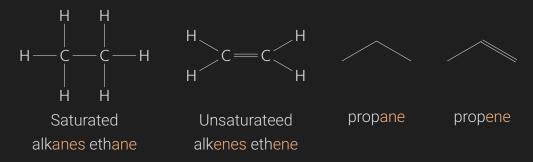
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14: Alkenes

Alkenes Basics/Review

▷ Alkanes vs alkenes:



- ▶ 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

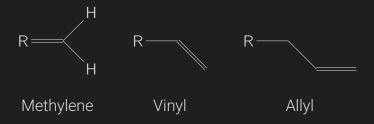
Basic types of alkenes:



Internal Alkene

• Types of terminal alkenes:

Terminal Alkene



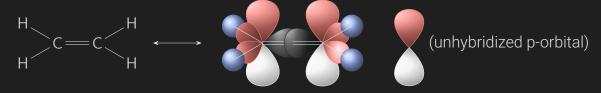
• "R" always tells you it's a carbon containing functional group, or hydrogen.

Cyloalkene

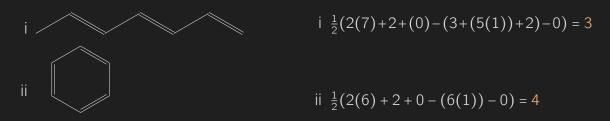
• "A" can be used to represent any functional group.

Relevant Review

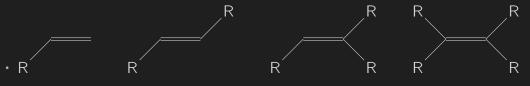
- **Electronegativity**: negative charges on atoms with lower hybridization result in greater stability due to proximity (overlap) to positive nucleus. More s character results in greater stability.
 - I.e., $sp(50\% s) > sp^2(33\% s) > sp^3(25\% s)$
 - E.g., ethene has two carbons that are both sp^2 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?



• **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

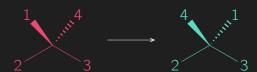
- Associated Patterns for Oxygen
 - A negative (○) charge corresponds with 1 bond and 3 lone pairs.
 - The absence of charge corresponds with 2 bonds and 2 lone pairs.
 - A positive (⊕) charge corresponds with 3 bonds and 1 lone pair.
- Associated Patterns for Nitrogen
 - A negative charge corresponds 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: 2ⁿ
 - · n: number of chiral centers
 - $\frac{2^n}{2}$: max pairs of enantiomers.

Cahn-Ingold-Prelog System

- **Chan-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 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:



• 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.

$$C = C + A - B \longrightarrow C - C - C$$

- 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.

$$C = C \xrightarrow{\text{Syn}} A = B \\ C = C \xrightarrow{\text{Syn}} C =$$

• 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.

$$C_1 = C_2$$

$$A - B$$

$$A - B$$

$$A - C_1 - C_2$$

$$A - C_1 - C_2$$

$$A - C_1 - C_2$$

$$A - C_2$$

$$A - C_2$$

$$A - C_1 - C_2$$

$$A - C_2$$

Hydrogenation

- **Hydrogenation**: a chemical reaction between molecular hydrogen H₂ 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 H₂ with catalyst to trigger syn addition:

$$H_2$$
 $Pd-c$
 H_2
 H_3
 H_4
 H_4

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

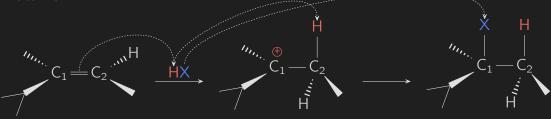
Hydrogenation Practice Problems

1.
$$\frac{H_2}{Pd-c}$$
 $\frac{H_2}{Pd-c}$

$$H_2$$
 Pd-c +

Hydrohalogenation

- **Hydrohalogenation**: the electrophilic addition ($\pi \to 2\sigma$ 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.



most stable carbocation intermediate

final product

• 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 regionselective 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

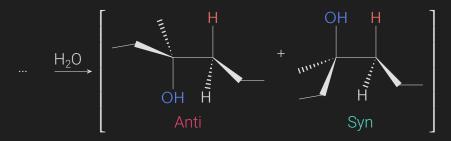
$$\begin{array}{c|c} & & & \\ &$$

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.
- 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: H₂SO₄ is a strong acid and can be generalized to H⁺ or HA.
- Note: I occasionally use red for cations, acids, and E^{\oplus} (electrophile). I also use blue for anions, bases, and nu^{\ominus} (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:

$$H_2O/H^+$$
 \oplus

- 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:
 - 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?"

