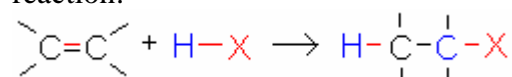


electrophilic additions initiated by protonation

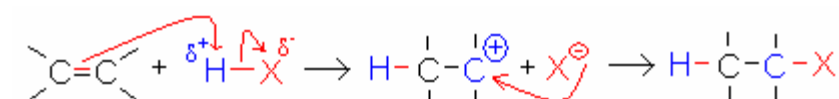
alkene + haloacid: hydrohalogenation

reaction:



X = Br, Cl, or I

mechanism:



regiochemistry:

Markovnikov—X attaches to the more substituted carbon.

(H adds first, forming the more substituted, and hence more stable, carbocation; X adds second, attaching to the carbocation.)

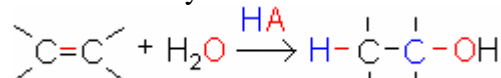
stereochemistry:

If one of the alkene carbons becomes a stereocenter, then both possible stereoisomers are formed.

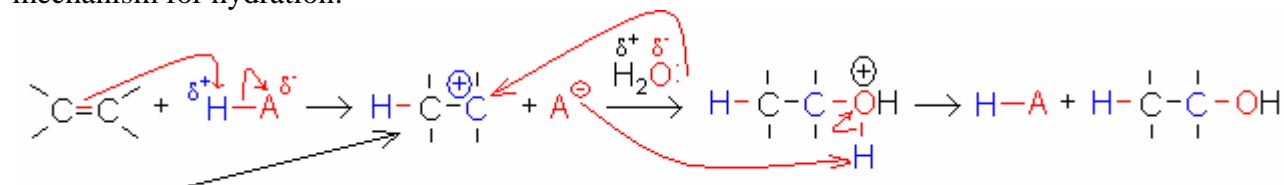
(H can attack either face of the trigonal planar alkene; X can attack either face of the trigonal planar carbocation intermediate)

alkene + catalytic acid + nucleophile: hydration, cationic polymerization, etc.

reaction for hydration:



mechanism for hydration:

This carbocation produced by protonation of the alkene can be attacked by other nucleophiles besides H₂O, such as ROH or another molecule of >C=C< (cationic polymerization).

regiochemistry:

H on less substituted C, nucleophile on more substituted C.

(H adds first, forming the more substituted, and hence more stable, carbocation; nucleophile adds second, attaching to the carbocation)

stereochemistry:

Produces both possible configurations at both carbons, for a maximum of four possible stereoisomers.

(H can attack either face of the trigonal planar alkene; nucleophile can attack either face of the trigonal planar carbocation intermediate)

synthetic utility:

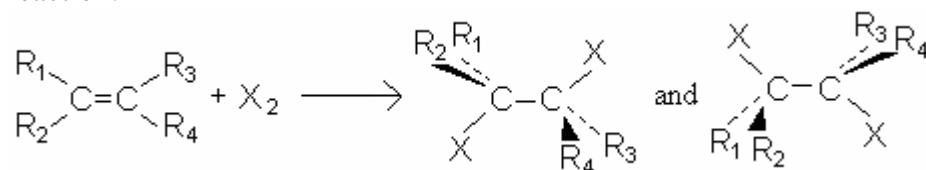
Hydration makes an alcohol, with the OH on the more substituted C; compare hydroboration-oxidation, which makes an alcohol with the OH on the less substituted C.

