

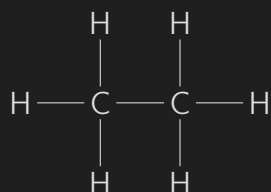
Organic Chemistry II

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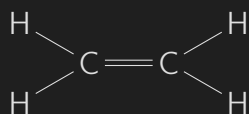
Chapter 14: Alkenes

Alkenes Basics/Review

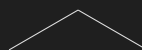
▷ Alkanes vs alkenes:



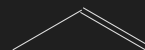
Saturated
alkanes ethane



Unsaturated
alkenes ethene



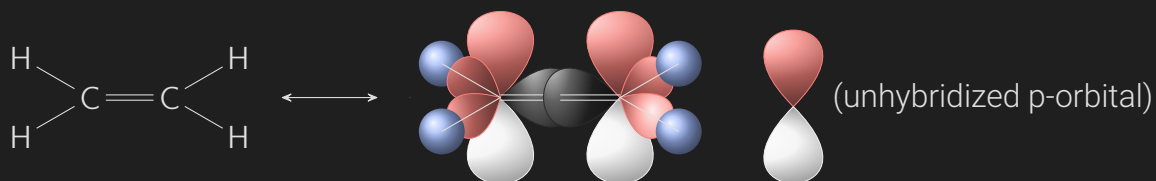
propane



propene

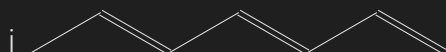
Practice and Review

- **Electronegativity:** negative charges on atoms with lower hybridization result in greater stability due to proximity (overlap) to positive nucleus. More s character results in greater stability.
 - I.e., sp (50% s) > sp^2 (33% s) > sp^3 (25% s)
 - E.g., ethene has two carbons that are both sp^2 due to one unhybridized p-orbital. This gives ethene a trigonal planar geometry.



- **Hydrogen deficiency index (HDI):** the measure of degrees of unsaturation.
 - E.g., two degrees of unsaturation results in a HDI of 2.
 - Degrees of freedom help represent possible structures, indicating possible double bonds, triple bonds, rings, or various combinations of each.
 - Only helpful when molecular formula is known for certainty.
 - Formula: $HDI = \frac{1}{2}(2C + 2 + N - H - X)$
 - X: halogen atoms.

- What is the HDI for the following molecules?



i $\frac{1}{2}(2(7) + 2 + (0) - (3 + (5(1)) + 2) - 0) = 3$



ii $\frac{1}{2}(2(6) + 2 + 0 - (6(1)) - 0) = 4$

- **Degree of substitution:** not a substitution reaction, but the **number of groups** connected to the double bond.



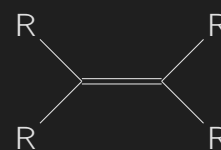
Monosubstituted



Disubstituted



Trisubstituted



Tetrasubstituted

Types of Alkenes

- Basic types of alkenes:



Terminal Alkene

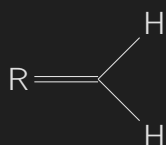


Internal Alkene



Cycloalkene

- Types of terminal alkenes:



Methylene



Vinyl



Allyl

- “R” always tells you it’s a carbon containing functional group, or hydrogen.
- “A” can be used to represent any functional group.

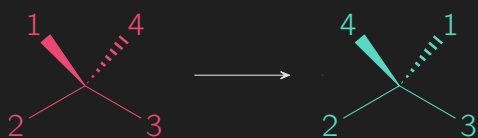
Chirality

- **Achiral (nonsuperimposable):** when an object’s mirrored version is identical to the actual object.
- **Chiral:** objects that are not superimposable.
 - The most common source of molecular chirality is the presence of a **carbon bearing four different groups**.
- All three-dimensional objects can be classified as either chiral or achiral.
- **Enantiomer:** the nonsuperimposable mirror image of a chiral compound.
 - Can be used in speech the same way the word **twin** is used
 - The easiest way to draw enantiomers is to simply change wedges and dashes, but there are multiples ways to mirror a molecule, so it can be more complex.

