

Note: the alkene is drawn in perspective.
Imagine it lying flat on a table - the H is coming toward you, that's why it's drawn as a "wedge"

Additions to Alkenes

"Master Organic Chemistry"
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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.

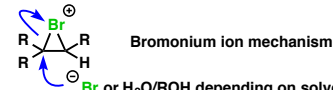
Reaction		"Regiochemistry"	"Stereochemistry"
Hydroboration		Anti-Markovnikoff	syn addition
Oxymercuration		Markovnikoff	syn + anti
Acid-catalyzed addition of H2O (hydration)		Markovnikoff	syn + anti
Addition of HX		Markovnikoff	syn + anti
Addition of HX		Markovnikoff	syn + anti
Bromination		N/A	anti addition
Halohydrin Formation		Markovnikoff	anti addition
Chlorination		N/A	anti addition
Dihydroxylation		N/A	syn addition
Dihydroxylation		N/A	syn addition
Epoxidation		N/A	syn addition
Hydrogenation		N/A	syn addition
Radical addition of HBr		Anti-Markovnikoff	syn + anti
Ozonolysis (Reductive workup)			
Ozonolysis (Oxidative Workup)			
Cyclopropanation		N/A	syn addition

Sometimes you might see $\text{BH}_3\cdot\text{THF}$ or B_2H_6 used here: it's the same reagent in a slightly different form. The base (can be NaOH , KOH , identity unimportant) helps make H_2O_2 more reactive. The reaction is *anti*-Markovnikoff 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).

This reaction goes through 3-membered "mercurinium" ion. The NaBH_4 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). Alternatively, an alcohol used in place of water will produce an ether.

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. HSO_4^- anion is not strongly nucleophilic, hence it does not add. Gives a mixture of syn and anti products due to 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. Gives a mixture of syn and anti



Br or H₂O/ROH depending on solvent

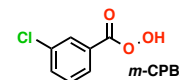
The key detail in these reactions is solvent: water and alcohol solvents will form the halohydrin products (the ones containing the OH and Br). All other solvents (you might see CCl_4 , CHCl_3 , hexane, etc.) provide the dibromide.

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 NaHSO_3 , H_2S , or $\text{Na}_2\text{S}_2\text{O}_3$ is also given as a reactant in this reaction - minor detail, it's used to remove the osmium from the hydroxyl groups.

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

RCO_3H is a peroxyacid. A common peroxy acid for this reaction is *m*-CPBA (*m*-chloroperoxybenzoic acid). If H_3O^+ , heat is written afterwards, this is opening of the epoxide to give the diol (anti-selective)



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

Peroxides generate the $\text{Br}\cdot$ 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-Markovnikoff product. It gives a mixture of syn and anti because it goes through a free radical process.

Reductive workup: Zinc (Zn), or dimethyl sulfide (DMS, Me_2S) is a reducing agent. It reduces excess ozone, allowing for isolation of the aldehyde.

Oxidative workup: Hydrogen peroxide is used to obtain the carboxylic acid instead of the aldehyde.
Can also use KMnO_4 and acid

This reaction goes through addition of a *carbene* (actually, "carbenoid") to the double bond. The reaction is stereospecific. Another set of conditions to provide a cyclopropane is CHCl_3 with strong base (NaOH), which makes the dichlorocyclopropane.

Omissions, Mistakes, Suggestions?

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