

Organic Chemistry II

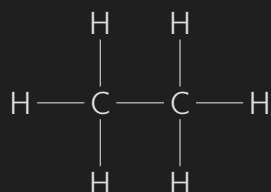
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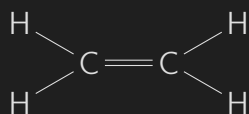
14: Alkenes

Alkenes Basics/Review

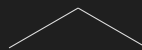
▷ Alkanes vs alkenes:



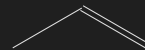
Saturated
alkanes ethane



Unsaturated
alkenes ethene



propane



propene

▷ We will fully investigate the nomenclature of alkenes ↗ later.

▷ Some relevant facts to start:

- **Alkene**: a hydrocarbon that contains a carbon-carbon double bond.
 - IUPAC recommends using alkene for only acyclic hydrocarbons with just one double bond; an **olefin** is a hydrocarbon with one or more double bonds.
- Generally prepared through beta elimination, which results in the formation of alkenes from alkanes.

Types of Alkenes

- Basic types of alkenes:



Terminal Alkene

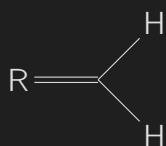


Internal Alkene

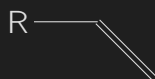


Cycloalkene

- Types of terminal alkenes:



Methylene



Vinyl

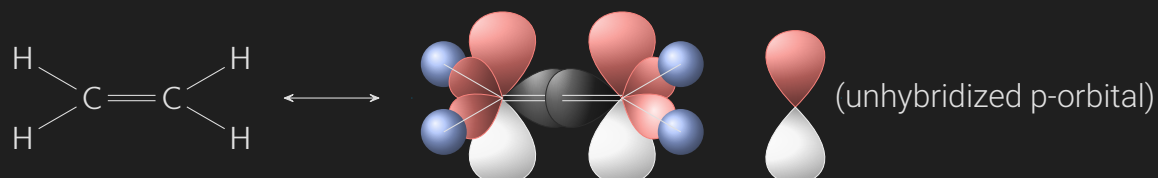


Allyl

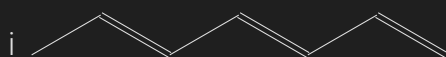
- “R” always tells you it’s a carbon containing functional group, or hydrogen.
- “A” can be used to represent any functional group.

Relevant 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 bounds, triple bounds, 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.



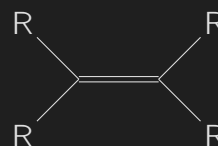
Monosubstituted



Disubstituted



Trisubstituted



Tetrasubstituted

Common Patterns Between Formal Charge and Lone Pairs

◦ Associated Patterns for Oxygen

- A negative (\ominus) charge corresponds with 1 bond and 3 lone pairs.
- The absence of charge corresponds with 2 bonds and 2 lone pairs.
- A positive (\oplus) charge corresponds with 3 bonds and 1 lone pair.

◦ Associated Patterns for Nitrogen

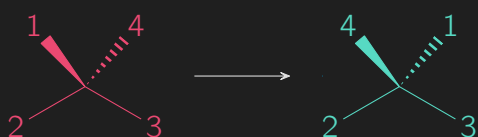
- A negative charge corresponds with 2 bonds and 2 lone pairs.
- The absence of charge corresponds with 3 bonds and 1 lone pair.
- A positive charge corresponds with 4 bonds and 0 lone pairs.

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*, *rectus*, *right*) or counterclockwise (*S*, *sinister*, *left*).
- If there is a tie between the atoms connected, then continue outward until a difference is found.
 - Do not add the sum of 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.

Rearrangements

- There are several kinds of rearrangements, but only those relating to carbocation rearrangements are focused here.
- **Hyperconjugation:** carbocations that can be stabilized by neighboring groups due to molecular orbitals that slightly overlap with empty *p* orbitals, placing some of its electron density there.

- Primary (1°), secondary (2°), and tertiary (3°): refers to the number of groups directly attached to the carbocation.
- Tertiary are the most stable (more slight overlap) and primary are the least (less overlap)
- **Hydride shift:** involves the migration of a H^- .
 - Involves the rearrangement of the carbocation to a more stable variant due to change migration of the H^- .
- **Methyl shift:** similar to a hydride, except a whole methyl group is migrated instead.
 - The methyl group must be attached to the carbon atom that is adjacent to the carbocation for this to occur.

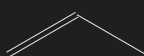
Nomenclature of Alkenes

Basic Alkene Nomenclature Rules

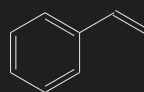
- Alkenes are named using the same four steps in the previously used nomenclature, though the suffix of "ane" is replaced with "ene."
- When choosing the parent chain, choose the parent chain that **includes** the double bond.
- When numbering the parent chain, the double bond should receive the **lowest** number possible.
 - Define the location k of the double bond as being the number of its first carbon.
 - The locant (k) of the double bond should be placed right before the suffix of "ene," though, it was previously recommended before the parent (both are acceptable), e.g., 2-pentene = pent-2-ene
- Name and the side groups (other than hydrogen) according to the appropriate rules.
- Define the position of each side group as the number of the chain carbon it is attached to.
- E-Z notation:** recommended instead of *cis* and *trans* in order to account for cases that has more than two different groups attached to the double bond by first determining the **CIP priority** ↗.
 - E**, *entgegen*, "opposite".
 - Z**, *zusammen*, "together"; "on ze zame zide."
- Commonly recognized alternative names:



Ethylene



Propylene



Styrene

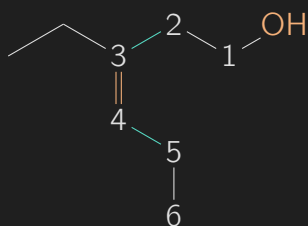
- Groups containing C=C have common names as well, which can be found under **types of alkenes** ↗.

Alkenes Containing an Alcohol

- If there is **more than 1** functional group, then the **alcohol** has the **higher priority** over alkenes.
- There are more rules depending on functional groups, but for now the distinction between alcohol and alkenes are all that is needed.

- I.e., find the longest chain and number in a way that the carbon containing the OH gets the lowest possible number while still including both the OH and alkene.

- An example with alcohol:

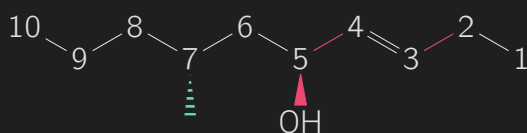


(3Z)-3-propyl-hex-3-en-1-ol

or

(3Z)-3-propyl-3-hexen-1-ol

- An example with OH still being lowest (name still ends with -ol), but alkene happens to be lower:



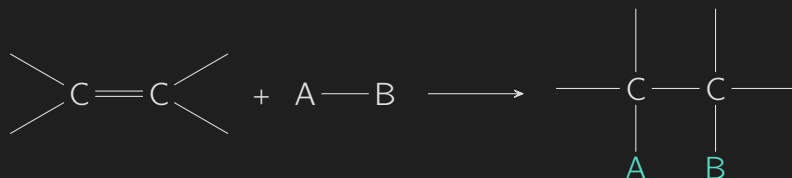
(3E,5S,7R)-4-methyl-3-en-5-ol

- Note: if planar geometry was not given, R and S could not be determined. Check out the [Cahn-Ingold-Prelog System](#) ↗ for review.