Cationic polymerization synthesizes new C-C bonds; compare with RMgX plus carbonyl or epoxide.

electrophilic additions initiated by halogens

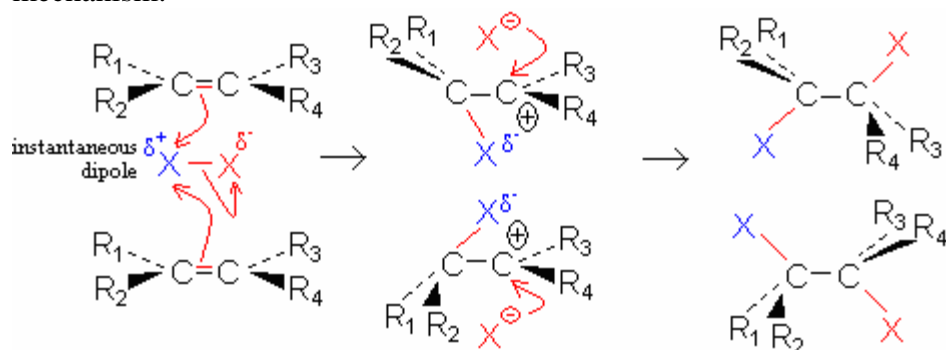
halogenation

reaction:



X = Br or Cl

mechanism:

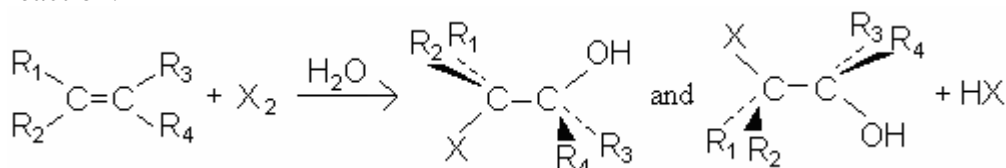


stereochemistry: two trans-addition products

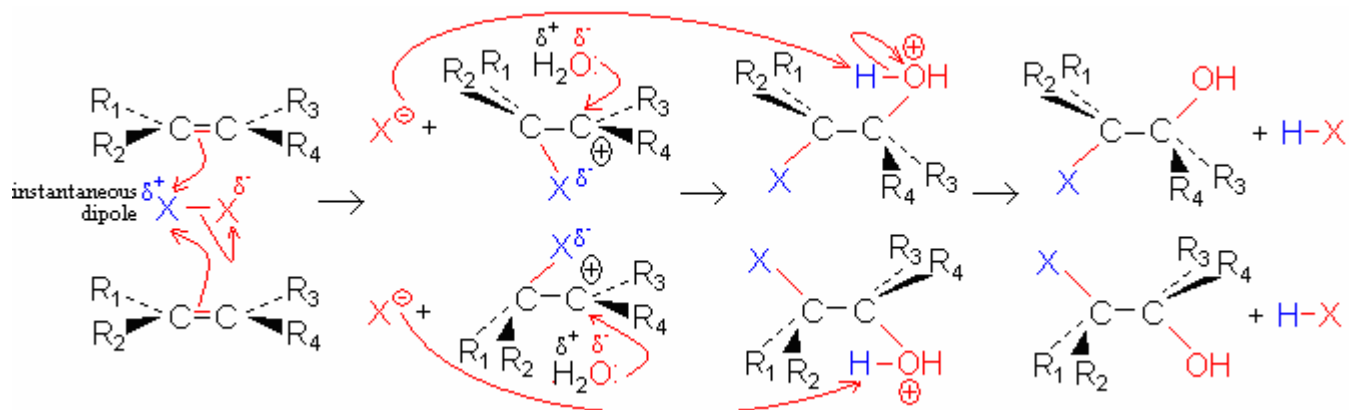
The first X blocks one face, so the second X attacks the other face.

haloalcohol and haloether synthesis

reaction:

A similar reaction occurs with X₂ in ROH.

mechanism:



stereochemistry: two trans-addition products

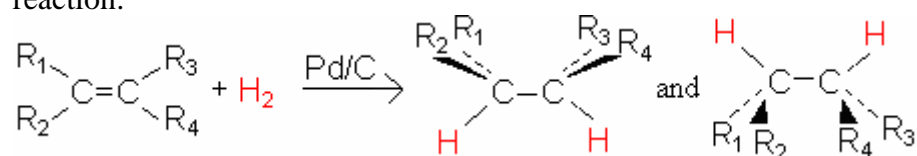
(The X blocks one face, so the H₂O attacks the other face.)

regiochemistry: The OH adds to the more-substituted carbon.

