, although sometimes one product will be slightly favored due to lower sterics or other factors. Here are some more examples of hydrogen halide addition following Markovnikov's rule:





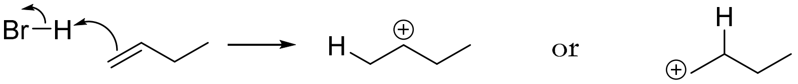


These are likely to be formed in about equal amounts, since both carbons are equally substituted

Loudon Ch. 4 Review: Alkene Structure & Reactivity

Jacquie Richardson, CU Boulder – Last updated 9/2/2020

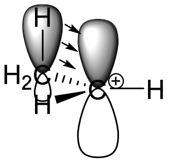
Why do things happen this way? During the first step, the alkene acts as a base and attacks the proton in HX. This means the pi bond is gone, and one of the carbons has picked up the proton. The other carbon is left with a positive charge since it lost electrons and did not form any new bonds. A positively-charged carbon is called a carbocation or C^+ for short. As it turns out, the more substituted a carbocation is, the more stable it is.



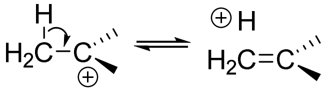
More substituted carbocation: more stable

Less substituted carbocation: less stable

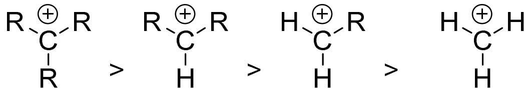
Why is this? Similar to what we saw in acid/base strength, the more you can stabilize a charge by distributing it out to the rest of the molecule, the more stable it will be. Carbocations can distribute out a little of their charge to surrounding R groups through **hyperconjugation**. Carbocations are sp^2 hybridized, so they have their three bonds in trigonal planar geometry, with an unhybridized p orbital pointing out above and below the plane. If there are nearby carbon atoms with bonds to other H or C atoms, then they can donate a small amount of electron density out of their sigma bonds towards the empty p orbital on the carbocation.



The C-H bonds in neighboring R groups get partially broken as a result of this, meaning that bonds between C atoms adjacent to the C+ have weaker, longer bonds to their R and H groups than would normally be expected. (The book uses a resonance arrow to show this happening, instead of an equilibrium arrow. It's a bit of a grey area – we're breaking a sigma bond but it's a weak sigma bond – so we'll just show equilibrium for now.)



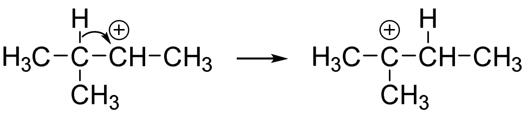
So the order of stability for carbocations, from most stable to least, is tertiary, secondary, primary, and methyl.



$3^o\ C^+$ $2^o\ C^+$ $1^o\ C^+$ Methyl C^+

In fact, this preference for stability is so strong that carbocations will rearrange themselves if there's any opportunity for them to become more stable. **Carbocation rearrangement** can occur by either **hydride shift** (an H moves over, bringing its electrons with it), or **alkyl shift** (an R group moves over, bringing its electrons with it).

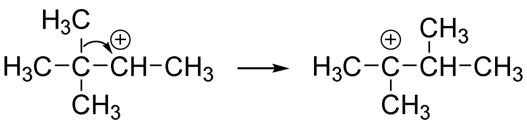
Hydride shift:



$$H_3C-\overset{H}{\underset{CH_3}{C}}-\overset{\oplus}{C}H-CH_3 \longrightarrow H_3C-\overset{\oplus}{\underset{CH_3}{C}}-\overset{H}{C}H-CH_3$$

$2^o\ C^+$ $3^o\ C^+$

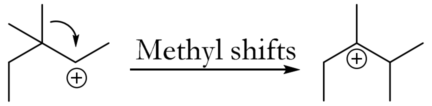
Alkyl shift:

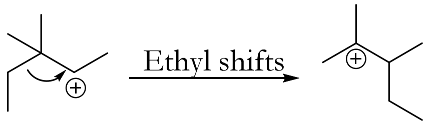


$$H_3C-\overset{H_3C}{\underset{CH_3}{C}}-\overset{\oplus}{C}H-CH_3 \longrightarrow H_3C-\overset{\oplus}{\underset{CH_3}{C}}-\overset{CH_3}{C}H-CH_3$$