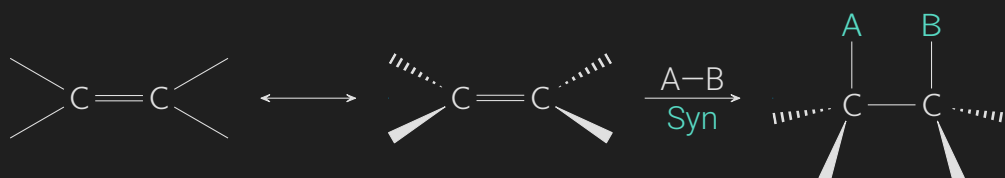
Addition Reactions of Alkenes

Syn Addition

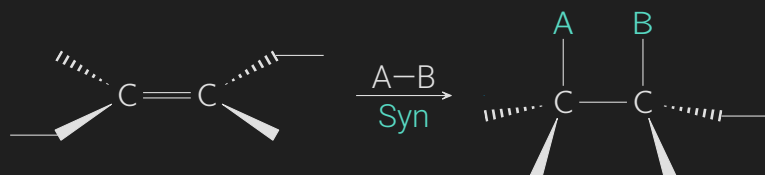
- Syn addition means that both components (A & B) came in from the same side.



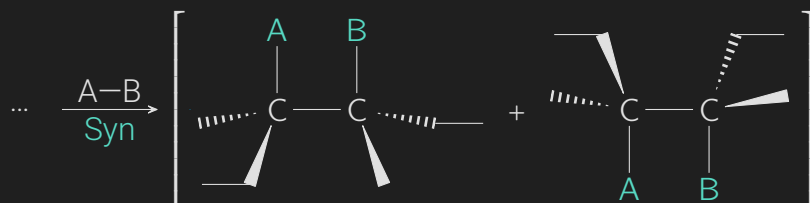
- When there is mixture of products, then the stereochemistry is important—A & B could come from different directions.
- Switching to a 3D perspective, with groups pointing towards and away from the viewer, rather than a flat view:



- 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.

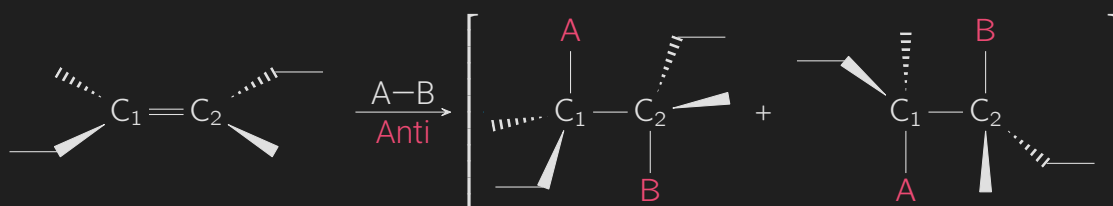


- The product in this case has **chiral centers** ↗, so enantiomers must be considered.



Anti Addition

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



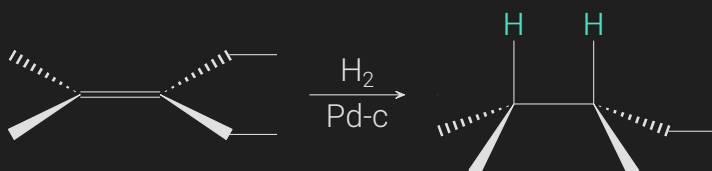
Hydrogenation

- **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** (π bonds) or **saturate** (add hydrogens) 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.
 - 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:

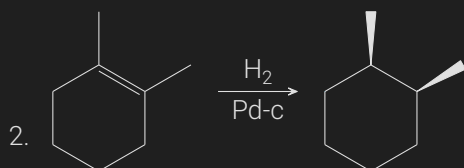
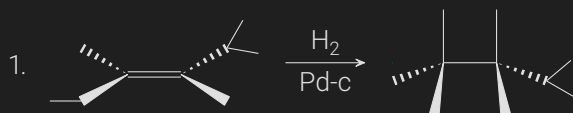


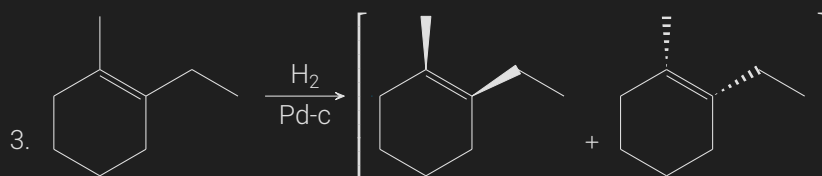
- Then apply H_2 with catalyst to trigger syn addition:



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

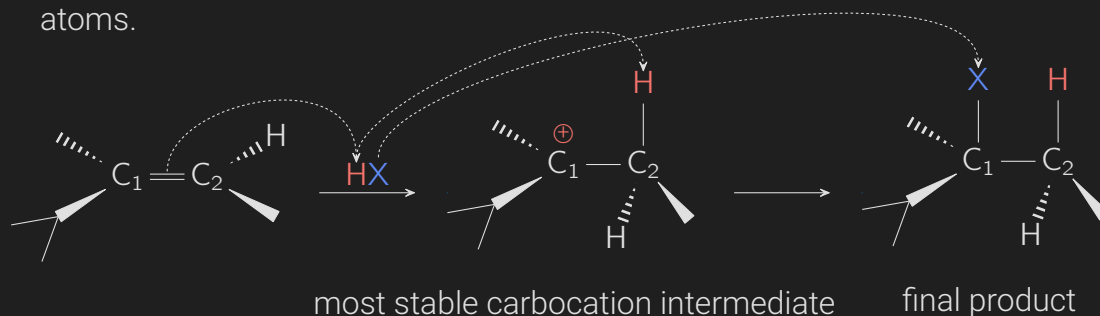
Hydrogenation Practice Problems



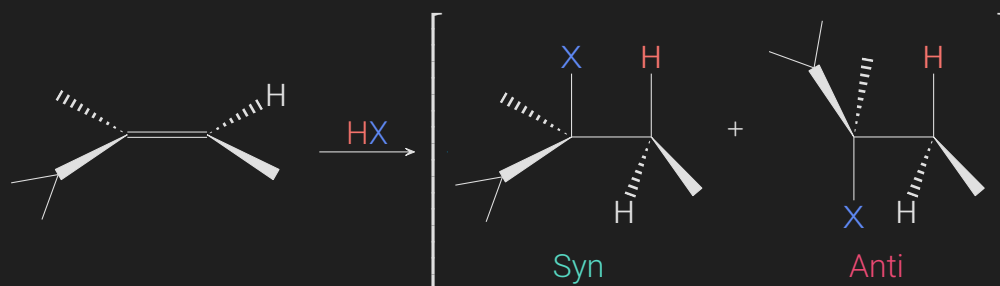


Hydrohalogenation

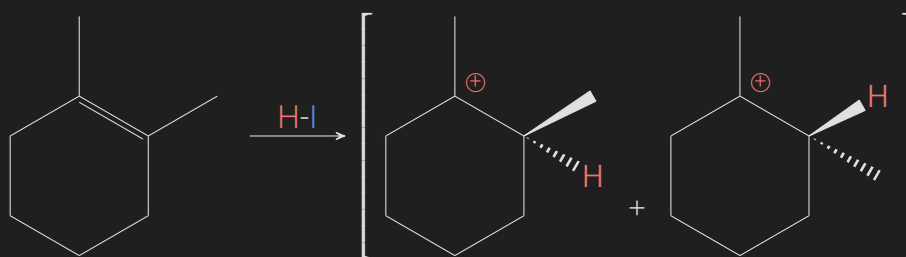
- **Hydrohalogenation:** the electrophilic addition ($\pi \rightarrow 2\sigma$ bonds) of hydrohalic acids (HX, e.g., HCl or HBr) to alkenes to yield the corresponding haloalkanes.
- **Markovnikov's Rule:** an addition of a protic acid (HX) or other polar reagent to an asymmetric alkene results in the **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.