- **Diastereomers:** non-identical stereoisomers (nonsuperimposable) that are **not mirror images** of one another.
 - Enantiomers have the same physical properties, while diastereomers have **different physical properties**.
 - Differences between enantiomers and diastereomers are especially relevant when comparing compounds with **more than one chiral center**.
 - **Maximum** (could be less) number of stereoisomers: 2^n
 - n : number of chiral centers
 - $\frac{2^n}{2}$: max pairs of enantiomers.

Cahn-Ingold-Prelog System

- **Cahn-Ingold-Prelog system:** a system of nomenclature for Identifying each enantiomer individually.
 1. Assign priorities to each of the four groups based on atomic number; the highest atomic number has the highest priority.
 2. Rotate the molecule so that the fourth priority group is on a dash (behind)
 3. Determine the configuration, i.e., sequence of 1–2–3 groups.
 - **clockwise (R)** or **counterclockwise (S)**.
- If there is a tie between the atoms connected, then continue outward until a difference is found.
 - Do not add the sum all atomic numbers attached to each atom, just the first in which the atoms differ.
 - Any multiple bonded atom, (2 or 3) is treated as if connected to multiple atoms equal to number of bonds.
- Switching any two groups on a chiral center will invert the configuration, e.g.,



- Switching twice results in a change without changing configuration, e.g.,



- **Configuration in IUPAC nomenclature:**

- The configuration of the chiral center is indicated at the beginning of the name, italicized, and surrounded by parentheses.
- When multiple centers are present, then each must be preceded by a locant.

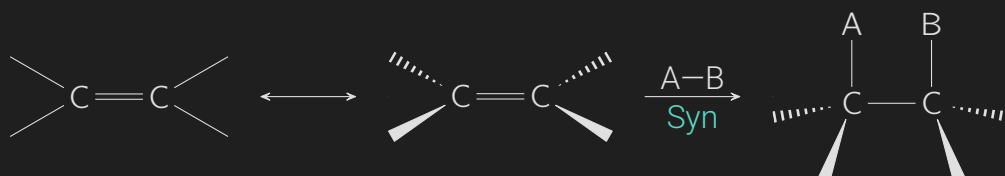
Addition Reactions of Alkenes

Syn Addition

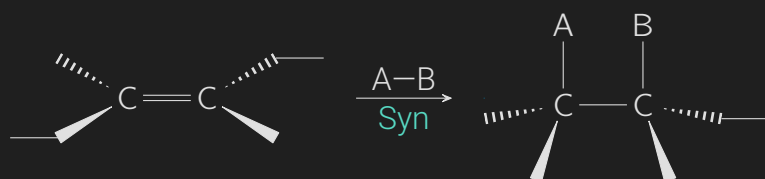
- Syn addition means that both components (A & B) came in from the same side.



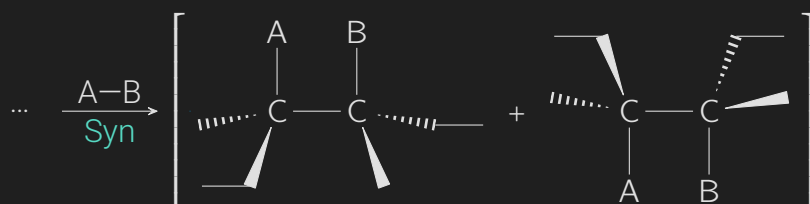
- When there is mixture of products, then the stereochemistry is important—A & B could come from different directions.
- Switching to a 3D perspective, with groups pointing towards and away from the viewer, rather than a flat view:



- The final product above results in no chiral compounds (no carbons contain four different groups). If a product does have chiral compounds, you must show the other possible products.

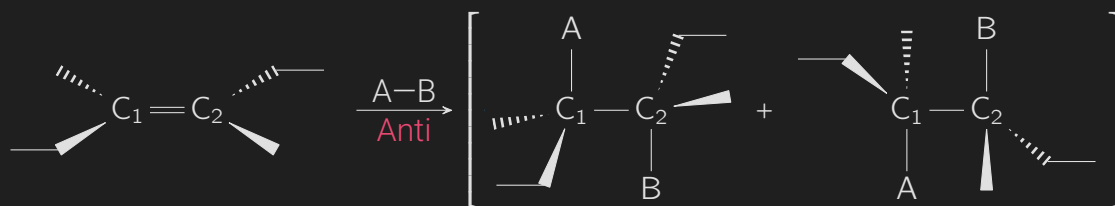


- The product in this case has chiral centers, so enantiomers must be considered.



