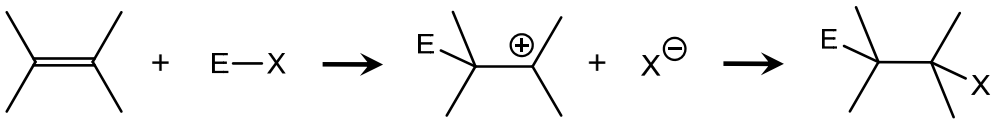
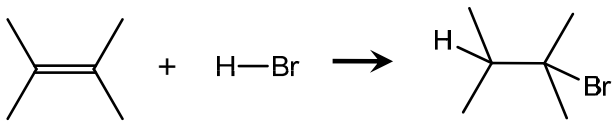
Electrophilic Addition to Alkenes

General Scheme:



E = *electrophilic group*
X = *leaving group*

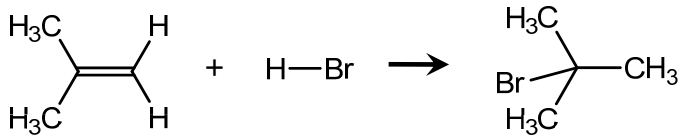
Example: Hydrohalogenation (addition of HX).



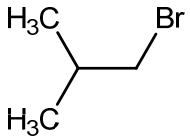
Markovnikov's Rule of Electrophilic Addition

Electrophiles typically add such that the most stable cation intermediate is formed. *(Usually, so that the electrophile is bound to the less substituted carbon.)*

Hydrohalogenation example:



selectively.

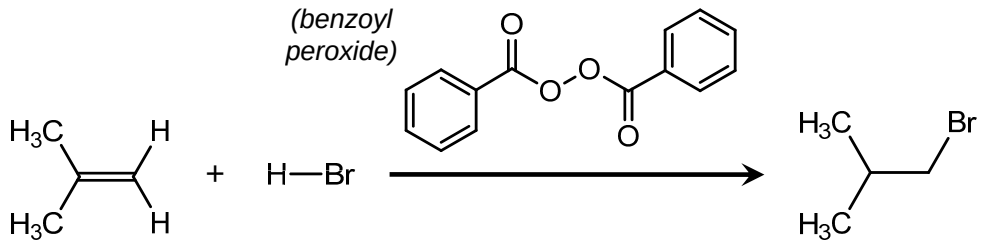


not observed.

We would call this reaction *regioselective*.

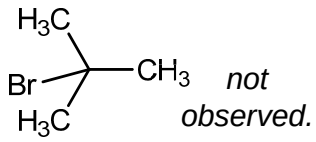
Anti-Markovnikov Hydrohalogenation with HBr + Peroxide

For most Markovnikov-rule electrophilic additions, there are alternative conditions that generate anti-Markovnikov preference.



selectively.

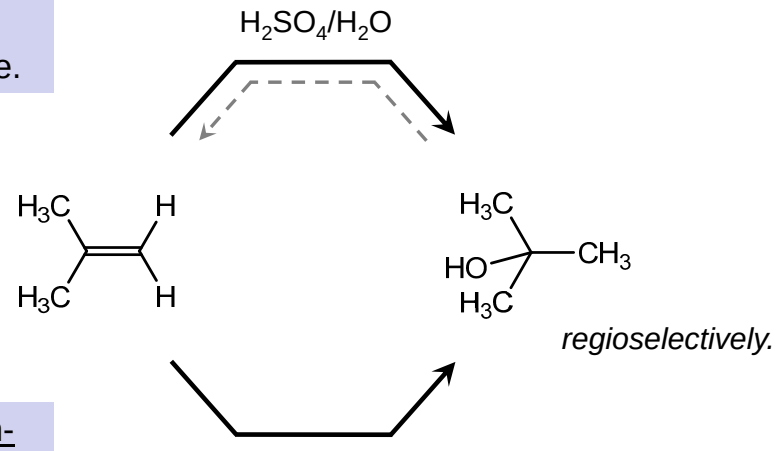
Again, *regioselective*.



not observed.

Markovnikov Addition of H_2O to Alkenes

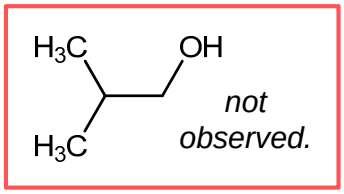
<u>Hydration</u>
Harsh and reversible.



regioselectively.

