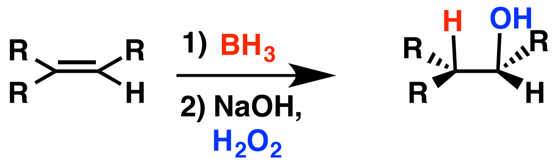
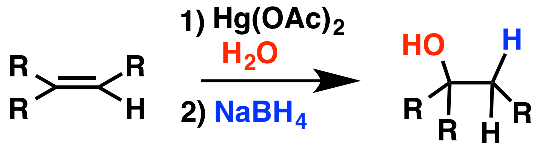
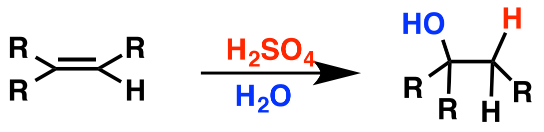
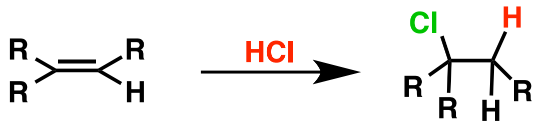
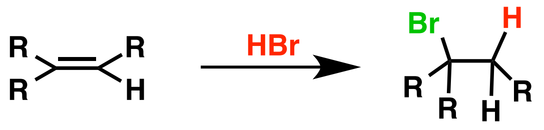
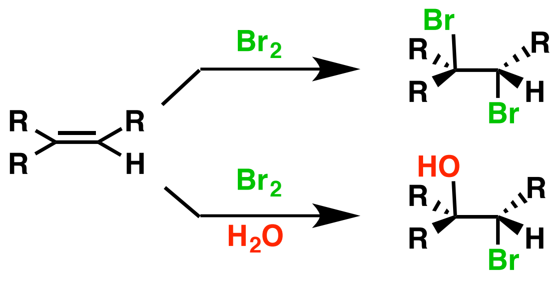
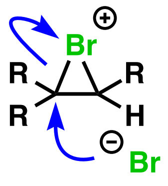
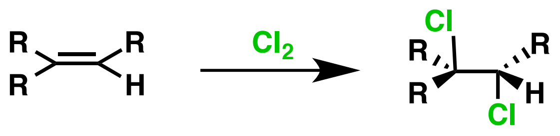
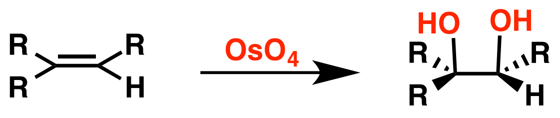
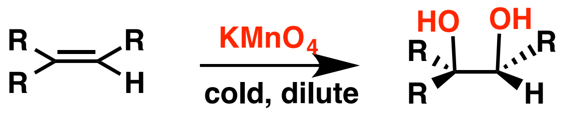
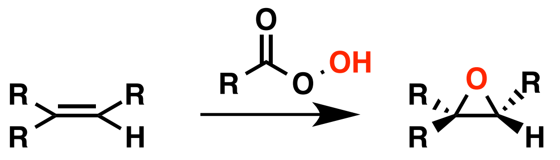
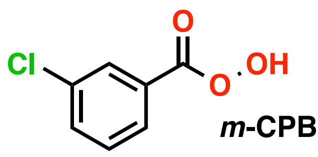
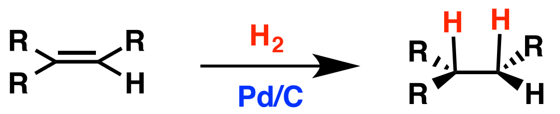
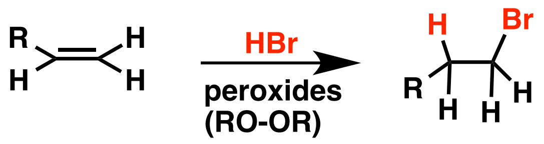
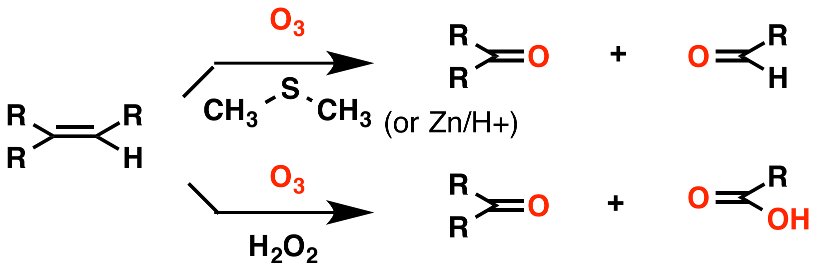
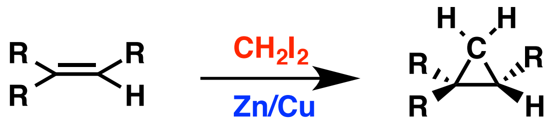
Additions to Alkenes

"Master Organic Chemistry"
masterorganicchemistry.com

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**	Sometimes you might see BH_3•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).
Oxymercuration		**Markovnikoff**	syn + anti	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.
Acid-catalyzed addition of H_2O (hydration)		**Markovnikoff**	syn + anti	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.
Addition of HX		**Markovnikoff**	syn + anti	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
Addition of HX		**Markovnikoff**	syn + anti	
Bromination		N/A	**anti addition**	 **Bromonium ion mechanism** **Br or H_2O/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.
Halohydrin Formation		**Markovnikoff**	**anti addition**	
Chlorination		N/A	**anti addition**	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).
Dihydroxylation		N/A	**syn addition**	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 $Na_2S_2O_3$ is also given as a reactant in this reaction - minor detail, it's used to remove the osmium from the hydroxyl groups.
Dihydroxylation		N/A	**syn addition**	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). NOTE: "anti" hydroxylation can be achieved through epoxidation followed by treatment with NaOH (basic) or aqueous acid (H_3O^+)
Epoxidation		N/A	**syn addition**	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) **m-CPBA**
Hydrogenation		N/A	**syn addition**	The catalyst can vary - you might see Pt or Ni as well. All provide the same product with the same stereochemistry.
Radical addition of HBr		**Anti-Markovnikoff**	syn + anti	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-Markovnikoff product. It gives a mixture of syn and anti because it goes through a free radical process.
Ozonolysis (Reductive workup)				**Reductive workup:** Zinc (Zn), or dimethyl sulfide (DMS, Me_2S) is a reducing agent. It reduces excess ozone, allowing for isolation of the aldehyde.
Ozonolysis (Oxidative Workup)				**Oxidative workup:** Hydrogen peroxide is used to obtain the carboxylic acid instead of the aldehyde. **Can also use $KMnO_4$ and acid**
Cyclopropanation		N/A	**syn addition**	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?

james@masterorganicchemistry.com