Anti Addition

- Anti addition means that the added components come in from different sides.



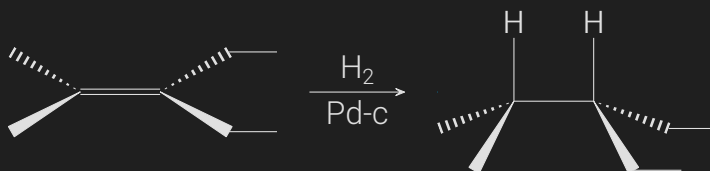
Types of Addition Reactions

- **Hydrogenation:** a chemical reaction between molecular hydrogen H_2 and another compound or element, usually in the presence of a catalyst such as nickel, palladium (typically Pd , due to cost) or platinum.
 - Commonly employed to reduce or saturate organic compounds.
 - Usually constitutes the addition of pairs of hydrogen atoms to a molecule, often an alkene.
 - Catalysts are required for the reaction to be usable; non-catalytic hydrogenation takes place only at very high temperatures.
 - **Reduces** double and triple bonds in hydrocarbons.
 - Always occurs with **syn addition**, with hydrogen entering from the least hindered side.
- Hydrogenation of 2-methyl-3-ethyl-2-pentene:

- First convert to 3D view:

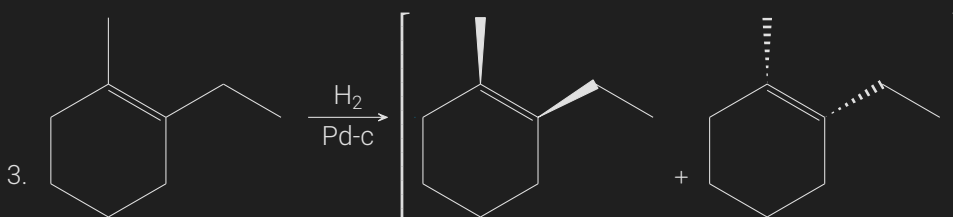
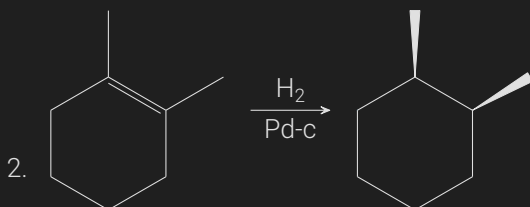
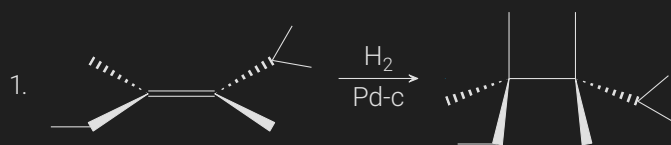


- Then apply H_2 with catalyst to trigger syn addition:

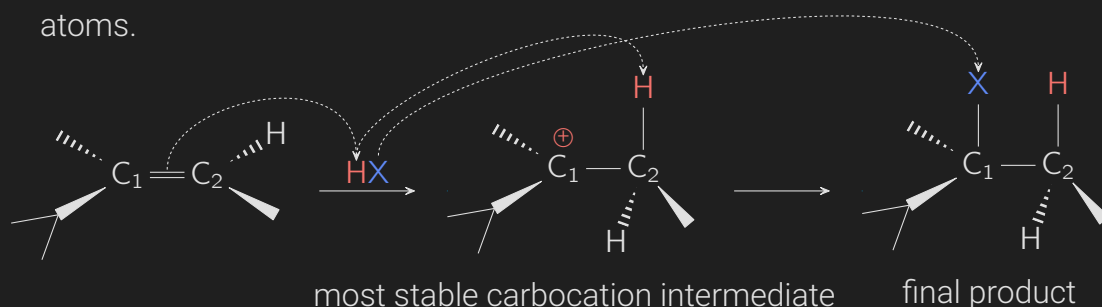


- Product is achiral; no enantiomers. Bottom would attack just flips the orientation; not a different product.

