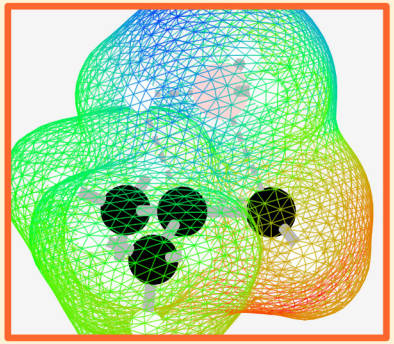
HIGHLIGHTS

- *Anti*-Markovnikov addition of H–Br by using peroxides.
- The radical chain mechanism.
- Hydroboration-oxidation gives the *anti*-Markovnikov addition of water across an alkene.
- Concerted addition of B–H.
- Migration or alkyl shift during oxidation.



The common addition of electrophiles across an alkene leads to ***Markovnikov addition*** product, where a hydrogen atom adds to the least substituted end of an alkene, and the heteroatom adds to the more substituted carbon. There are methods to reverse the regioselectivity and form the ***anti-Markovnikov product***. The first method uses radical chemistry to give the *anti*-Markovnikov addition of H–Br. By forming a bromine radical addition leads to bromine being on the least substituted carbon of the alkene and the electron deficient carbon radical stabilized on the more substituted end. The second method is hydroboration-oxidation that gives the *anti*-Markovnikov addition of water across an alkene. Not only is this reaction regioselective, but it is also stereospecific with boron and hydrogen undergoing *syn* addition. Oxidation of the boron then gives an alcohol, this occurs with retention of stereochemistry.

CHEMISTRY CLASSICS

π NUCLEOPHILES PART 2

ANTI-MARKOVNIKOV ADDITION

Anti-Markovnikov addition

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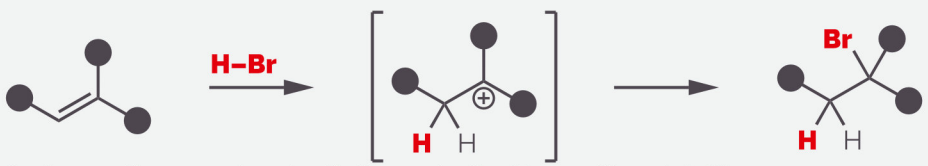
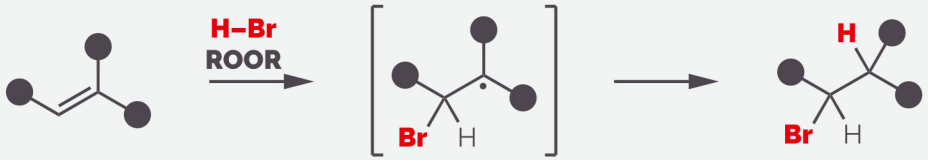
1. The addition of H–Br to an alkene

Markovnikov addition



ionic reaction - regioselectivity controlled by ***cation*** stability

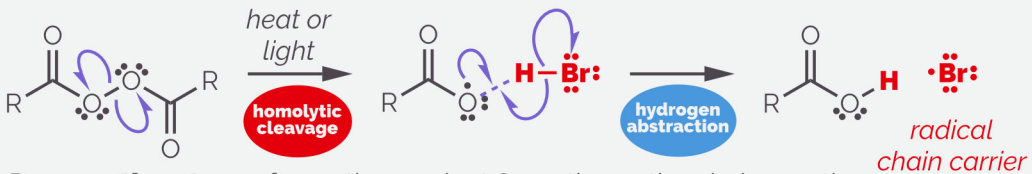
Anti-Markovnikov addition



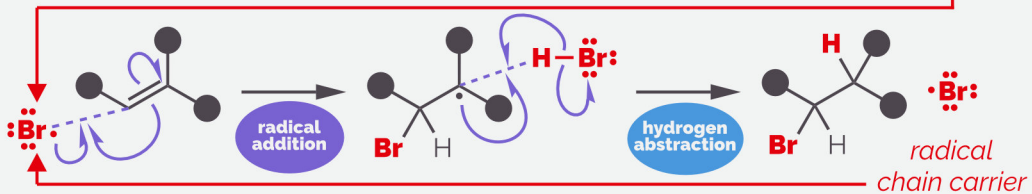
radical reaction - regioselectivity controlled by ***radical*** stability