H
$$H_2O$$
 H_2O
 H_2O
 H_3 ° carbocation intermediate

- 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.
- \circ Reminder, H₂O 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 is makes them trigonal planar, so nu^{\odot} can attack from top or bottom.
 - C^{\oplus} 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 (AcO-Hg-OAc) in aqueous solution to yield the addition of an acetoxymercury (HgOAc) group and a hydroxy (OH) group across the double bond.

$$CH_3 - C - OH$$
 $CH_3 - C - O^-$

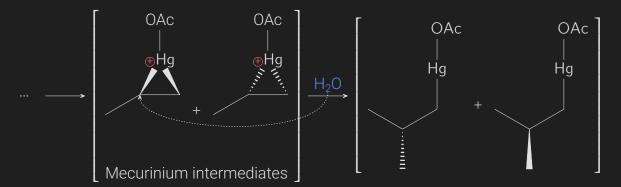
$$\parallel \qquad \qquad \parallel \qquad \qquad \parallel$$

$$O \qquad \qquad O$$
acitic acid, OAc acitate, AcO $^-$

- 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^{\odot} ; ROH can be used instead.
- THF has no function directly; it is the solvent.
- NaBH₄ 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 attack the carbon with the grater 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:

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 BH₃, B₂H₆, R₂BH are used. The presence of Boron is key.
- Like H₂O and ROH, it's useful to think of them in the following way:

$$\mathsf{BH3} \longleftrightarrow \mathsf{H} - \mathsf{BH}_2 \qquad \mathsf{R2BH} \longleftrightarrow \mathsf{H} - \mathsf{BR}_2$$

• 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:

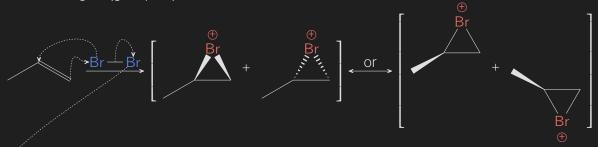
$$BH_2$$
 BH_3 H_2O_2 , NaOH OH

• Revisiting a practice example, using different reagents:

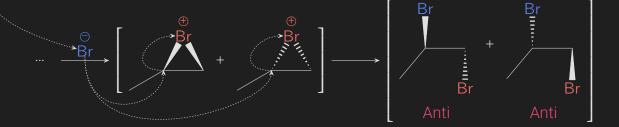
If the untouched methyl happened to be above or below the plane initially, then you
would keep that the same, e.g.

Halogenation

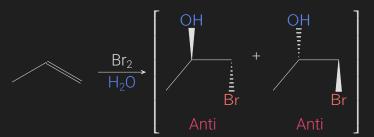
- **Halogenation**: a reaction that involves the addition of one or more halogens to a compound or material.
 - The addition of halogens to alkenes proceeds via intermediate halonium ions.
 - **Halonium ion**: any onium ion containing a halogen atom carrying a positive charge. This cation has the general 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^{\odot} :



• Alternatively, if you did the reaction in H_2O , then water would become the dominant nu^{\odot} , leaving OH.



15: Alkynes

Alkynes Basics/Review

- ▶ Alkynes: an unsaturated hydrocarbon containing at least one carbon—carbon triple bond.
 - o Contains two unhybridized p-orbitals (sp) on each carbon.

$$\delta$$
+ δ - δ - δ + H—C \equiv C—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).
- \circ Traditionally known as acetylenes, though acetylene referrers specifically to C_2H_2 (ethyne)

Acetylides

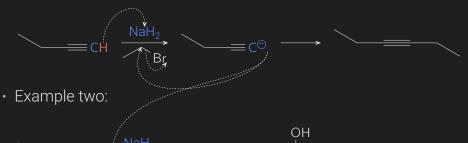
▶ **Acetylide**: an alkyne with a negatively charged carbon on one end, e.g.,

$$H-C\equiv C-H \xrightarrow{:B} H-C\equiv C^{\ominus} + BH$$

- :B is a name of generic base, typical bases used:
 - NaNH₂ → sodamide, or NaH → sodium hydride.
- Acetylide acts as a nucleophile when it reacts with an epoxide, 1°-halide, or a methyl-halide.

$$\begin{array}{cccc}
 & 1^{\circ} & \\
 & X & \text{CH3-X} \\
\end{array}$$
epoxide 1°-halide metyhl-halide

- Is a S_N 2 reaction.
- · Can be used for chain extension, e.g.,



- 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.

