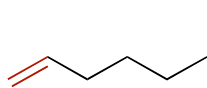


Chapter 6 - Alkenes: Structure and Reactivity

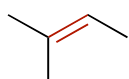
Nomenclature

Alkene naming adds a few twists to what we already know of the IUPAC systematic naming.

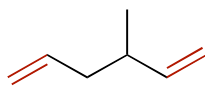
- 1) Find the longest chain containing the double bonds (or multiple double bonds). Alkenes get priority over other substituents
- 2) Number the chain from the end nearest the double bond. Double bonds, again, get priority. Only after that do you consider other substituents and give them the lowest number possible.
- 3) Name the molecule using -ene as the suffix to replace the -ane. If necessary, number the double bond with the carbon it starts with (lowest number end). If there are more than one double bonds in a molecule, number each one and add -diene, -triene, etc. to the suffix. Cyclic alkenes are similar starting with number 1 being one end of a double bond. Number the ring toward the closest substituent.



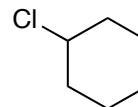
1-hexene



2-methyl-2-butene

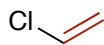
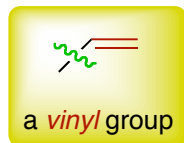


3-methyl-1,5-hexadiene

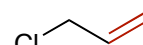
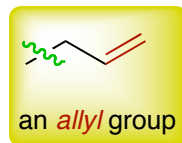
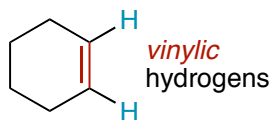


4-chlorocyclohexene

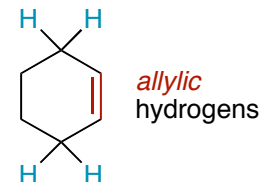
There are some common names associated with substituents containing a double bond. A vinyl group is a two carbon alkene attached to a larger molecule. Note that any H's attached to an alkene are referred to as vinylic hydrogens. An allyl group has an extra CH₂ in between the double bond and its attachment. Allylic hydrogens are on an sp³ carbon adjacent to a double bond.



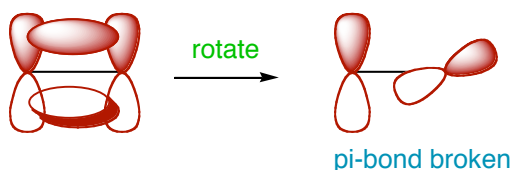
vinyl chloride



allyl chloride



Double bonds have restricted rotation due to the side-to-side overlap of the orbitals to create the pi-bond. Thus, if it were to rotate, the pi-bond would be broken. Similar to the rigidity of cycloalkenes, the rigid nature of a double bond creates cis/trans stereoisomers. This must be added to the front of the name.

