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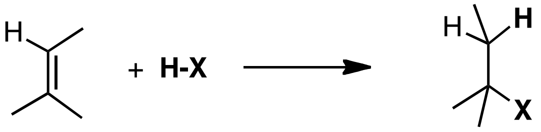
Chemistry 0310 - Organic Chemistry 1

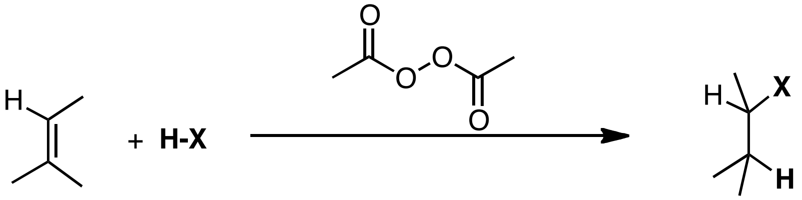
Chapter 12. Reactions of Alkenes

Addition reactions of X-Y to alkenes are thermodynamically favorable if the newly formed C-X and C-Y bonds are stronger than the π-bond (ca. 60 kcal/mol) and the X-Y bond. This is true for most halogens, halogen halides, peroxides, and H_2O. Kinetically, the addition of electrophiles to alkenes is fast due to the easily accessible π-electron cloud.

- **Addition of HX** to alkenes is regioselective and follows Markovnikov's rule: with unsymmetrical alkenes, the proton adds to the less substituted carbon of the double bond.

Changes in mechanism lead to exceptions from Markovnikov's rule; for example, the peroxide initiated addition of HX to alkenes (a radical chain mechanism) results in anti-Markovnikov products.

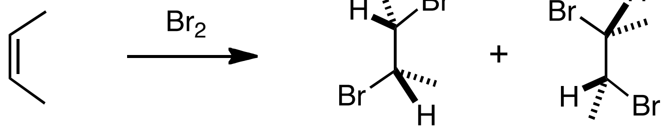




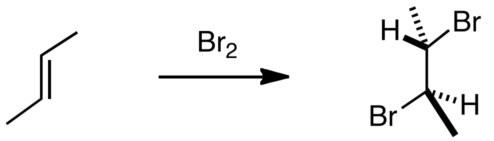
The radical polymerization of alkenes is similarly initiated with peroxides and involves repetitive additions of carbon-based radicals to the π-system of alkenes in the propagation steps.

- **Addition of H_2SO_4** to alkenes provides, after hydrolytic work-up, an alcohol product. This is an alternative to the acid-catalyzed hydration of alkenes. Both methods follow Markovnikov's rule. Since carbocations are intermediates, backbone rearrangements to the more stable carbocations can occur.

- **Addition of X_2** to alkenes generates vicinal dihalides via backside attack (*anti*-addition) on an intermediate halonium (e.g. bromonium, iodonium) ion. This is an example of a stereospecific reaction: a particular stereoisomer of the starting material leads to a specific stereoisomer of the product.

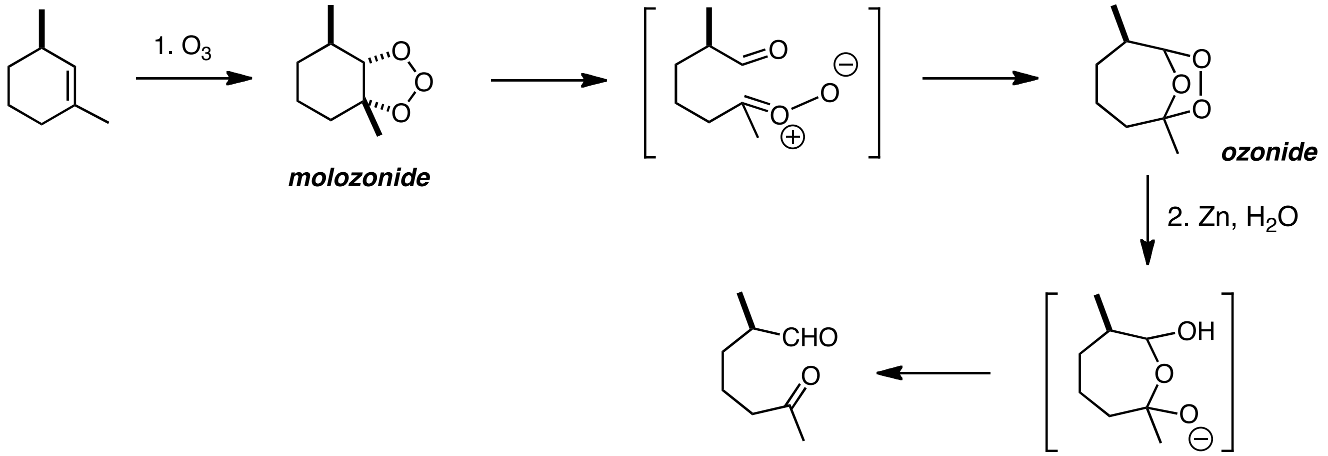


chiral 2,3-dibromobutane

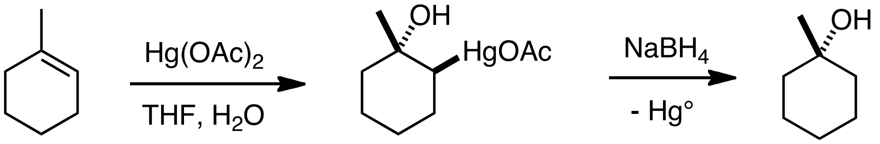


meso 2,3-dibromobutane

- **Halohydrin formation** involves treatment of alkenes with X_2 and H_2O (or HOX). Halonium ions are intermediates, and H_2O attacks at the more substituted carbon in unsymmetrical alkenes.
- ***Syn*-Hydroxylations** of alkenes are most conveniently performed with catalytic OsO_4 and NMO (N-methylmorpholine N-oxide) as the co-oxidant. Attack occurs from the less-hindered face of the alkene, and a vicinal *syn*-diol is isolated after reductive workup.
- **Oxidative cleavage** of 1,2-disubstituted alkenes with $KMnO_4$ provides carboxylic acids after *in situ* oxidation of the intermediate aldehydes. With more highly substituted alkenes, ketones are isolated. Ozonolysis of alkenes with O_3 followed by reductive workup gives aldehydes and/or ketones. The mechanism involves cycloaddition to the molozonide, rearrangement, a second cycloaddition to give an ozonide, and reductive cleavage of the O-O bond. This method is milder than oxidation with $KMnO_4$, and aldehydes are not oxidized to acids.



- **Oxidative addition of H_2O**: The Wacker process converts alkenes into aldehydes.
- **Oxymercuration** of alkenes according to Markovnikov's rule. Addition of H_2O to the intermediate mercurinium ion occurs regioselectively and results in an organomercury compound that is generally reduced with $NaBH_4$ to give an alcohol:



- **Hydroboration** of alkenes proceeds with overall anti-Markovnikov selectivity. Sources for BH_3 (diborane, BH_3·THF) or sterically more hindered boranes (9-BBN) add to alkenes to give intermediate organoboranes which can be oxidized with H_2O_2 or hydrolyzed with aqueous acid to give alcohols and alkanes, respectively. The regioselectivity of hydroboration is determined by electronic (polarization of the B-H bond) and steric factors. The more highly hindered the substituents on borane, the higher the regioselectivity in the addition to unsymmetrically substituted alkenes. The mechanism for hydroboration involves a *syn*-addition across the B-H bond. In the oxidation, the organic residue migrates under retention of configuration.