



CHEM 2400/2410

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 best authority.

Reaction	Reagents	Product	Regioselectivity	Stereochemistry
Hydroboration	1) BH ₃ 2) MeOH, H ₂ O ₂		Anti-Markovnikov	syn addition
Oxymercuration	1) Hg(OAc) ₂ 2) H ₂ O		Markovnikov	syn + anti
Acid-catalyzed addition of H ₂ O (Hydration)	H ₂ O, H ⁺		Markovnikov	syn + anti
	HCl		Markovnikov	syn + anti
Addition of HX	HBr		Markovnikov	syn + anti
Bromination	Br ₂ , H ₂ O		Anti-Markovnikov	anti addition
Hydrolysis of an Alkyl Halide	OH ⁻		Anti-Markovnikov	anti addition
Chlorination	Cl ₂		N/A	anti addition
Dihydroxylation	OsO ₄		N/A	syn addition
Dihydroxylation	KMnO ₄ , cold, dilute		N/A	syn addition
Epoxidation	mCPBA		N/A	syn addition
Hydrogenation	H ₂ , Pd/C		N/A	syn addition
Reductive addition of HBr	HBr, Zn		Anti-Markovnikov	syn + anti
Oxidative (Reductive workup)	OsO ₄ , NMO, Zn		N/A	syn addition
Oxidative (Oxidative Workup)	OsO ₄ , Na ₂ S ₂ O ₈		Anti-Markovnikov	syn + anti
Cyclopropanation	CH ₂ , Zn/Cu		N/A	syn addition

Sometimes you might see BH₃-THF or BH₃ used here; the same reagent is a slightly different form. The issue here is that BH₃ is a very strong Lewis acid and it reacts with the alkene to form a carbocation intermediate. The issue is that the carbocation intermediate is not strongly nucleophilic, hence it does not add. Gives a mixture of syn and anti products due to the free carbocation.

The reaction goes through a carbocation intermediate. The H₂O₂ step removes the mercury. While the addition is anti, the overall reaction is stereoselective because the step involves a carbon based free radical (usually not discussed). Alternatively, an alcohol used in place of water will produce an ether.



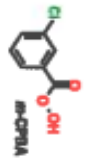
HCl and HBr (as well as HI, not shown) produce the same to give a free carbocation which can then be trapped by the halide anion. Gives a mixture of syn and anti.

The by-product in these reactions is a cyclic bromonium ion intermediate. The by-product is a mixture of syn and anti products. The by-product is a mixture of syn and anti products. The by-product is a mixture of syn and anti products.

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

Checklist is a transition state. The book won't be given in the course to fully understand how this reaction works. Occasionally a second reagent like NaHCO₃, H₂O, or Na₂S₂O₈ is also given as a reagent in the reaction - minor detail, its used to remove the cation from the spirocyclic groups.

Keywords are "cold, dilute". NOTE: if "heat" or "acid" is mentioned in the conditions, the diol will be formed to provide carbonyl compounds (same reaction as epoxidation with oxidative workup, NOTE: "wet" hydrolysis can be achieved through epoxidation followed by treatment with NaOH (aqueous) or aqueous acid (H₂O⁺).



RCO₂H is a peroxycarboxylic acid. A common peroxycarboxylic acid for this reaction is m-CPBA (3-chloroperoxybenzoic acid). If H₂O⁺, heat is written above, this is a sign of the epoxide to give the diol (anti-alkene).

The reagent can vary - you might see Br or HI as well. All provide the same product with the same stereochemistry.

Peroxide generates 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 regioselectivity for the anti-Markovnikov product. It gives a mixture of syn and anti because it goes through a free radical process.

Reductive workup: Zn (Zn), or dimethyl sulfoxide (DMSO, Me₂S) is a reducing agent. It reduces excess osmium, allowing for isolation of the alcohol.

Oxidative workup: Hydrogen peroxide is used to obtain the carboxylic acid instead of the alcohol. Can also use K₂Cr₂O₇ and acid.

Oxidation, Reduction, Synthesis
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