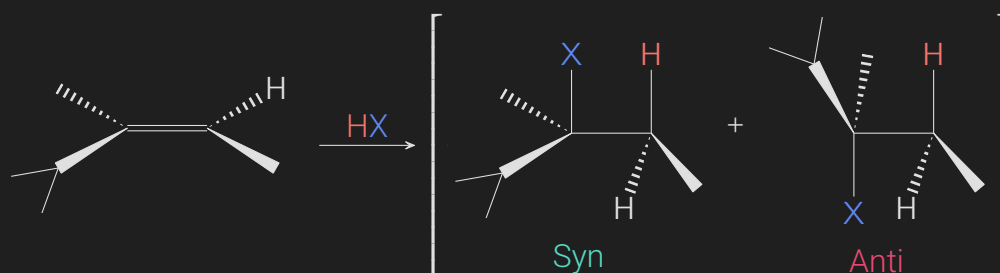
Hydrogenation Practice Problems



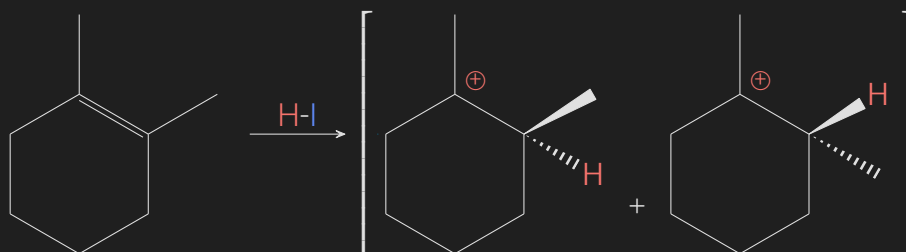
- **Hydrohalogenation:** the electrophilic addition ($\pi \rightarrow 2\sigma$ bonds) of hydrohalic acids (HX, e.g., HCl or HBr) to alkenes to yield the corresponding haloalkanes.
- **Markovnikov's rule:** an addition of a protic acid (HX) or other polar reagent to an asymmetric alkene results in the **electropositive part (usually H)** gets attached to the carbon with **more hydrogen substituents**, and the **electronegative part (usually the halide)** attaches to the carbon with **more alkyl substituents**.
 - Alternatively: H^+ is added to the carbon with the **greatest** number of hydrogen atoms while the X^- **component** is added to the carbon with the **fewest** hydrogen atoms.



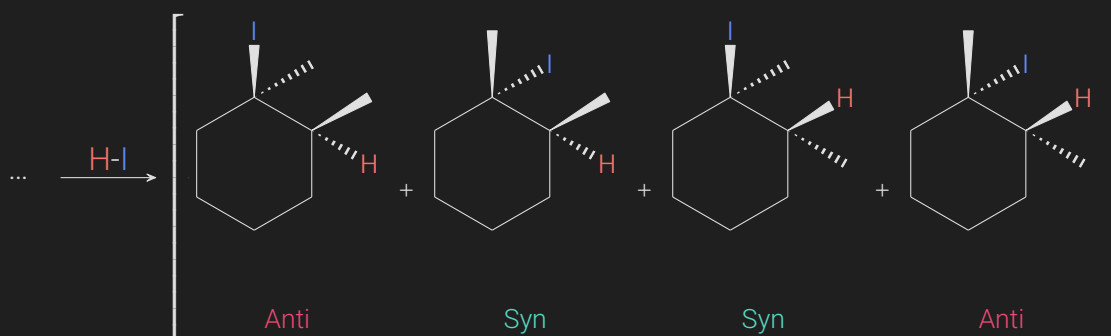
- However, we have a chiral carbon, so we have to take enantiomers into account:



- The previous example is an example of a regioselective reaction, i.e., it's a chemical reaction where one reaction site is preferred over another.
 - Markovnikov additions are common examples of regioselective reactions since there is a specific region in where the hydrogen is supposed to go.
- Another example that contains multiple products:

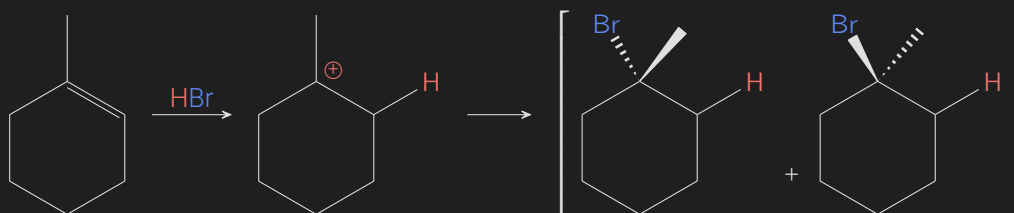


- Again, this first step shows the most stable carbocation intermediate, which helps determine where the H^+ will attach to. In this case either location works, so four products are formed, each with syn and anti enantiomers.



