

# Additions to Alkenes

**Addition of Hydrogen halides (HX)**

CC(C)=CC + HX >> CC(C)(X)CC (1,2-addition)

The reaction goes through a carbocation intermediate. This is the Markovnikov's rule saying that the proton binds to the less substituted carbon because by doing so the more substituted carbocation is formed. The halide ion attacks the carbocation from both sides, thus a mixture of enantiomers is produced.

CC(C)=CC + HX >> CC(C)C(C)X (anti-addition)

There is no stereoselectivity and a mixture of enantiomers can be formed.

**Radical addition of HBr**

CC(C)=CC + HBr >> CC(C)C(C)Br

Only this works for anti-Markovnikov addition. The reaction goes through a radical intermediate with anti and syn addition.

CC(C)=CC + HBr >> CC(C)C(C)Br (anti-addition)

CC(C)=CC + HBr >> CC(C)C(C)Br (syn-addition)

HBr is used to brominate the alkyl position of the double bond. In the experiments of the bromination, you can simply observe the alkyl position and check for bromine there.

However, the reaction is not an anti/bimolecular. It involves resonance stabilization of the alkyl radicals and other experiments are also required. In addition, the lack of stereoselective control makes predicting the possible products quite difficult. You can check <https://www.demonstrations.wisc.edu/alkene-bromination/> for more details.

**Alkyne Bromination**

CC#CC + Br2 >> CC(Br)C(Br)C

Anti-addition of bromine to alkynes.

**Anti-catalyzed hydration**

CC(C)=CC + H2O >> CC(C)(OH)CC

Anti-catalyzed hydration follows the Markovnikov's rule. However, enantiomers are possible because of the carbocation intermediate.

CC(C)=CC + H2O >> CC(C)(OH)CC (anti-addition)

**Hydroboration**

CC(C)=CC + BH3 >> CC(C)C(C)B

Anti-addition of BH3 to alkenes. The main reason for using hydroboration is preventing possible rearrangements that happen during acid-catalyzed hydration. The mechanism goes through a three-membered ring where you can run into other nucleophiles such as alcohols, amines and acids.

CC(C)=CC + BH3 >> CC(C)C(C)B

**Hydroboration Oxidation**

CC(C)=CC + BH3 >> CC(C)C(C)OH

Hydroboration oxidation follows the Markovnikov's rule. However, Markovnikov is a concerted, syn addition, so the OH and OH2 groups are on the same side in the product. For better stereochemistry, today aldehydes react with 9-BBN (9-borabicyclo[3.3.1]nonane) instead of BH3.

CC(C)=CC + BH3 >> CC(C)C(C)OH

**Hydroxylation**

CC(C)=CC + H2O2 >> CC(C)(OH)CC(OH)C

Like for any other reaction involving the carbon chain will help a lot.

In order for the reaction to proceed, there must be the presence of carbon with a double bond.

**Anti-Markovnikov hydration**

CC(C)=CC + H2O >> CC(C)C(C)OH

The anti-Markovnikov hydration with OsO4, works only at low temperatures. If heat is applied, the double bond is cleaved.

CC(C)=CC + H2O >> CC(C)C(C)OH

**Anti-Markovnikov hydration**

CC(C)=CC + H2O >> CC(C)C(C)OH

In aqueous solution, hydroboration-oxidation is used for both Markovnikov hydroboration. Hydroboration is a concerted, syn addition, so the OH and OH2 groups are on the same side in the product. For better stereochemistry, today aldehydes react with 9-BBN (9-borabicyclo[3.3.1]nonane) instead of BH3.

CC(C)=CC + H2O >> CC(C)C(C)OH

**Hydroxylation**

CC(C)=CC + H2O2 >> CC(C)(OH)CC(OH)C

Hydroxylation is the key to tetrahydroxylation of a double bond. It flows through a cyclic intermediate (cyclic hydroperoxide) in a concerted, syn addition of the two hydroxyls and the overall reaction can run with and then the opposite side flow, from enantiomers formed by anti-addition.

CC(C)=CC + H2O2 >> CC(C)(OH)CC(OH)C

**Hydroxylation**

CC(C)=CC + H2O2 >> CC(C)(OH)CC(OH)C

Same mechanism as hydroxylation. Only the hydroperoxide is attacked by the water here. Key point for regioselectivity: the water attacks the more substituted carbon of the ring. Key point for stereoselectivity: the OH and OH2 are on the same side (syn) attack from the opposite side.

CC(C)=CC + H2O2 >> CC(C)(OH)CC(OH)C

**Hydrogenation**

CC(C)=CC + H2 >> CC(C)CC

Other catalyst such as Pt or Ni can also be used for the catalytic hydrogenation of alkenes. It is a syn addition. For heterogeneous reactions, Wilkinson's catalyst is used instead of acids.

CC(C)=CC + H2 >> CC(C)CC (Wilkinson's catalyst)

Catalyzed syn addition.

**Epoxide-alkene reaction**

CC(C)=CC + H2O2 >> CC(C)1OC1

It is a stereoselective reaction and depending on the configuration of the alkene, one or two products is obtained.

CC(C)=CC + H2O2 >> CC(C)1OC1

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