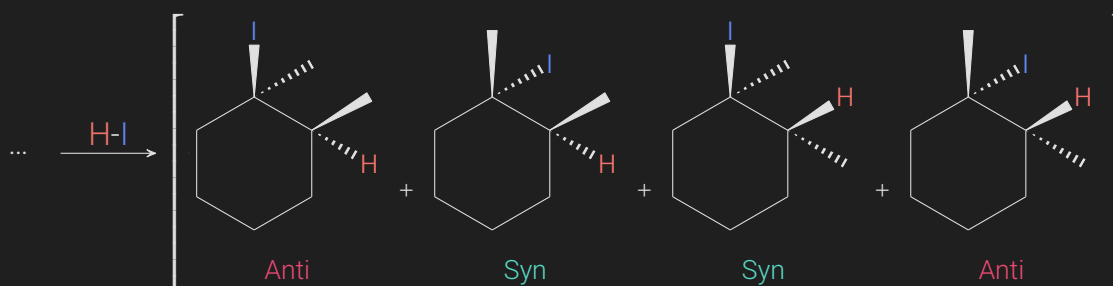
- However, we have a chiral carbon, so we have to take enantiomers into account:



- 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:

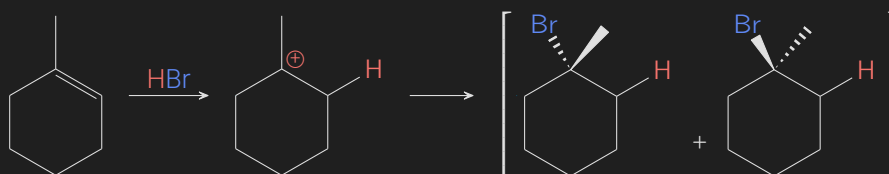


- Again, this first step shows the most stable carbocation intermediate, which helps determine where the H^+ will attach to. In this case either location works, so four products are formed, each with syn and anti enantiomers.



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

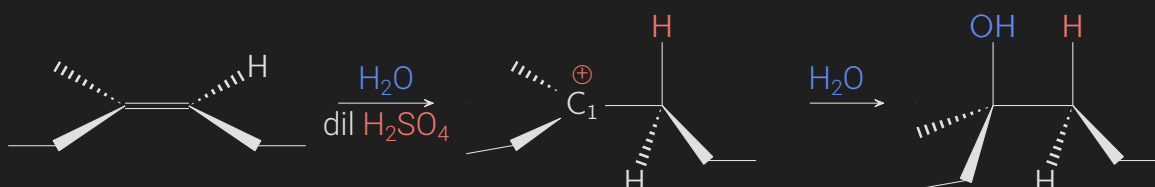
Hydrohalogenation Practice Examples



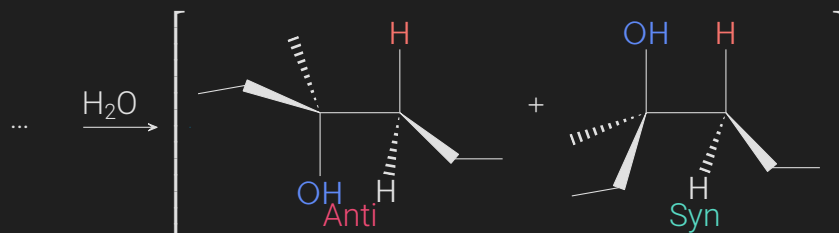
Addition of Water or Alcohol

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.

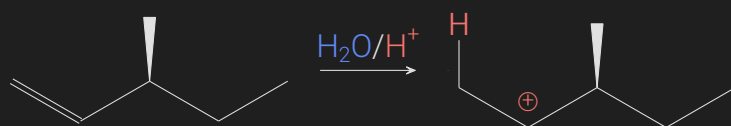
- Note: the hydronium ion (H_3O^+) forms via the reaction of H_2SO_4 with H_2O , and is the source of the proton that reacts with the starting alkene.
- $\text{H}-\text{OH}$ and $\text{RO}-\text{H}$ helps to visualize where the proton is coming from. What ever works with water also works with alcohol 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 **cations**, **acids**, and E^+ (electrophile). I also use **blue** for **anions**, **bases**, and nu^- (nucleophile) to help easily keep track of things. This is an arbitrary color choice, but it holds weight in these notes. However, not all bases/acids are nucleophile/electrophiles, so keep that in mind.
- Again, this reaction is stereoselective, so there is actually more than one product:

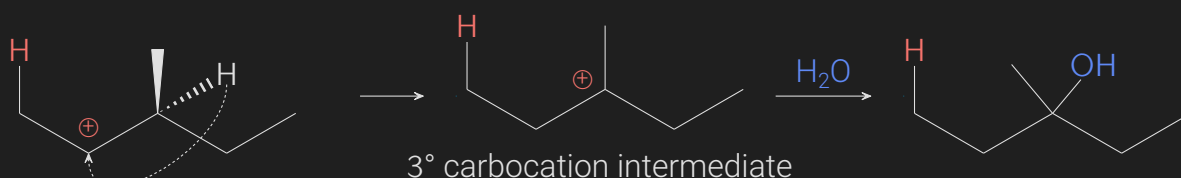


- Example 2:

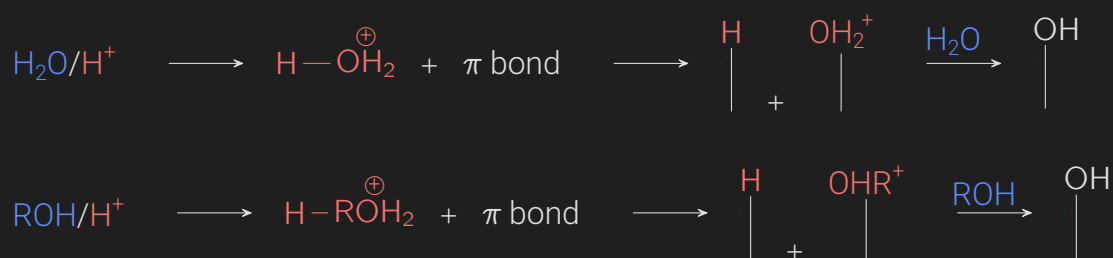


- **Rearrangement** \rightarrow is always a possibility to be considered when cation are generated. In this case, a 2° carbocation was generated, but we can do better:

- Note: showing H is not necessary, but useful to visualize the hydride shift and avoid the urge to move the methyl. "Why move a sofa when you can move a chair?"



- Note: the carbocation intermediate changes planar geometry due to change in hybridization ($sp^3 \rightarrow sp^2$).
- Top and bottom attacks do not need to be considered in this case, as there are chiral centers; no enantiomers.
- Reminder, H_2O and alcohols (ROH) behave very similarly; the reduction of the π bond generates 2σ bonds, one of which that takes a **hydrogen**, and the other (with possible carbocation rearrangement first) which first takes up the **cation** generated in the medium, then interacts with **base**, removing an **H** and leaving **OH**.
- Note: the OH is not actually negatively charged on the end, I just keep the blue there to help show where it's coming from; it helps determine syn/anti if needed.



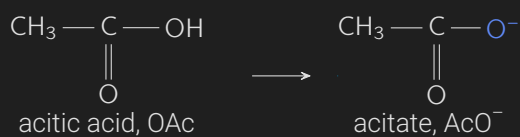
◦ **Problems of going through carbocation intermediate:**

- Carbocations are sp^2 , which makes them trigonal planar, so nu^- can attack from top or bottom.
- C^+ can cause rearrangements leading to **multiple products**.