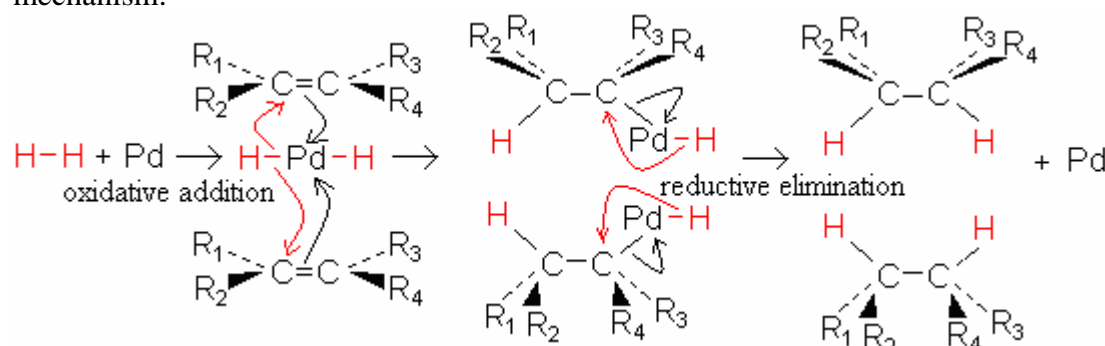
(Addition of X creates the more stable—i.e., more substituted—carbocation.)

hydrogenation

reaction:



mechanism:



stereochemistry: two syn-addition products

(Both H's attack the same face because they're both attached to the same particle of Pd.)

If one face is hindered, the major product comes from attack on the unhindered face.

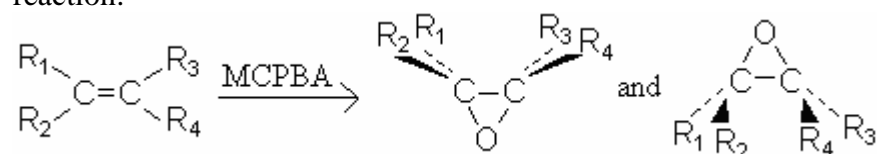
synthetic utility: Defunctionalizes—i.e., replaces a functional group with H's or D's.

Compare with $RMgX + H_3O^+$

oxidations

MCPBA oxidation

reaction:



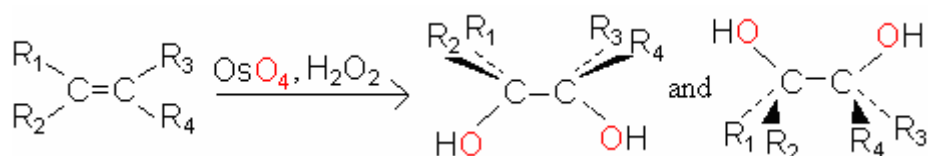
stereochemistry: 2 cis-addition products (the single O attacks both alkene C's from the same side)

synthetic utility: MCPBA oxidation followed by attack with HO^- results in trans dihydroxylation.

Compare with osmium-catalyzed cis dihydroxylation.

osmium catalyzed dihydroxylation

reaction:

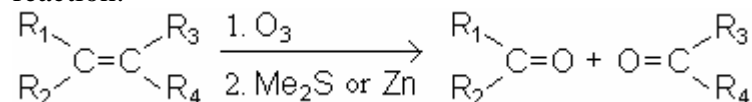
stereochemistry: two cis-addition products (both O's add concertedly from the same OsO_4)

synthetic utility: Osmium catalyzed dihydroxylation is cis.