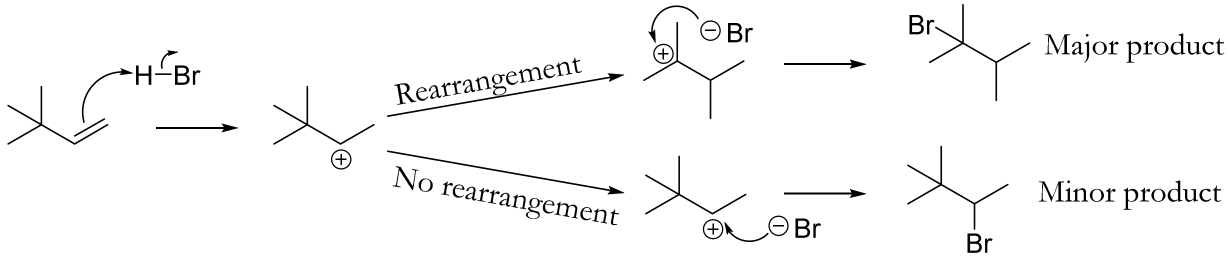
$2^o\ C^+$ $3^o\ C^+$

For both of these, the shifting group can only hop over from a carbon adjacent to the carbocation. However, multiple consecutive rearrangements can occur, so long as there is a gain in stability on every step. For example, it might be possible for a 1° C^+ to rearrange to a 2° C^+, and then to a 3° C^+. But you are unlikely to see a 2° C^+ rearranging to another 2° C^+, unless doing so gives it additional stability from some other source.
Sometimes there are multiple possibilities:



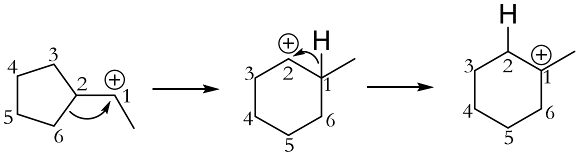


When you're trying to predict the carbocation rearrangements for a molecule, look for highly-substituted carbons neighboring the carbocation and try shifting a group over to see if stability is improved. If a carbocation rearrangement is favorable, then that will give the major product for a reaction, and the unrearranged carbocation will give the minor product.

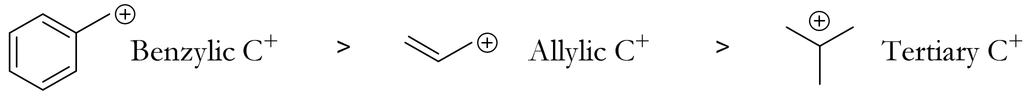


Usually if either a hydride or an alkyl shift could occur, then the hydride shift is more favorable, since this leaves more R groups on the new carbocation.
It is also possible for R groups to shift even when they're part of a larger ring containing the carbocation. These are ring-expansion rearrangements. They follow all the same rules for regular carbocation rearrangements, but it can be difficult to track which atom goes where. Numbering is extremely helpful, and so is writing out which atoms gain or lose bonds to each other.