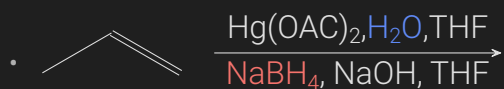
Oxymercuration-Demercuration

◦ **Oxymercuration-Demercuration** is another electrophilic addition organic reaction that transforms an alkene into a neutral alcohol.

- Reacts with mercuric acetate ($\text{AcO}-\text{Hg}-\text{OAc}$) in aqueous solution to yield the addition of an acetoxymcury (HgOAc) group and a hydroxy (OH) group across the double bond.

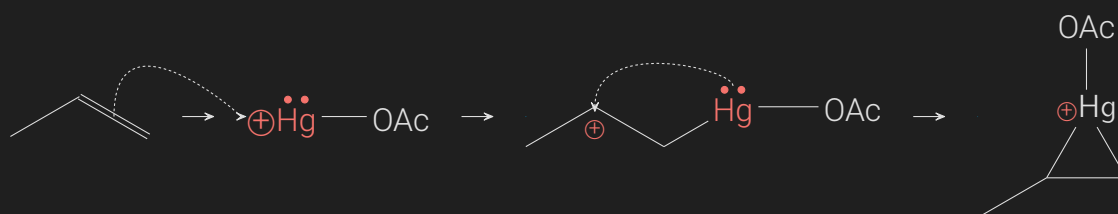


- Carbocations are not formed in this process and thus rearrangements are not observed.
 - The reaction follows **Markovnikov's rule**.
 - The reaction is stereospecific—it is always an **anti addition**.
- Example using propylene:

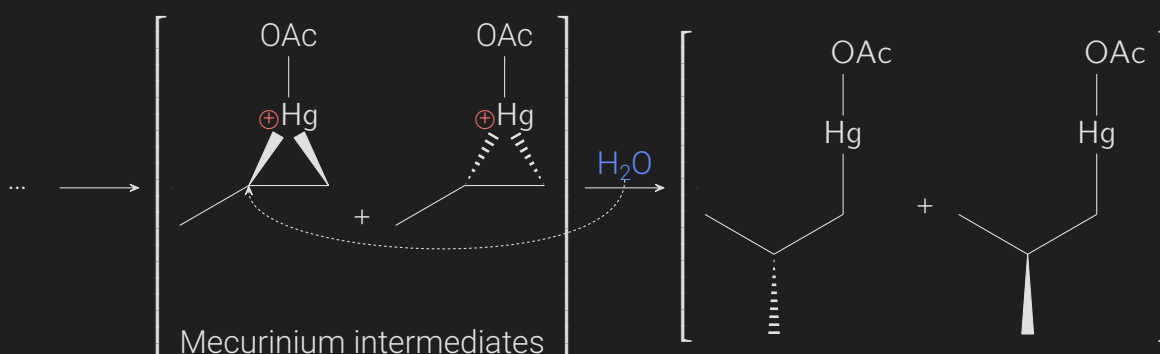


- H_2O is nu^- ; ROH can be used instead.
- THF has no function directly; it is the solvent.
- NaBH_4 is the reducing agent.



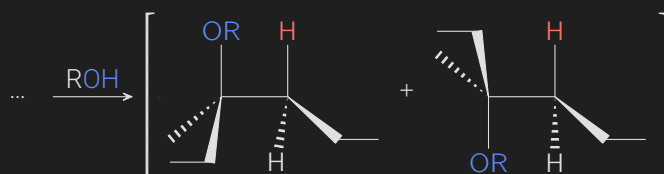
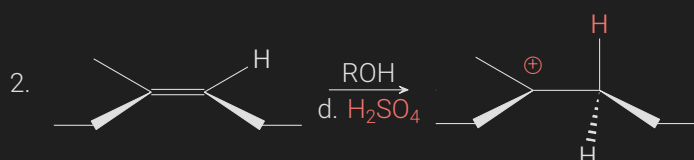
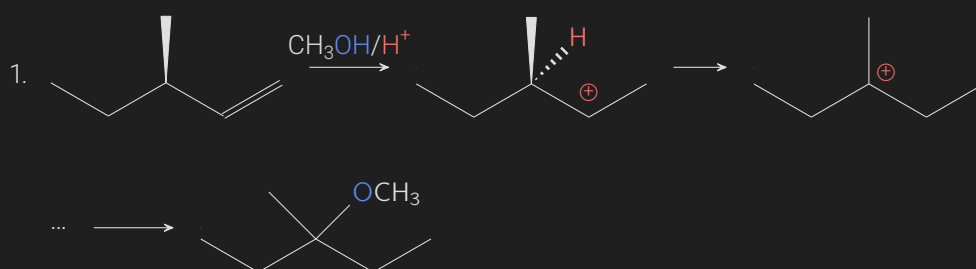


- Note: the above is a concerted (one step) process, but drawn out for illustration.
- Also, we are not done, we have a chiral center that forms, plus it is just an intermediate step, a nucleophilic attack will occur on the strained (highly reactive) epoxide:

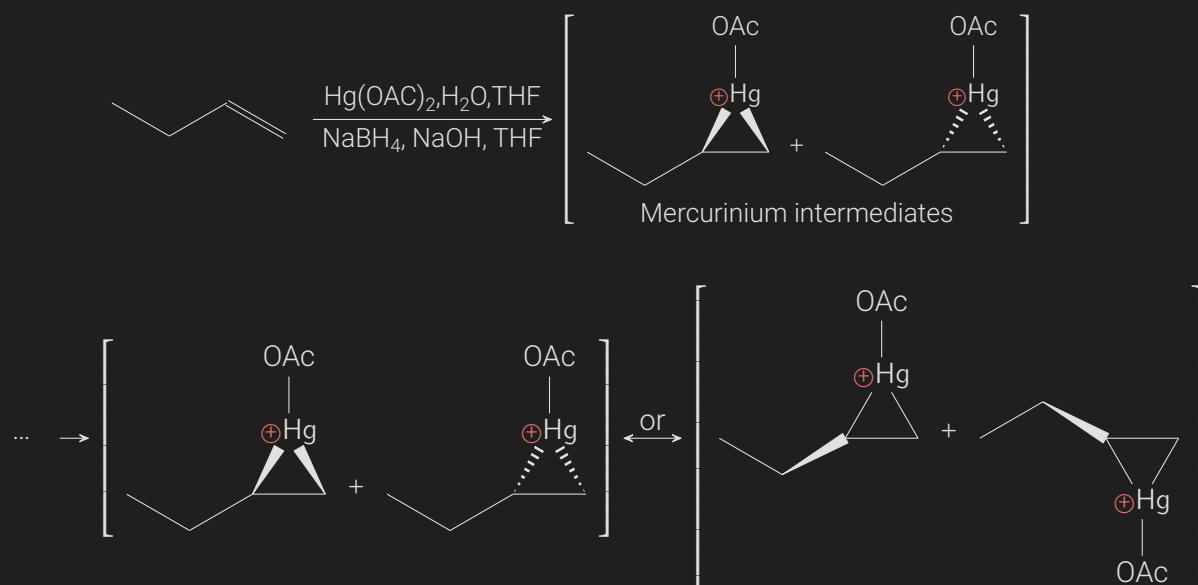


- Notice the nucleophile attacks the carbon with the greater flow of electrons (more substituted), since there was a positive charge on mercury. Epoxides with no charge are attacked on the side with less steric hindrance.
- Also, the nucleophilic attack occurs on the opposite side of the plane since there is less hindrance on that side.