- The above products are all **stereoisomers** of each other. Note: not all chemical reactions produce all possible stereoisomers.

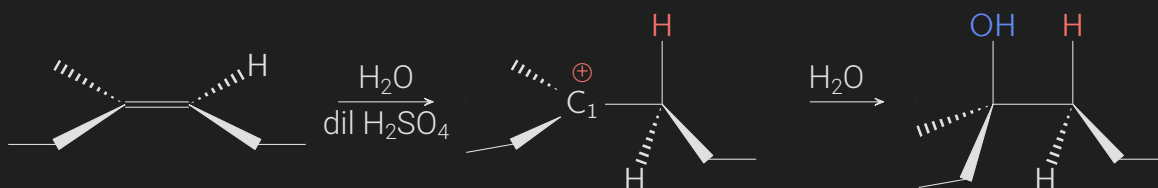
Hydrohalogenation Practice Examples



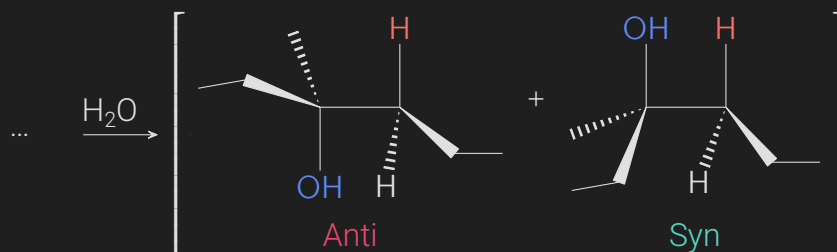
Addition of Water or Alcohol (ROH): analogous to that of hydrohalogenation (HX); both of which involve a carbocation intermediate, syn/anti stereochemistry, and Markovnikov regioselectivity.

- Note: the hydronium ion (H_3O^+) forms via the reaction of H_2SO_4 with H_2O , and is the source of the proton that reacts with the starting alkene.

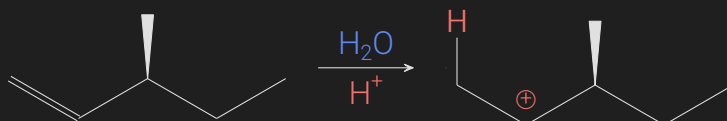
- H–OH and RO–H helps to visualize where the proton is coming from. What ever works with water also works with alcohol and vice versa.
- An example that is very similar to the example from hydrohalogenation ↗:



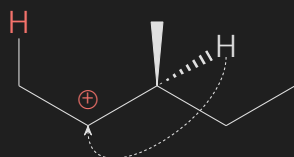
- Note: H_2SO_4 is a **strong acid** and can be generalized to H^+ or HA.
- Note: I occasionally use **red** for both **cations** and **acids**. I also use **blue** for **anions** and **bases** to help easily keep track of things. This is an arbitrary color choice, but it holds weight in these notes.
- Again, this reaction is stereoselective, so there is actually more than one product:



- Example 2:



- Rearrangement is always a possibility to be considered when cation are generated. In this case, a 2° carbocation was generated, but we can do better:



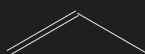
Nomenclature of Alkenes

- ▷ Generally prepared through beta elimination, which results in the formation of alkenes (series of unsaturated hydrocarbons contain that a π bond).
- ▷ Alkenes are named using the same four steps in the previously used nomenclature, though the suffix of "ane" is replaced with "**ene**".
- ▷ When choosing the parent chain, choose the parent chain that **includes** the π bond.

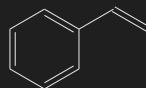
- ▷ When numbering the parent chain, the π bond should receive the **lowest** number possible.
- ▷ The locant of the π bond should be placed right before the suffix of “ene,” though, it was previously recommended before the parent (both are acceptable).
- ▷ Commonly recognized alternative names:



Ethylene



Propylene



Styrene