Break C2-C6 bond
Form C1-C6 bond
C2 loses R group,
gets + charge



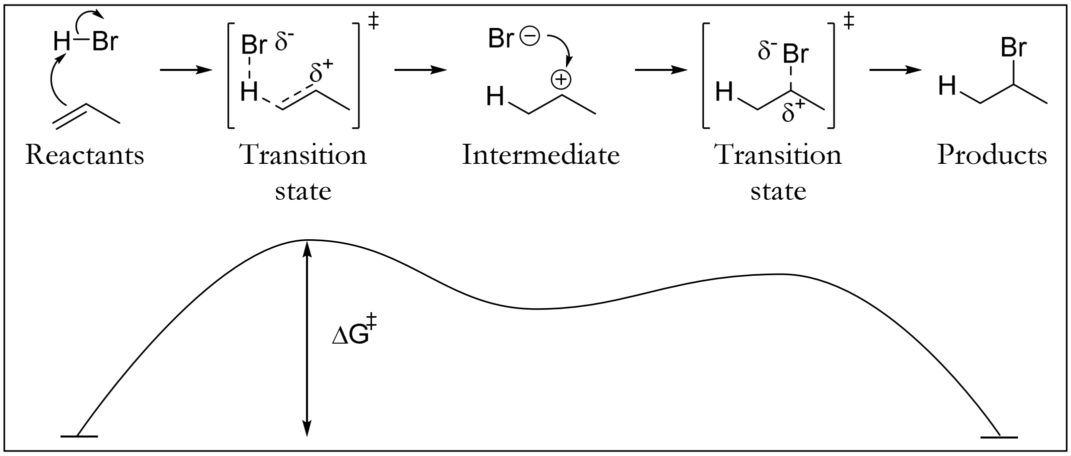
In this example, there are two separate rearrangements: first an alkyl shift to change the ring from a five-membered to a six-membered ring, both with secondary carbocations. (This turns out to be favorable because six-membered rings are the most stable rings – more about this in Ch. 7.) The second step is a hydride shift to become a tertiary carbocation.
The most important message from this section is **<u>any time a carbocation is formed, in any reaction, always check for rearrangements!</u>** We'll see this again in the future.
One final note: carbocations are even better than 3° if they're resonance-stabilized (one carbon away from a double bond or aromatic ring). These are allylic or benzylic C^+.



Reaction Rates
Each step of a reaction passes through a **transition state**, which is an in-between state where bonds are partially broken or formed and charges are in a partial state. The transition state (or TS) is indicated by square brackets and a double dagger symbol (‡).

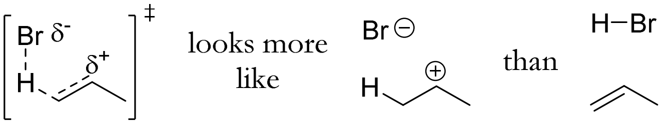
Loudon Ch. 4 Review: Alkene Structure & Reactivity

Jacquie Richardson, CU Boulder – Last updated 9/2/2020

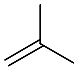


Transition states are not normally shown as part of the mechanism but they can sometimes be drawn out explicitly if something about them is important for explaining a reaction. Showing the partially-formed bonds in a TS is a little like showing them in a resonance form – you indicate a partially-formed bond with dotted lines. For example, during the first step the left C forms a bond to H, so there is a dotted line between C and H in the TS. Meanwhile the H-Br bond is breaking, so that is also shown as a dotted line. We can also show the energy for these structures underneath each one, to make a reaction energy diagram. Whichever step has the highest-energy transition state is the **rate-determining step** (RDS), and the bottleneck for the entire reaction. This is measured by $\Delta G^{\ddagger}$, the activation energy or energy barrier. The rate of the reaction is very dependent on the size of the energy barrier: a small change in energy gives a huge difference in rate. We can give the molecules more energy to get over this barrier by increasing the temperature of a reaction. As a rule of thumb, increasing the temperature by 10°C roughly doubles the rate.

When we show transition states as structures, there's some ambiguity about how much the bonds are broken or formed at the actual peak of the energy barrier. **Hammond's Postulate** says that a transition state more closely resembles whichever of the two states on either side of it is closest to the transition state in energy. If there's an intermediate, this is usually closest in energy to the TS.

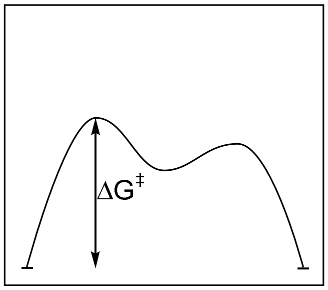


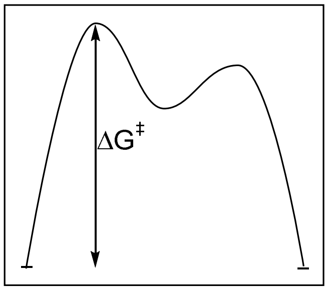
This also means that if an intermediate is very unstable, the associated TS is also very unstable and the reaction proceeds more slowly overall.