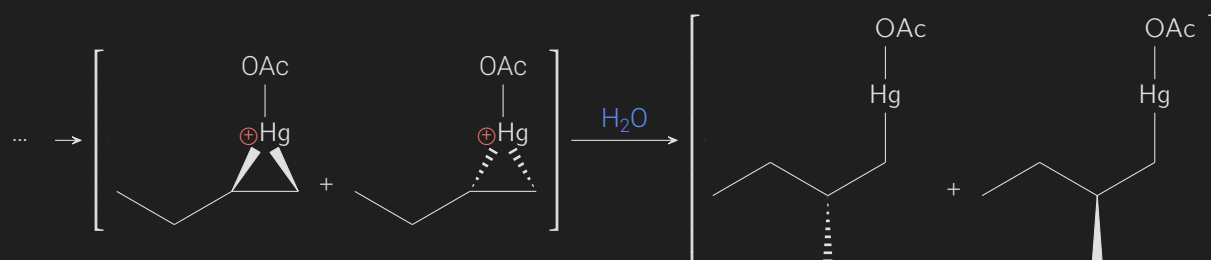
Related Practice Problems



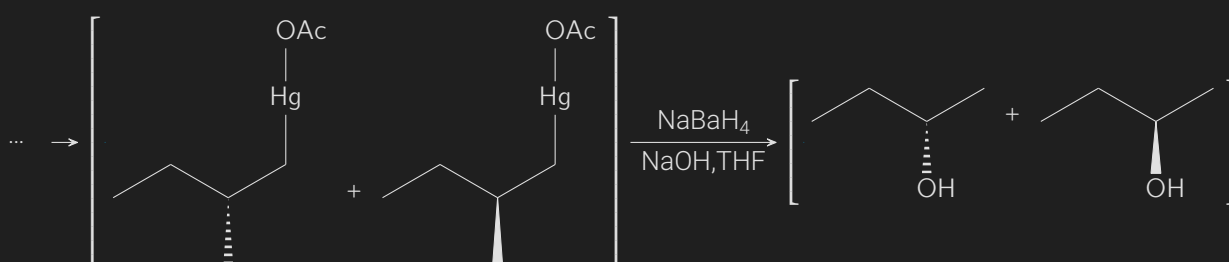
3. + Alternate ways of drawing rings (was done in lecture):



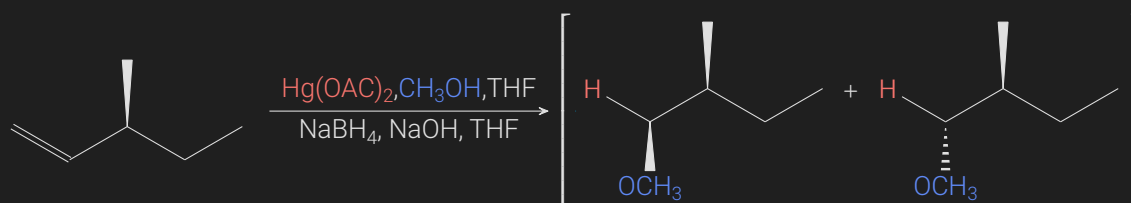
Oxymercuration:



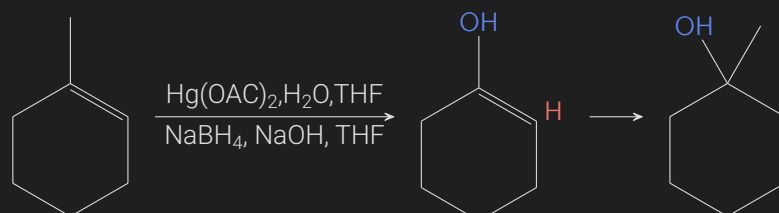
Demercuration:



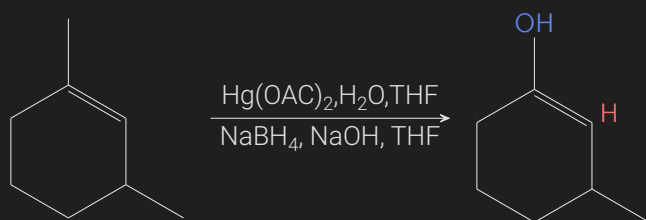
4.



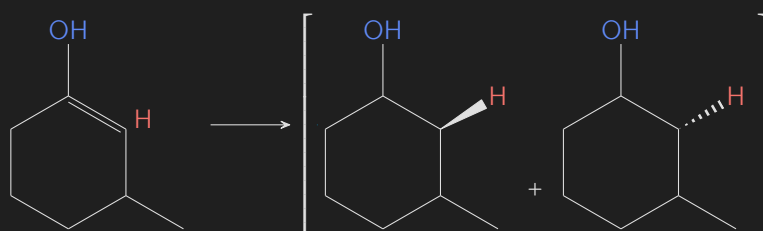
5.



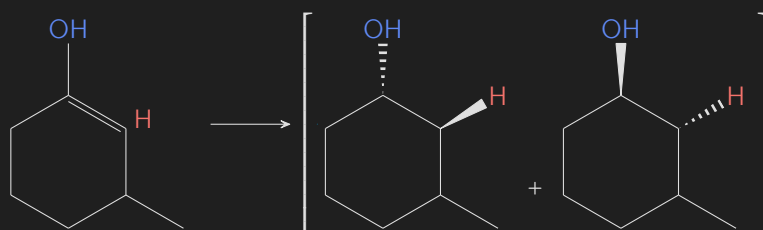
6. (was done in lecture)



- We know these are the locations of the H and OH, so we can start by labeling them.



- The methyl will be the same no matter what, so we can ignore that.
- H has two options, which gives us the above.
- Since oxymercuration-demercuration is always an **anti addition**, then we know OH must be **anti** to the hydrogen in both of the products:

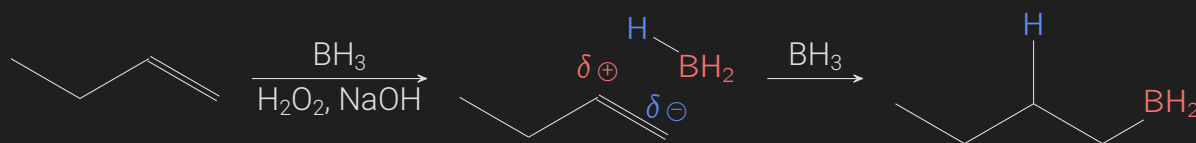


Hydroboration-Oxidation

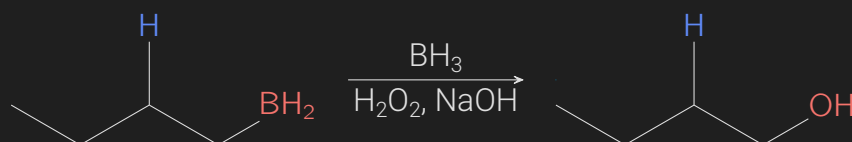
- **Hydroboration-Oxidation:** a two-step hydration reaction that converts an alkene into an alcohol.
 - Results in the **syn addition** of a hydrogen and a hydroxyl group where the double bond had been.
 - An **anti-Markovnikov reaction**—the hydroxyl group attaches to the less-substituted carbon.
 - Provides a more stereospecific and complementary regiochemical alternative to other hydration reactions such as acid-catalyzed addition (stereoselective) and oxymercuration-demercuration (stereospecific for anti).
 - Usually BH_3 , B_2H_6 , R_2BH are used. The presence of Boron is key.
- Like H_2O and ROH , it's useful to think of them in the following way:



- Unlike water/alcohol, the hydrogen is now the partial negative component and the boron is the positive.



