

Nuggets of Knowledge for Chapter 11 – Alkenes (I)
Chem 2310

I. Introduction to Alkenes

Bond structure

- A double bond consists of one sigma bond and one pi bond.
 - The sigma bond is formed by the overlap of two sp^2 orbitals.
 - The pi bond is formed by the overlap of two p orbitals.
 - The carbon atoms must therefore have sp^2 hybridization in order to have an unhybridized p orbital with which to make the pi bond.
 - The pi bond is more reactive than the sigma bond because it is farther from the carbon nuclei and is therefore higher in energy.
- The geometry of the carbons in the double bond is trigonal planar.
 - Because of this, they cannot have atoms coming forward or backward from them.
 - When forming $C=C$ from tetrahedral atoms (such as in an E2 or E1 reaction), it is important to rearrange the atoms coming out of the $C=C$ so that they are trigonal planar.

Classifying Alkenes

- There are several categories that can be used to describe compounds containing carbon-carbon double bonds.
 - alkenes – hydrocarbons containing a $C=C$ (not in a benzene ring)
 - aromatic – compounds containing a benzene ring
 - unsaturated – compounds containing a $C=C$ (not in a benzene ring); may have atoms besides carbon and hydrogen
 - Alkenes and other unsaturated compounds undergo certain reactions because of the $C=C$, which we will study in this chapter and the next. We will focus on alkenes to avoid complications with other functional groups.
 - Aromatic rings undergo a different set of reactions (we will study these in chapter 16).
- When a compound contains more than one carbon-carbon double bond, it is classified by the relationship between the two double bonds.

- isolated C=C's are separated by at least one sp^3 carbon
 - the pi bonds cannot overlap each other, so they behave just like a single C=C
- conjugated C=C's are separated only by a single bond
 - the pi bonds overlap with each other, creating a single pi system
 - they are more stable than regular C=C's
 - they can absorb UV light if there are at least 3, with a sufficient number they absorb visible light and cause the compound to be colored
 - their reactions will be covered in chapter 15
- cumulated C=C's share a carbon atom
 - in order for the middle carbon to have two pi bonds, it is sp hybridized, and the pi bonds are at right angles to each other (similar to a triple bond)
 - they are less stable than regular C=C's
 - they often isomerize to form triple bonds
 - their reactions are beyond the scope of this course, but we will discuss their stereochemistry briefly in chapter 15

Reactivity of Alkenes

- The pi bond can act as a weak nucleophile or base, or it can be attacked by a radical.
 - If the pi bond acts as a base, it will attack a strong acid, leaving a carbocation that will continue to react.
 - If the pi bond acts as a nucleophile, it will attack a strong electrophile, also leaving a carbocation that will continue to react.
 - If the pi bond is attacked by a radical, the bond will break, and one electron will join with the radical to form a new bond, leaving a radical on the other carbon, which will continue to react.

Physical Properties

- The physical properties of alkenes are very similar to those of alkanes.
 - Alkenes are nonpolar, having only van der Waals forces.
 - Alkenes are insoluble in water, since they can't break into the hydrogen bonding network of the water molecules.
 - Alkenes are highly flammable. They react with oxygen to form carbon dioxide and water (or carbon monoxide and soot if there isn't enough oxygen or heat).

- Alkenes are less dense than water, so they float on top of the water as a separate layer when placed in contact with water.
- Alkene boiling points are similar to alkanes. They increase with molecular weight, and decrease slightly with branching because of the reduced surface area.