$3^{o}\ C^{+}$

More stable intermediate
More stable TS
Smaller barrier
Faster rxn





$1^{o}\ C^{+}$

Less stable intermediate
Less stable TS
Larger barrier
Slower rxn

Loudon Ch. 4 Review: Alkene Structure & Reactivity

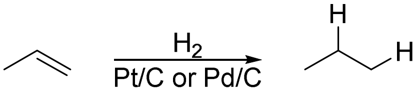
Jacquie Richardson, CU Boulder – Last updated 9/2/2020

Catalysts

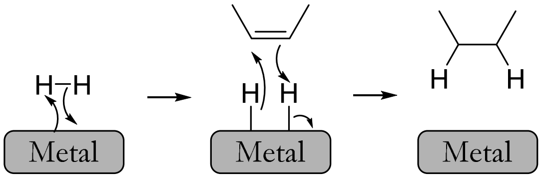
We can cheat and lower the barrier by using a catalyst. This stabilizes the transition state so the reaction goes faster. Catalysts are not consumed by the reaction, so they are only needed in small amounts. They can be **heterogeneous** (different phase from the reactants, like the catalytic converter in a car), or **homogeneous** (same phase as the reactants, like enzymes in living organisms). We'll look at one example from each category for now.

Hydrogenation of Alkenes

The overall reaction for this takes an alkene and adds an H to each carbon. Since there is no difference between the two groups being added, Markovnikov's rule has nothing to say about this reaction. The catalyst used is either platinum or palladium coated onto tiny particles of carbon – this is a heterogeneous catalyst. This is to maximize the surface area for the metal, since Pd and Pt are both expensive and the reaction occurs only at the surface.

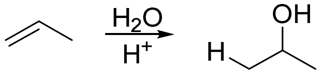


The mechanism for this is a little beyond the scope of regular arrow-pushing, but the gist of it is that the hydrogen molecule splits up and attaches to two points on the metal surface. The alkene then adds both hydrogen atoms at the same time, to the same face of the molecule. This will be important later on.

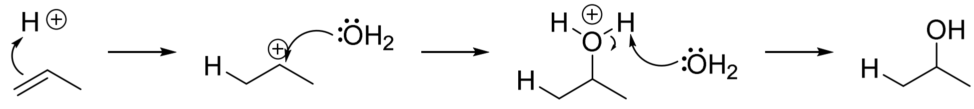


Hydration of Alkenes

This reaction is quite similar to hydrogen halide addition, only we are adding H_2O instead and we need an acid catalyst to start this reaction. The acid is in solution, making this a homogeneous catalyst. This can be written as an actual acid in water (like $H_2O + H_2SO_4$), or it can be written in a more generic way (like $H_2O + H^+$ or H_2O + acid cat. or H_3O^+). For the purposes of this mechanism, these are all equivalent to each other.

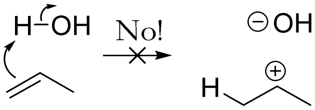


The mechanism for this starts out like HX addition – the alkene picks up an acidic proton, creating a carbocation which gets attacked by a nearby molecule with lone pairs (H_2O instead of X^-). However, this gives us a positive charge on oxygen afterwards, so it has to get deprotonated as an extra final step. Whether you show this deprotonation being done by water, or whether you just show the O-H bond breaking towards O so the H can drift off as H^+, it's fine either way. The end result adds an H and an OH, following Markovnikov's rule. Since a carbocation is generated, all the same issues apply as for other carbocations – more substituted is more stable, and rearrangements can occur.



Note that we are not showing the initial step happening by deprotonating water. This is because there is a much better proton donor available, and generating HO^- in the presence of a strong acid is very unfavorable. **<u>Carbocations cannot exist in the presence of a</u>**

<u>strong base</u> (any base whose conjugate acid has a pKa of about 15 or higher). The pKa of H_2O is 15.7, so its conjugate base, OH^-, is strong and carbocations can't exist around it.



Aromatic Reactivity

None of the alkene reactions we'll cover apply to aromatic rings. Even though these have C-C double bonds, they react under totally different conditions. In a molecule with both an alkene and an aromatic ring, only the alkene reacts.