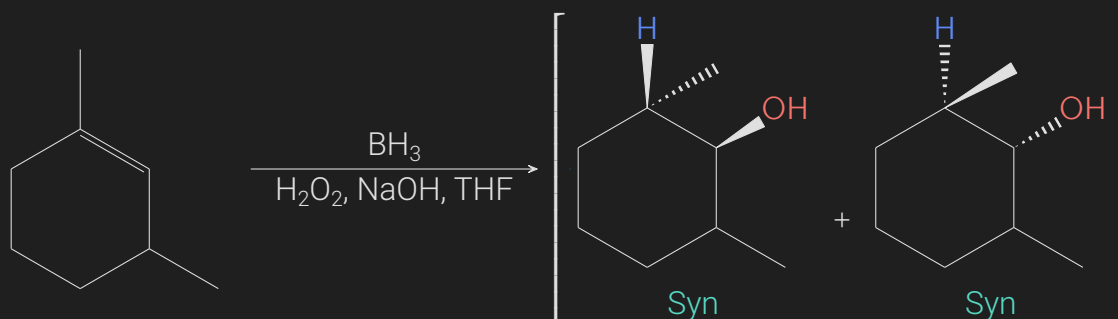
- There are no chiral centers, but there is still one more step—the oxidation:



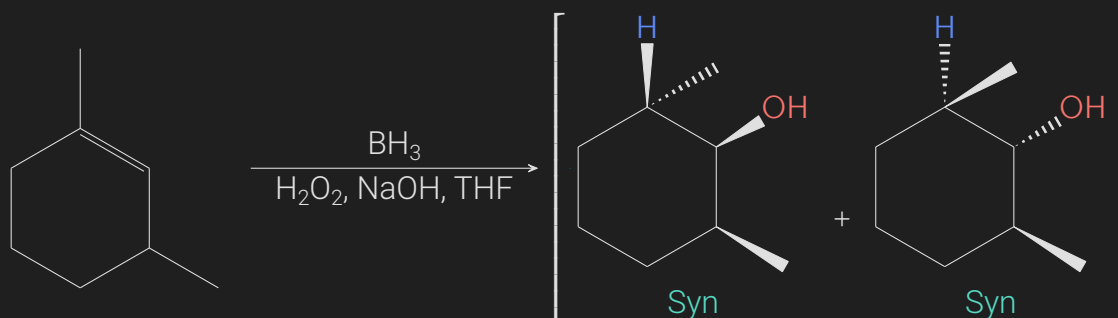
- If we had used $\text{Hg}(\text{OAc})_2$, then the above reaction would be different; partial charges change the possible final products: $\text{H}-\text{BH}_2$ vs. $\text{H}-\text{OH}_2$:



- Revisiting a practice example, using different reagents:

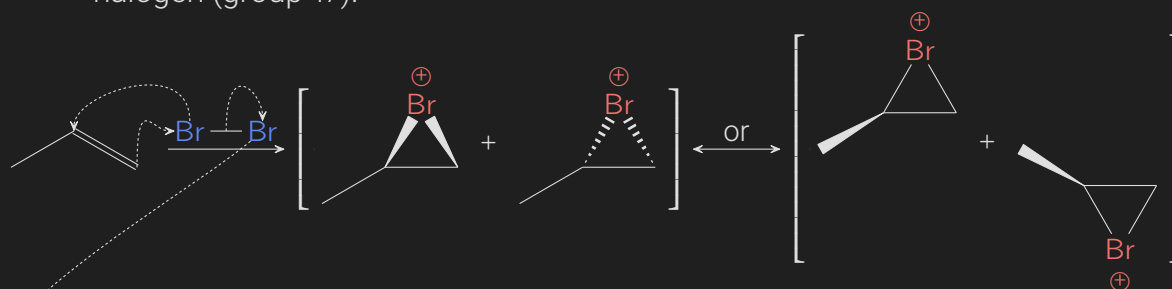


- If the untouched methyl happened to be above or below the plane initially, then you would keep that the same, e.g:

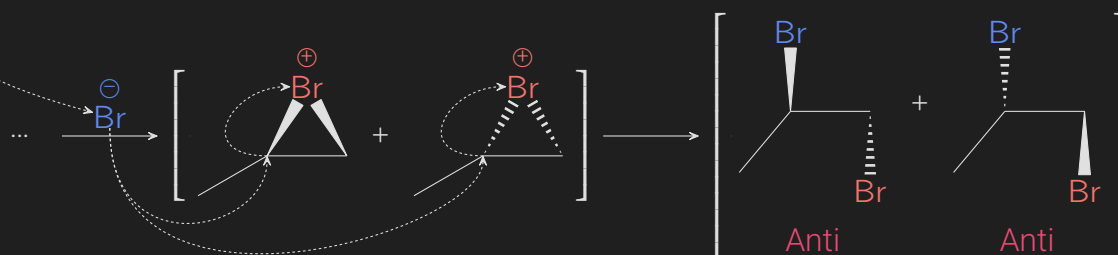


Halogenation

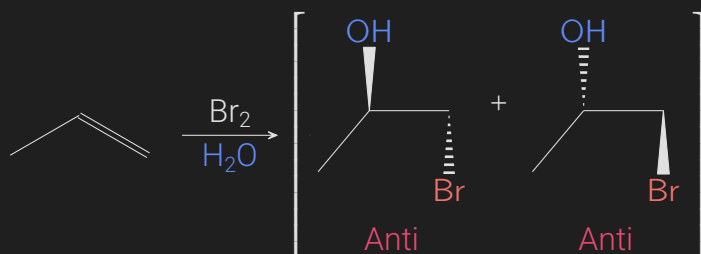
- **Halogenation:** a reaction that involves the addition of one or more halogens to a compound or material.
- The addition of halogens to alkenes proceeds via intermediate halonium ions.
- **Halonium ion:** any onium ion containing a halogen atom carrying a positive charge. This cation has the general structure: $R-^+X-R'$
- **Onium ion:** a cation formally obtained by the protonation of mononuclear parent hydride of a pnictogen (group 15 of the periodic table), chalcogen (group 16), or halogen (group 17).



- In the above example we see a cyclic bromonium ion intermediate being formed. Next, one bromine is now left to act as the nu^\ominus :



- Alternatively, if you did the reaction in H_2O , then water would become the dominant nu^\ominus , leaving OH .



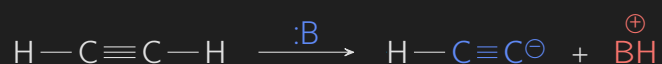
15: Alkynes

Alkynes Basics/Review

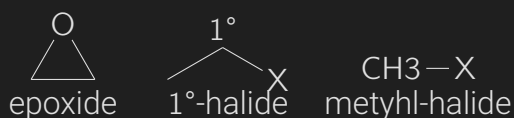
- ▷ **Alkynes**: an unsaturated hydrocarbon containing at least one carbon—carbon triple bond.
 - Contains two unhybridized p-orbitals (sp) on each carbon.
 - $\delta^+ \quad \delta^- \quad \delta^- \quad \delta^+$
 $\text{H} - \text{C} \equiv \text{C} - \text{H}$
 - Large amount of s character (sp: 50% s) makes the hydrogens very acidic and the carbons very basic.
 - 1 mole of base takes off 1 hydrogen (1 equivalent, equiv, eq), which can be done twice to take off both (2 equivalent).
 - Traditionally known as acetylenes, though acetylene refers specifically to C_2H_2 (ethyne)

Acetylides

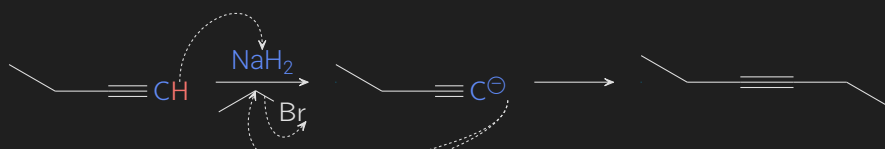
- ▷ **Acetylide**: an alkyne with a negatively charged carbon on one end, e.g.,



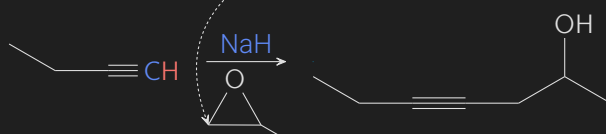
- :B is a name of generic base, typical bases used:
 - $\text{NaNH}_2 \rightarrow$ sodamide, or $\text{NaH} \rightarrow$ sodium hydride.
- Acetylide acts as a **nucleophile** when it reacts with an epoxide, 1°-halide, or a methyl-halide.