Preparation of Alkynes

 Introductory example of a geminal dihalide going through two E2 reactions to generate an alkyne:

$$R \xrightarrow{Br} H$$
 $R' \xrightarrow{NaNH_2} R$ $R' \xrightarrow{NaH_2} R$ $R' \xrightarrow{R'} R'$

Related example with a vicinal dihalide (halide on adjacent carbons):

$$R \xrightarrow{Br} R' \xrightarrow{NaNH_2} R \xrightarrow{R'} R \xrightarrow{NaH_2} R \xrightarrow{R'} R'$$

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.

- There 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 difficultly 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

Basic Alkyne Nomenclature

- All other basic IUPAC rules still apply; the suffix is "yne".
- Find the longest carbon chain that includes both carbons of the triple bond.
- Number the longest chain starting at the end closest to the triple bond.
- Compounds with > 1 triple bond are called diynes, triynes, etc.
- Enynes are compounds that contain both double and triple bonds, and enynols also contain an alcohol.
- The functional groups have their assigned carbon numbers written directly before their name.

Priority Rules

- More functional groups will change the as we get introduced to more, but for now we only need to know the following (somewhat follows electronegativity):
 - 1. Alcohol
 - 2. Alkenes
 - 3. Alkynes
 - 4. Alkyls
 - 5. Halogens
- Preference for naming order if multiple functional groups are present in the same chain: OH + DB + TB > OH + DB > OH + TB.
- When alkynes are substituents, then they are named as k-alkynyl. (k = locant)
- Example containing all three:

(3R,4E)-butylnon-4-en-7-yn-3-ol

Addition Reactions of Alkynes

Hydrohalogenation of Alkynes

Introductory example:

$$R \xrightarrow{H} H \xrightarrow{H-Br} R \xrightarrow{\oplus} H \xrightarrow{Br} Br \xrightarrow{H} H$$
vinyl halide

- 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:

$$R \longrightarrow R' \xrightarrow{HCl} R \xrightarrow{\oplus} H \xrightarrow{Cl} \begin{bmatrix} R & H & Cl & H \\ R' & R' & R' & R' \end{bmatrix}$$
zusammen entegen

- Cl is higher priority than any carbon containing gruop (R), and any R' is higher than H, so both top and bottom attacks are possibile.
- 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:

$$R \longrightarrow H \xrightarrow{H_2O} H \xrightarrow{H_2SO_4} R \xrightarrow{\oplus} H \xrightarrow{H_2O} OH \xrightarrow{R} H$$
enol

- 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.
- \circ HgSO₄ is frequently used instead of d. H₂SO₄, 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:

$$R \longrightarrow R' \xrightarrow{H_2} R \xrightarrow{H} H$$

$$R \longrightarrow R'$$

$$H \rightarrow H$$

$$H \rightarrow H$$

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

$$R - = R' \xrightarrow{H_2} \xrightarrow{H} \xrightarrow{R'}$$

 Alkyne → trans-alkene; using generation of free radicals (•, single electron) that pair up with another electron generated by the dissociation of Na → Na⁺+ e⁻ to create a free pair of electrons that then receive a hydrogen from NH₃:

$$R \xrightarrow{R'} R' \xrightarrow{\text{Na}} R' \xrightarrow{\text{R'}} R' \xrightarrow{\text{R$$

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

Halogenation of Alkynes

• Introductory example:

$$R \longrightarrow R' \xrightarrow{I_2} R \xrightarrow{P} R' \xrightarrow{I_0} R$$

- 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:

$$R = R' \xrightarrow{I_2} R \xrightarrow{I_2} R \xrightarrow{I_2} R' \xrightarrow{R'} R' \xrightarrow{R'} R'$$

 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.