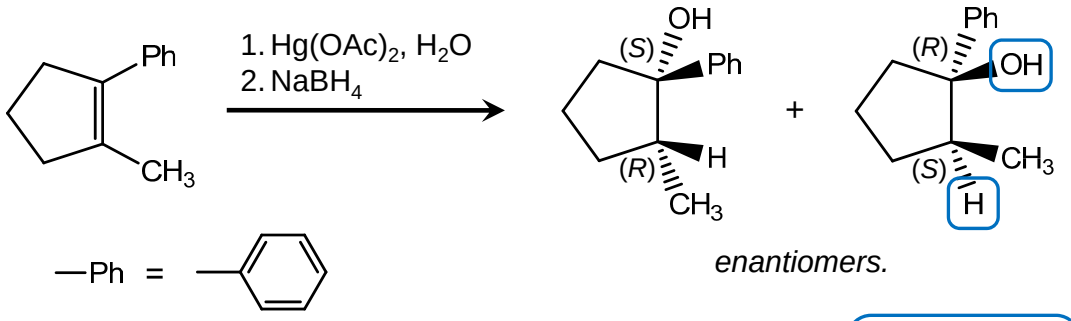
<u>Hydroxymercuration-Demercuration</u>
Milder, higher yielding.

1. $Hg(OAc)_2$, H_2O
2. $NaBH_4$



not observed.

Stereoselectivity of Hydroxymercuration-Demercuration



—Ph =

enantiomers.

H & OH add to opposite faces of alkene.

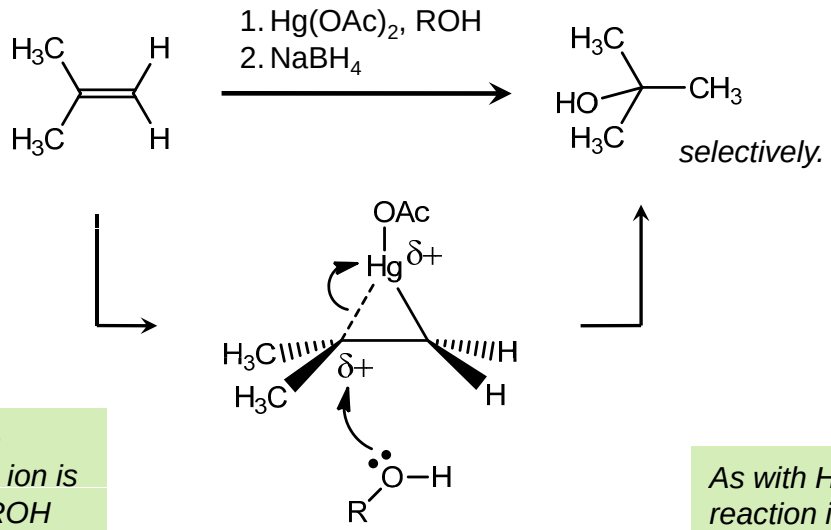
This reaction is ***diastereoselective***:
(*R*,*R*) and (*S*,*S*) products are *not* produced.

The reaction is **not *enantioselective***:
There is no preference for (*R*,*S*) enantiomer over (*S*,*R*) enantiomer; the product is racemic.

Markovnikov Addition of ROH

Alkoxymercuration-Demercuration

(analogous to Hydroxymercuration-Demercuration.)



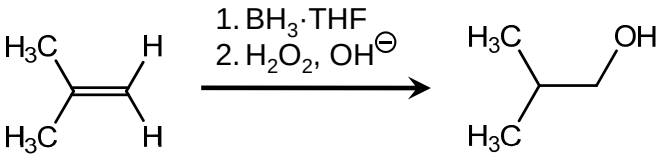
selectively.

Intermediate mercurinium ion is trapped by ROH instead of H_2O.

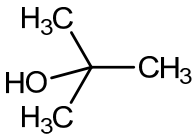
As with H_2O, reaction is also stereospecific.

Anti-Markovnikov Addition of H_2O

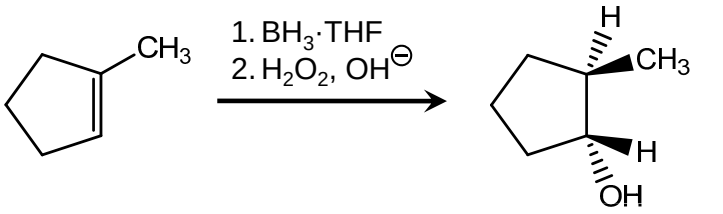
Hydroboration



regioselectively.



not observed.



H & OH add to same face of alkene.