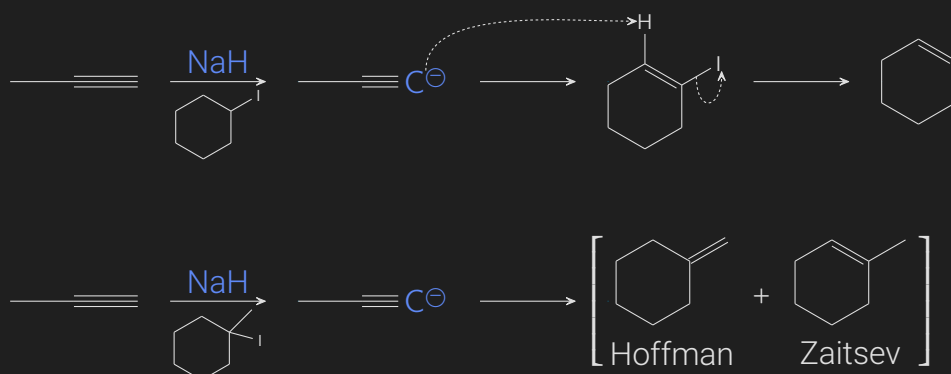
- Is a $\text{S}_\text{N}2$ reaction.
- Can be used for chain extension, e.g.,



- Example two:



- Acetylide acts as a **base** when it reacts with 2°-halide or a 3°-halide due to steric crowding.
 - Is an E2 reaction.



- The Zaitsev product is more likely to be the major product due to the thermodynamics (more energetically stable) than the Hofmann product; a bulkier base would likely increase the Hofmann product.

Regioselectivity and Stereospecificity of E2 Reactions

- **Regiochemistry**: when a chemical reaction is said to produce two different regiochemical outcomes.
 - **Regiochemical**: preference of chemical bonding or breaking **direction**.
- **Regioselective**: when there is a preference in products of a regiochemical reaction.
- **Zaitsev product**: name of the **more substituted** alkene that is generally observed to be the major product.
- **Hofmann product**: name of the **less substituted** alkene.
- The ratio between the Zaitsev and Hofmann product is dependent on a number of factors and often difficult to predict.
 - Steric hindrance of the base often plays a major role, often increasing the Hofmann product.
 - The outcome of E2 reactions can often be carefully **controlled by choosing the base**, despite difficulty in overall prediction.
- **Stereospecific**: when the stereoisomeric product of the E2 process depends on the configuration of the starting stereoisomeric substrate.
 - The stereospecificity is only relevant when the **β position has only one proton**.
- **Stereoselective**: when the substrate itself is not necessarily stereoisomeric, but can yield two stereoisomeric products, one of which that often has a higher yield.
 - Occurs when there are **more than one proton in the β position**.

- **Coplanar**: when the proton in the β position, the leaving group, and the two carbons atoms that form a double bond lie on the same plane.
 - Often leads only one stereoisomer product being formed, thus more often stereospecific.
 - If it stereoselective, then usually *trans* conformation is favored.
 - **Periplanar**: when the proton and leaving group are **nearly** coplanar; often is used in place of coplanar to incorporate both situations.
- **Syn-coplanar**: when the proton and the leaving group are **eclipsed** in a coplanar conformation.
 - Elimination in this state involves a higher energy transition state due to eclipsed geometry, and is **slower** than anti-coplanar arrangement.
- **Anti-coplanar**: when the proton and the leaving group are **staggered** in a coplanar conformation.
 - Elimination in this state involves a lower energy transition state due to staggered geometry, leading to a **faster** reaction relative to syn-coplanar.

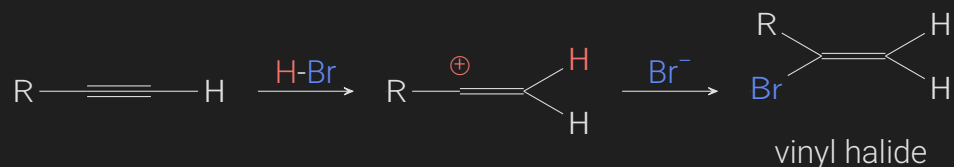
Alkyne Nomenclature



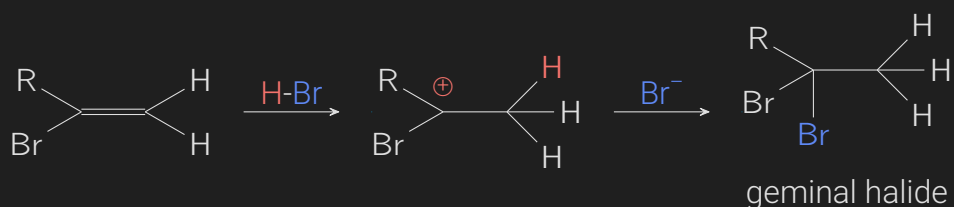
Addition Reactions of Alkynes

Hydrohalogenation of Alkynes

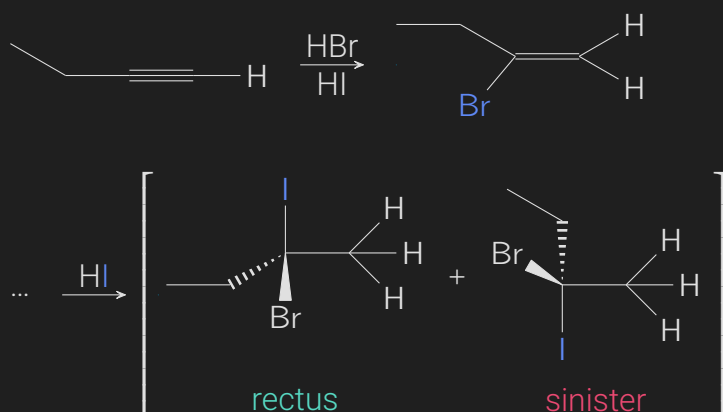
- Introductory example:



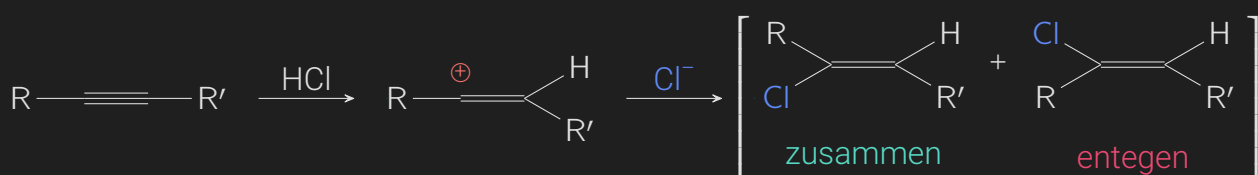
- Is Regioselective ↗
- Follows Markovnikov's Rule ↗
- This reaction can be done again (2 equiv):