Occurrence and uses of alkenes

- Alkenes themselves are not very common in nature, though unsaturated compounds are more common.
 - Two exceptions are alpha-pinene, a compound found in the oils of coniferous trees such as pine trees, and muscalure, the sex attractant of the common housefly.
- Alkenes are used in industry as starting materials and intermediates. The most commonly used is ethylene – 49 billion pounds are produced each year, which is more than any other organic compound.
 - Ethylene is used to make a variety of other compounds. Examples include:
 - polyethylene, a common plastic in things like plastic bags and milk jugs
 - ethanol, used industrially as a solvent and as a gasoline additive
 - acetic acid, used as an acid catalyst and as a solvent
 - ethylene glycol, used as antifreeze

Spectroscopy

- IR spectra of alkenes can be recognized by their characteristic bands. Please learn these frequencies.
 - C-H on C=C is at 3100-3000 cm^{-1}
 - C=C is at 1680-1620 cm^{-1}
- NMR spectra of alkenes can be recognized by the chemical shift of the vinyl hydrogen atoms, and the complex splitting that occurs.
 - Hydrogen atoms directly attached to the C=C appear at 4.5-6.5. Please learn this range.
 - Peaks caused by hydrogen atoms attached to the C=C often show complex splitting. This occurs because the coupling constants between different hydrogens are not the same, making it so that a hydrogen split by two neighbors is not a triplet, but instead a doublet of doublets, and so on.

Stability of alkenes

- The stability of alkenes affects which ones are favored in reactions that form them, such as E2 and E1.

- Alkenes are stabilized by overlap of the pi orbital with nearby C-H bonds (similar to carbocations and radicals). Because of this, the most substituted C=C are the most stable.
- With C=C that have the same number of carbon substituents, steric hindrance will affect their stability. Trans C=C's are more stable than cis C=C's, and geminal C=C's are in between. (Remember that this is a smaller affect than substitution.)
- Cyclic alkenes can also be less stable because of strained angles. Cyclobutene and cyclopropene are unusually reactive because of their highly strained C=C's.
- Trans C=C's can exist in rings with 8 carbons or more. Smaller rings cannot have trans C=C's because there aren't enough carbons to make the chain. When the ring is large enough, the ring is more stable in the trans geometry.

II. Unsaturation Number

- The formula of a compound can be used to determine the number of double bonds or rings that the compound must contain. This is called the unsaturation number.
- The presence of either a double bond or a ring will cause two less H's to be needed. We can use the formula $(2C + 2) - H / 2$ to determine the unsaturation number for hydrocarbons.
- The presence of other atoms can also affect the number of H's, and this must be taken into account in order to determine the unsaturation number.
 - Oxygen atoms do not change the number of H's needed.
 - Halogen atoms take the place of a H, and the number of H's needed is one less for every halogen atom present.
 - Nitrogen atoms require one more H, and the number of H's needed is one more for every nitrogen atom present.
- The formula that can be used for all compounds to determine the unsaturation number is: $(2C + 2 - X + N) - H / 2$

III. Nomenclature of Alkenes

- Naming alkenes is very similar to naming alkanes and alkyl halides. The difference is that the C=C takes priority in both the choosing of the principle chain or ring, and the numbering of the chain.
- Priorities in choosing the principle chain or ring:

- It must contain the C=C. If there is more than one C=C, it must contain all of them, if possible.
- If there is more than one chain or that contains the C=C, choose the one that is the longest.
- If there is more than one chain or ring that contains the C=C and are the same length, choose the one that has the most substituents.
- Priorities for numbering the principle chain or ring:
 - Give the C=C the lowest number. The numbers must go across the C=C, with the lower number being used to label it's location.
 - If there are two ways to number that both give the lowest number to the C=C, then give the lowest number to the first substituent, then the second, etc.
 - If there are two ways to number that give the same numbers, give the lowest number to the substituent that comes first in the alphabet.
 - A ring with only one C=C and no substituents does not need to be numbered.
- If there is one C=C in the chain or ring, the ending of the name is changed from "ane" to "ene".
 - For example, a chain of 5 carbons with one C=C is a pentene.
 - The number giving the location of the C=C is added at the beginning of the name – for example, 2-pentene.
- If there is more than one C=C, a "di" or "tri" is inserted before the "ene", and an "a" is added to make the name easier to say.
 - For example, a chain of 5 carbons with two C=C's is a pentadiene.
 - The numbers giving the locations of the C=C's are added before the name – for example, 1,3-pentadiene.
- The two smallest substituents containing a C=C have common names.
 - vinyl – a C=C attached directly to the chain or ring
 - allyl – a C-C=C attached so that the C=C is one carbon away from the chain or ring
- All other substituents containing C=C's must be named by adding "en" just before the "yl" on the end of the alkyl name – for example, butyl becomes butenyl.