Compare with MCPBA oxidation followed by attack with HO^- , which gives trans dihydroxylation.

ozonolysis

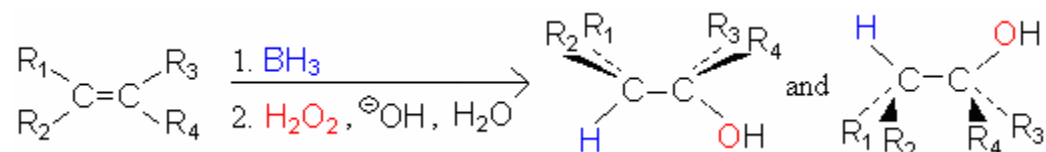
reaction:



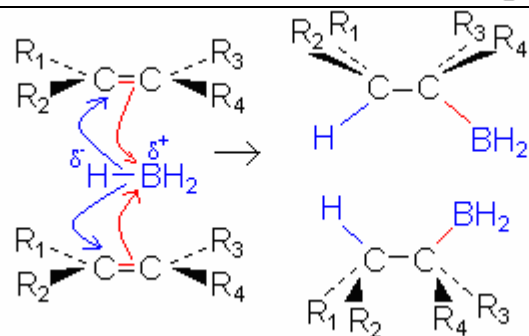
synthetic utility: cleaves carbon-carbon bonds; creates carbonyls

hydroboration-oxidation

reaction:

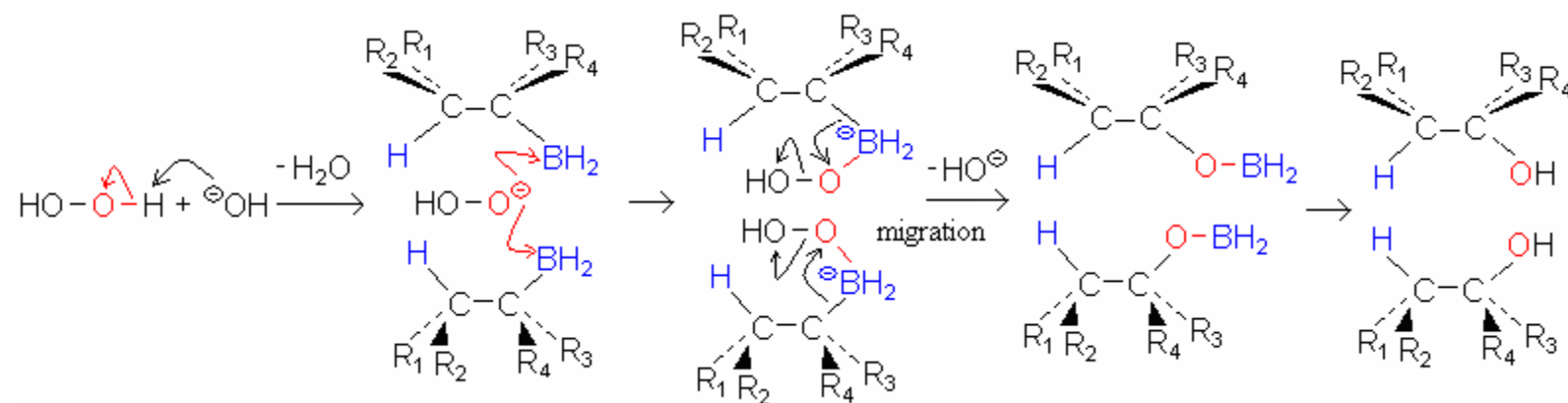


mechanism of hydroboration:



If the alkene is not too hindered,
the B will go on to attack two more

mechanism of oxidation:



stereochemistry: two cis-addition products (the H and BH₂ add to the same side since they come from the same molecule of BH₃ and add concertedly; migration to the O occurs with retention of configuration at the C)

regiochemistry: The B (in the hydroboration) and OH (in the oxidation) add to the less-substituted C. (the B adds to the less-substituted carbon to reduce steric hindrance; during migration the O trades places with the B)

synthetic utility: Hydroboration-oxidation makes an alcohol with the OH on the less substituted C; compare with hydration (alkene + H₂SO₄+ H₂O), which makes an alcohol with the OH on the more substituted C.