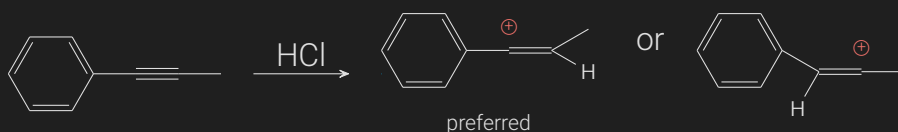
- Geminal halide: a carbon that contains two halides.
- Related practice problem that generates chiral carbon due to use of different reagents for each equivalence (needs to be verified still, I might be wrong):



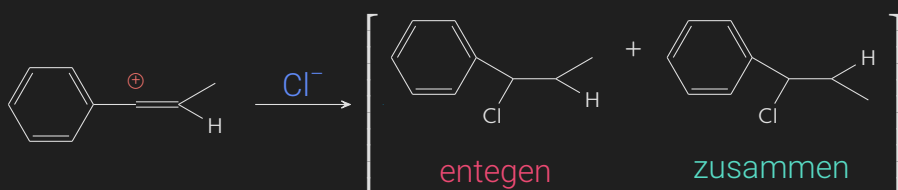
- Example with an internal alkyne; either side can be chosen if the R groups are not specified:



- Cl is higher priority than any carbon containing group (R), and any R' is higher than H, so both top and bottom attacks are possible.
- Related practice problem:

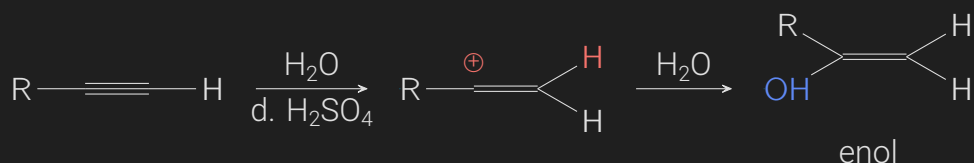


- The former carbocation intermediate is preferred due to resonance of the benzene ring, which does a better job stabilizing the carbocation.
- Continuing the reaction:

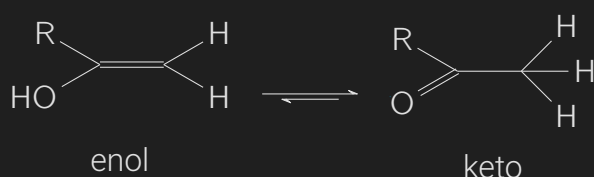


Hydration of Alkynes

- Introductory example:



- Follows **Markonikov's Rule** ↗
- However, enols readily interconvert with more stable form:



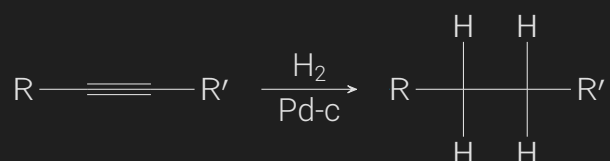
- **Tautomers:** a class of structural isomers (constitutional isomers) that readily interconvert, commonly due to the relocation of a proton (protonation-deprotonation) across a π bond.
 - The chemical reaction is called tautomerization; the concept is referred to tautomerism, which is sometimes desmotropism.
- Keto-enol tautomerism major product is the keto form, which does not allow for a second addition reaction.
- HgSO_4 is frequently used instead of d. H_2SO_4 , due to the mercurinium intermediate vs. the carbocation intermediate, which is both **faster** and a means to **reduce the probability** of byproducts.

- Example of an alkyne in a hydroboration-oxidation reaction ↗:

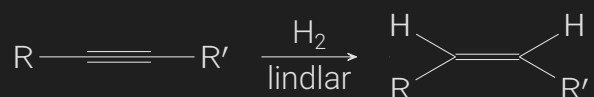
- **Aldehyde:** generally created by removing a hydrogen from an alcohol; in our case it is generated by the **anti-Markovnikov** reaction that results in a terminal enol, which then undergoes tautomerization and produces the aldehyde as the major product.

Hydrogenation of Alkynes

- Complete hydrogenation of an alkyne:



- Alkyne \rightarrow cis-alkene; use of lindlar catalyst (Pd-c poisoned with lead) limits further reduction by controlling hydrogens available:

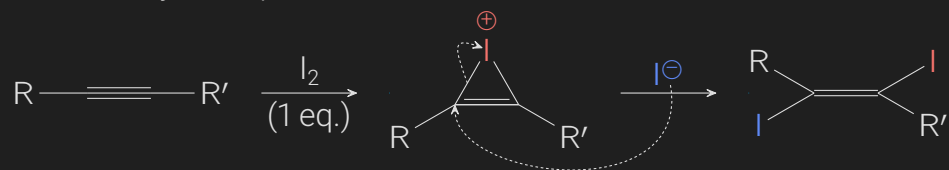


- Alkyne → **trans**-alkene; using generation of free radicals (•, single electron) that pair up with another electron generated by the dissociation of $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$ to create a free pair of electrons that then receive a hydrogen from NH_3 :

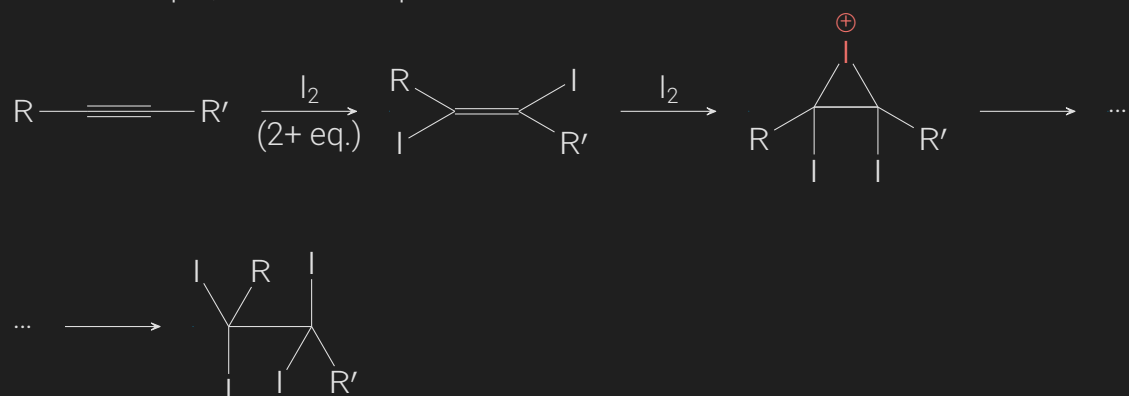
- Note, in lecture the added hydrogens were drawn separately; I am unsure, but I assume they happen near-simultaneously.

Halogenation of Alkynes

- Introductory example:



- The 3-membered cationic ring with a double bond is not very stable, so it does not form readily with a rate that is 10^3 – 10^7 times slower than that on an alkene.
- Same example, but with 2 equivalent or excess:



- Note: if you had controlled the second addition and added a different halide, then stereochemistry would have been important to consider since the products would have had chiral carbons.

16: Oxidation and Reduction

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17: Mass Spectrometry and Infrared Spectroscopy

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18: Nuclear Magnetic Resonance Spectroscopy

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19: Free Radical Reactions

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20: Conjugation and Resonance

...

21: Benzene and Aromaticity

...

22: Reactions of Aromatic Compounds

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