- The substituent must be numbered from the point of attachment, and the number added to the beginning of the substituent name – for example, 3-butenyl.
- Stereochemistry must be added to the beginning of the name if there are two possible isomers for the compound.
 - This will occur when the substituents on both sides of the C=C are different. See chapter 6 for a review of determining stereochemistry of C=C's.
 - trans and cis may be used when there are only two substituents on each side of the C=C, and when there is only one C=C in the molecule
 - E and Z may always be used. They must be used when there are three or more substituents on the C=C, or when there is more than one C=C in the molecule.
 - A number must be added before E or Z the when there is more than one C=C with stereochemistry in the molecule.
 - Rings with 8 or more carbons can have two stereoisomers, and the stereochemistry must be labeled. Rings with 7 or fewer carbons should not be labeled, as they can only be in the cis configuration.

IV. Introduction to Reactions of Alkenes

- There are three basic types of reactions: substitution, elimination, and addition.
 - In a substitution reaction, a nucleophile replaces a leaving group.
 - In an elimination reaction, a hydrogen and a leaving group are removed, leaving a C=C.
 - In an addition reaction, something is added to both sides of a double bond, giving a saturated compound with two new substituents.
 - Elimination and addition reactions are opposites of each other.
- Nearly all reactions of alkenes are addition reactions. We will see different mechanisms and different atoms added to the double bond, but all of them give the same type of result.
- The C=C in benzene rings do NOT undergo addition reactions. Benzene rings are not affected by the reagents that cause addition to C=C to occur.

V. Addition of HX to Alkenes

Carbocation Mechanism

- When alkenes react with hydrogen halides such as HCl, HBr, or HI, an alkyl halide is formed.
- The mechanism involves two steps:
 - protonation, in which the alkene attacks the hydrogen of the hydrogen halide, adding a hydrogen to the alkene and forming a carbocation and a halide ion
 - attack, in which the halide attacks the carbocation, forming the alkyl halide
- This reaction is regioselective. The halogen ends up only on the more substituted side of the C=C, because this is where the more stable carbocation will form and then be attacked by the halide.
 - If neither side is more substituted, two carbocations will form, and two products will be made.
- Since a carbocation is formed, rearrangements may occur. Products will be formed from both the original carbocation as well as the rearranged carbocation.
- This reaction is useful for converting alkenes to alkyl halides. When using this reaction for synthesis, make sure to consider the following:
 - Look at all of the alkenes that could have been used to make the alkyl halide. They must have the same carbon skeleton as the product, and the C=C must contain the carbon that will have the halide on it.
 - Next, make sure that the halogen will go to the side that will give the alkyl halide you are trying to make. If the halogen is on the less substituted side, the wrong product will be formed.
 - If the right product will be formed, next look at whether any other products would also be formed. A good synthesis gives only the desired product. Things to watch out for include:
 - If the C=C is equally substituted, two carbocations will form leading to two products.
 - If the initially formed carbocation can rearrange, another carbocation will form leading to additional products.
- This reaction is more effective at synthesizing alkyl halides than halogenation of alkanes because it does not form multiple products as often.

