

Summary Sheet - Additions to Alkenes

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If you understand just these 5 things, you'll be alright.

It's easy to get bogged down in details. Not all the details are equally important. Here are 5 key things to understand.

- Understand the order of carbocation stability.** Tertiary carbocations are most stable, followed by secondary and primary. Understand why.
- The most negative group will bond to the carbon best able to support positive charge.** This follows for the acid additions (e.g. HCl, HBr) AS WELL AS hydroboration, since H carries the negative charge in the H-B bond (due to the low electronegativity of B).
- Acids + alkenes = free carbocations.** With free carbocations, there can be no stereoselectivity (i.e. they are stereorandom). Also, be alert for the possibility of rearrangements, especially where tertiary carbocations can be formed.
- Halides + alkenes = bridging cations.** These will provide *anti* products. These cations never rearrange.
- If there's a metal involved, it's probably syn.** The only exception is oxymercuration.

(Sixth thing - less applicable, but still important)

6. If radicals are involved in the mechanism there can be no stereoselectivity. The two examples are oxymercuration (where NaBH₄ converts the C-Hg bond to C-H through a radical process) and the peroxide induced free radical addition.

Study Questions:

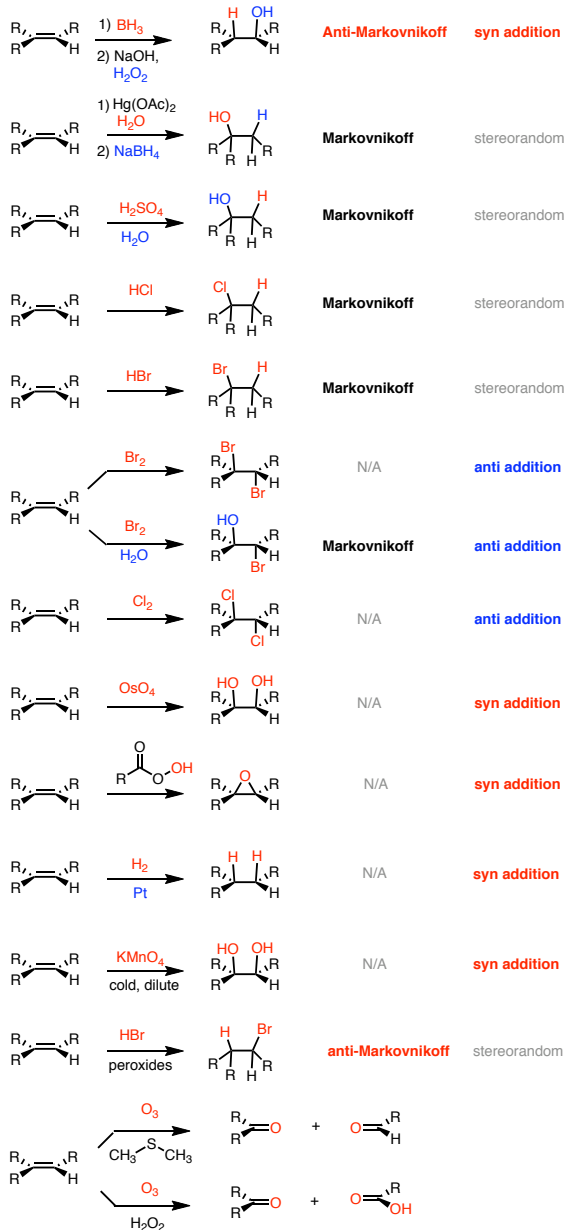
- What are some examples of Markovnikov-selective reactions?
- Why** are these reactions selective for the Markovnikov products?
- What are some examples of anti-Markovnikov selective reactions?
- Why** are they selective for the anti-Markovnikov products?
- What are some examples of anti-selective reactions. Why do they give the anti-products?
- What are some examples of syn-selective reactions?
- Write down combinations of alkene and reagent that would provide you with:
 - a primary alcohol
 - a secondary alcohol
 - a tertiary alcohol
 - an ether

Note - this sheet is not meant to be comprehensive. Your course may provide additional material, or may not cover some of the reactions shown here. Your course instructor is the final authority.

Omissions, Mistakes, Suggestions?

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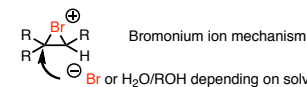


Sometimes you see BH₃·THF or B₂H₆ - it's the same reagent in a slightly different form. The base (can be NaOH, KOH, identity unimportant) helps make H₂O₂ more reactive. The reaction is *anti*-Markovnikov because the H-B bond is polarized toward H (electronegativity of H = 2.2, B = 2.0) - the H adds to the carbon best able to stabilize positive charge (i.e. the most substituted one).

Can use an alcohol in place of water. Goes through 3-membered "mercuronium" ion. NaBH₄ step removes the mercury. *While the addition is anti, the overall reaction is stereorandom* because this step involves a carbon based free radical (usually not discussed).

Strong acid protonates the alkene, generating free carbocation. Watch out for possibility of rearrangements when a tertiary carbocation could be generated through a 1,2 shift. HSO₄⁻ anion is not strongly nucleophilic, hence it does not add. Stereorandom because of the free carbocation.

HCl and HBr (as well as HI, not pictured) protonate the alkene to give a free carbocation which can then be trapped by the halide anion. Stereorandom

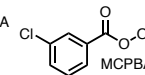


The key detail in these reactions is solvent: water and alcohol solvents will form the *halohydrin* products (the ones containing the OH and Br). All other solvents (you might see CCl₄, CHCl₃, hexane, etc.) provide the dibromide.

As with bromination, above. Although not depicted, use of water or alcohol as solvent will also lead to formation of the halohydrin product (also anti).

Osmium is a transition metal. The tools won't be given in this course to fully understand how this reaction works. Occasionally a second reagent like NaHSO₃, H₂S, or Na₂S₂O₃ is also given as a reactant in this reaction - minor detail, it's used to remove the osmium from the hydroxyl groups.

RCO₃H is a per-acid. A common peracid for this reaction is *m*-CPBA (*m*-chloroperbenzoic acid). If H₃O⁺, heat is written afterwards, this is opening of the epoxide to give the diol (anti-selective)



The catalyst can vary - you might see Pd/C or Ni as well. All provide the same product with the same stereochemistry.

Keywords are "cold, dilute". If "heat" is mentioned in the conditions, the diol will be cleaved to provide carbonyl compounds (same reaction as ozonolysis with **oxidative** workup, below).

Peroxides generate the Br[·] radical, which adds to the double bond in the way that will generate the most stable radical (i.e. the radical will go on to the most substituted carbon). This explains the selectivity for the anti-Markovnikov product. It's stereorandom because it goes through a free radical process.

CH₃SCH₃ (dimethyl sulfide) is a reducing agent, it will be oxidized to dimethyl sulfoxide.

Hydrogen peroxide is used to obtain the carboxylic acid instead of the aldehyde.