2. Radical chain mechanism for H–Br addition

Initiation steps - forms the first radicals, normally by homolytic bond breaking

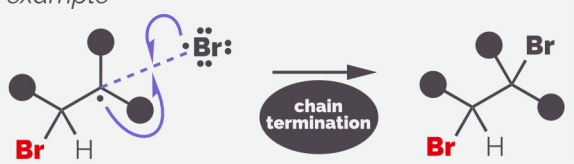


Propagation steps - forms the product & continues the chain reaction

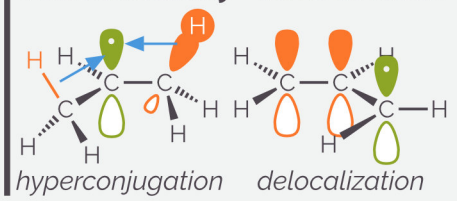


Termination steps - any two radicals meeting

example

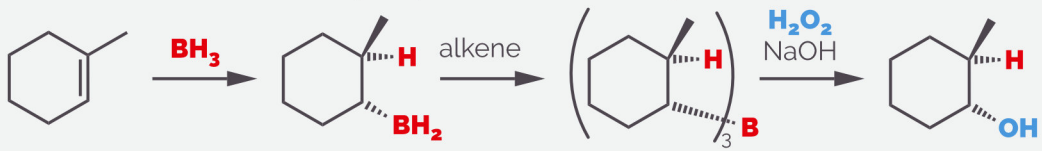


Radical stability - same as cation



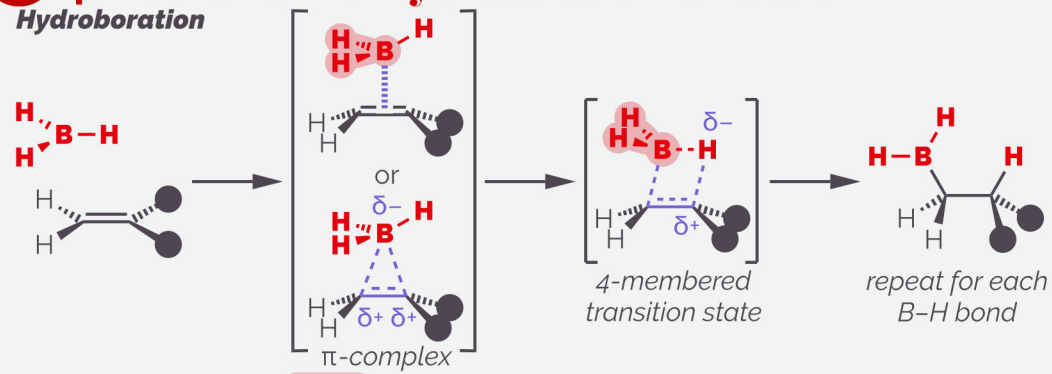
3. *Anti*-Markovnikov addition of H_2O

Anti-Markovnikov selectivity & syn addition (stereospecificity)



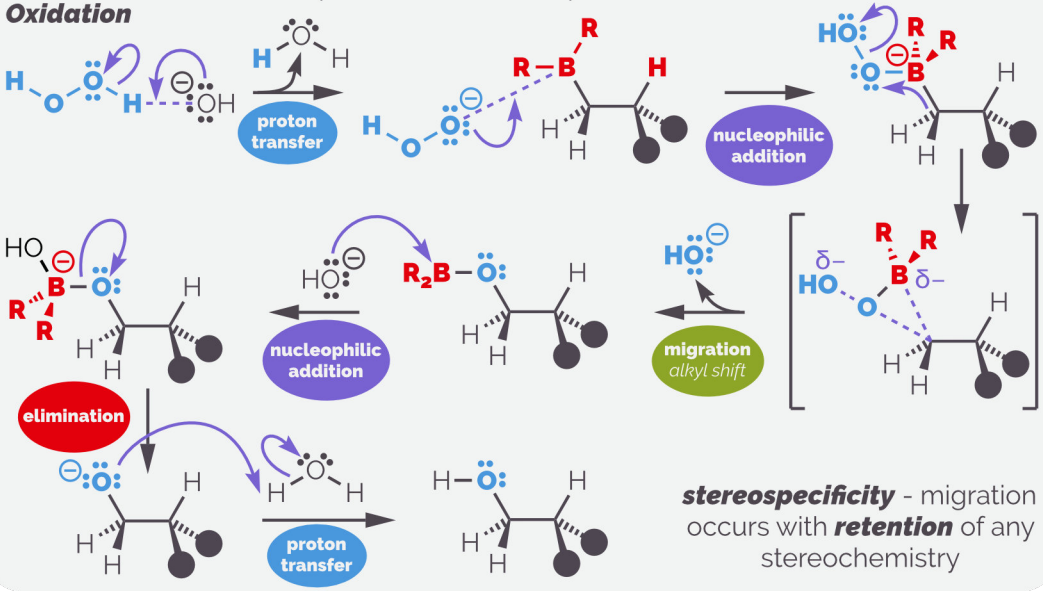
4. Mechanism of hydroboration-oxidation

Hydroboration



regioselectivity - **sterics** - bulky borane adds to least hindered end
- **electronics** - π complex leads to build up of δ+. Favored on substituted end

Oxidation



stereospecificity - migration occurs with ***retention*** of any stereochemistry