Radical mechanism

- The presence of organic peroxides such as CH_3OOCH_3 can cause the reaction of alkenes and HBr to follow a radical mechanism instead of one involving a carbocation.
- The oxygen-oxygen bond in the peroxide is very weak because both electronegative oxygen atoms are pulling on the electrons. Exposure to heat or light can cause this bond to break homolytically, creating two oxygen radicals.
 - The oxygen radical reacts with an HBr molecule, forming an alcohol and a bromine radical.
 - The bromine radical attacks the alkene, forming a carbon radical on the more substituted side, with the bromine on the less substituted side.
 - The carbon radical then reacts with an HBr molecule, taking a hydrogen and forming an alkyl halide and a bromine radical.
 - The creation of a new bromine radical during the reaction causes the peroxides to be catalytic. Only a small amount of peroxide is necessary to initiate the reaction; once it has started it can continue without any more peroxide breaking.
- The regioselectivity of the reaction is reversed when a radical reaction occurs.
 - In both cases, the reactive intermediate, a carbocation or carbon radical, is stabilized by hyperconjugation, and forms on the more substituted side of the $\text{C}=\text{C}$.
 - In the carbocation mechanism, the hydrogen is added first as the alkene attacks the acid, sending the hydrogen to the less substituted side and leaving the more substituted side for the carbocation, which is then attacked by the halide.
 - In the radical mechanism, the bromine is added first as the alkene is attacked by the bromine radical, sending it to the less substituted side and leaving the more substituted side for the carbon radical, which then attacks a hydrogen.
- The radical mechanism is only effective with HBr, not with HCl or HI. Even in the presence of peroxide, alkenes react with HCl and HI by a carbocation mechanism, giving alkyl halides with the chloride or iodide on the more substituted carbon.
- No rearrangements occur with the radical mechanism. Radicals cannot rearrange because the orbital is not empty, so a pair of electrons cannot slide into it.
- This reaction can be used to make alkenes into alkyl bromides.
 - It is a useful complement to the regular addition of HX to alkyl halides because it makes it possible to make alkyl halides in which the halide is attached to a carbon less

substituted than those around it. Also, it doesn't undergo rearrangements. However, it only works with bromine.

VI. Acid-catalyzed Hydration of Alkenes

- When sulfuric acid is used instead of a hydrogen halide, and the reaction takes place in the presence of water, an alcohol is formed instead of an alkyl halide.
- The mechanism of the reaction has three steps:
 - protonation – the pi bond of the alkene attacks the acid, adding a hydrogen and forming a carbocation and the conjugate base of sulfuric acid
 - attack – a water molecule attacks the carbocation, forming a protonated alcohol
 - deprotonate – another water molecule takes the hydrogen atom from the protonated alcohol, forming an alcohol and a hydronium ion (H_3O^+)
- The difference between the reaction of alkenes with HX and H_2SO_4 is caused by the conjugate bases.
 - Both reactions begin with protonation of the alkene to form a carbocation, but the halide can act as a nucleophile, while the HSO_4^- can't. The halide reacts as a nucleophile, giving an alkyl halide product; if water is present, it can act as the nucleophile, giving an alcohol product.
 - Phosphoric acid also has a non-nucleophilic conjugate base, and can be used in this reaction in place of sulfuric acid.
- This reaction is said to be acid-catalyzed because the hydronium ion formed in the last step can serve as the acid in the first step. Only a small amount of acid is necessary for all of the alkene to be converted to alcohol. However, a full equivalent of water is needed.
 - Since sulfuric acid reacts rapidly with water, the acid in the first step is actually hydronium ion (although it is frequently written as sulfuric acid itself). The sulfuric acid forms hydronium ion and then its conjugate base remains a spectator ion for the rest of the reaction.
- This reaction is called a hydration because the elements of water are added to the double bond – a H on one side and an OH on the other.
- This reaction is regioselective. The OH always goes to the more substituted side, because that is where the more stable carbocation will be formed, then attacked by a water molecule.
 - If both sides are equally substituted, two carbocations will be formed, giving two products.

- Since a carbocation is formed, rearrangements can occur. Products will be formed from both the original carbocation and the rearranged one.
- This reaction can be used to make alkenes into alcohols. When using this reaction for synthesis, make sure to consider the following:
 - Look at the alkenes that could be used to make the alcohol. They must have the same carbon skeleton, and the C=C must include the carbon that will have the alcohol on it.
 - Check to see if the alkene will give the correct product – the OH will go to the more substituted side.
 - Check to see if any other additional products will form because of equally substituted C=C's, or carbocations that can rearrange.
- We will see two more reactions that form alcohols from alkenes in the next chapter. We will also discuss several more addition reactions.