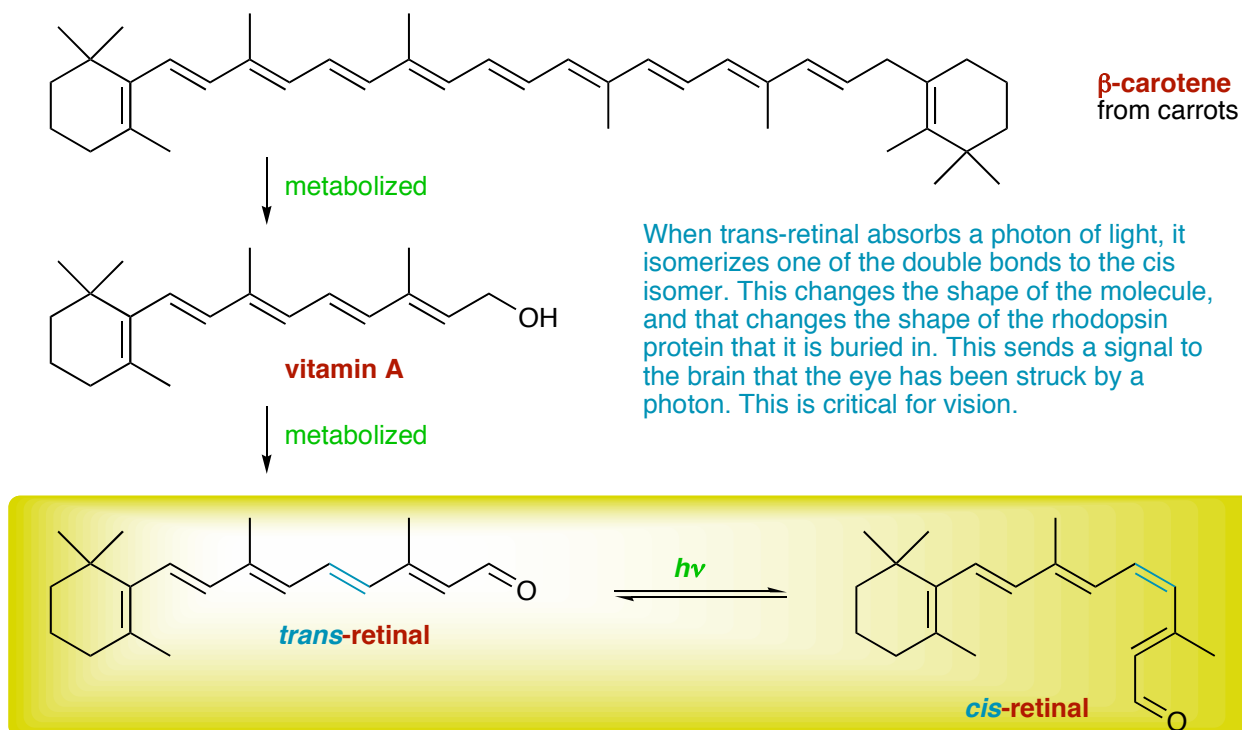


trans-2-butene



cis-2-butene

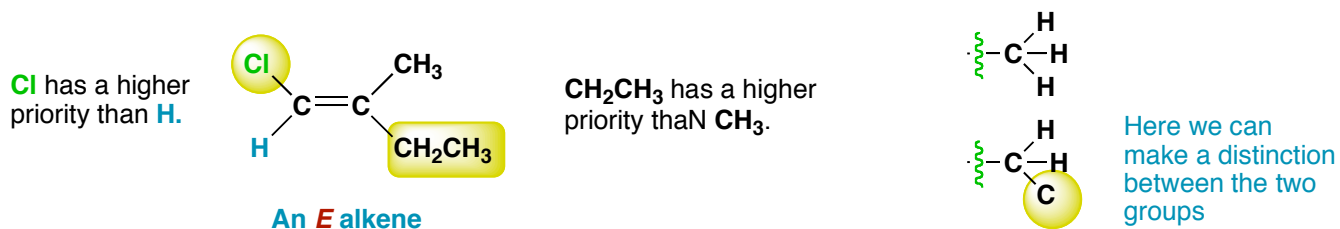
Double bond geometry is important in biology. For example, the trans to cis isomerization of retinal when struck by a photon is the signaling trigger for the brain's recognition of light. Thus, a double bond stereochemistry change is critical for vision.



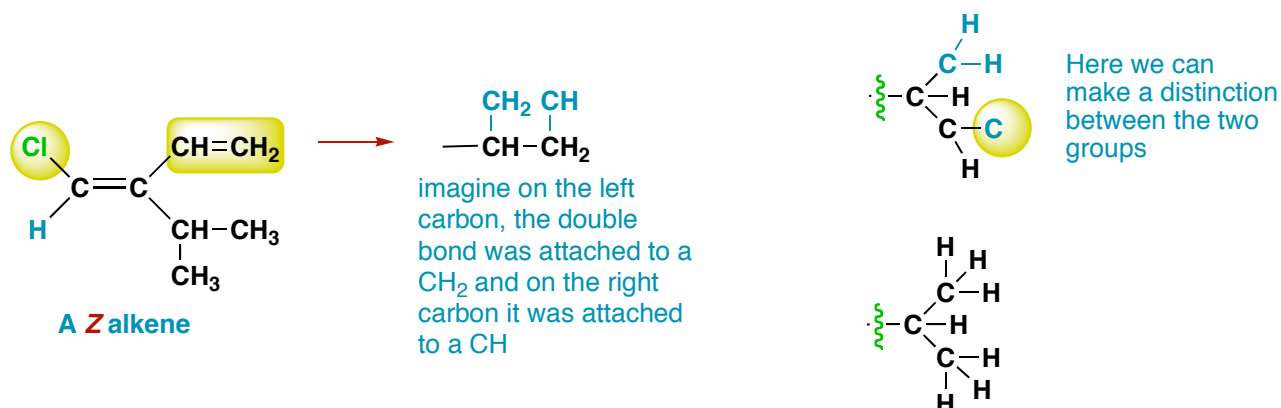
Alkenes with four different groups attached to it also have different stereoisomers. However, our cis-trans designation is not adequate for describing their difference because one wouldn't know which groups you were referring to as being on the same side or opposite sides. Thus, we have another designation that describes the relative positions of the groups on each end of the double bond that have the highest priority (see below). We identify the highest priority group on either end of the double bond and if they are on the same side of the alkene we designate it as a **Z isomer** (zusammen - "together"). If they are on opposite sides, we use the **E designation** (entgegen - "opposite").

Cahn-Ingold-Prelog rules for assigning priorities.

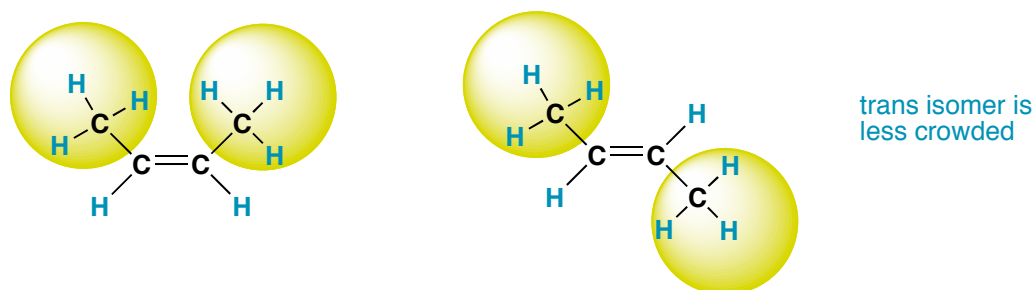
- 1) Look at the atom directly connected to the carbon of the double bond. Rank the atoms according to their atomic number. The higher atomic number gets priority over the lower.
- 2) If the distinction cannot be made after the first atom, look at the next level of atoms attached to those groups. Only look out as far as you need to make a distinction and **NO FURTHER**.



3) Multiple bonds are equivalent to the same number of single bonds IN BOTH DIRECTIONS. It is useful to draw out a group with multiple bonds adding in the imaginary groups.



Cis alkenes are less stable than trans alkenes. This is due to greater steric strain when putting substituents close to each other. For example, cis-2-butene is higher in energy by about 2.8 kJ/mol than the trans isomer.



Alkenes that have more alkyl substituents also show greater stability of the pi-bond. Everything else being the same, a tetrasubstituted alkene is more stable (lower energy) than a trisubstituted or disubstituted, etc.