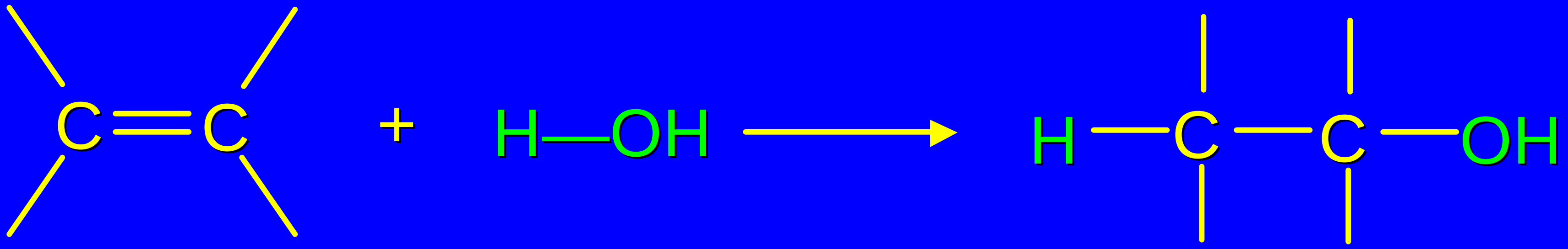
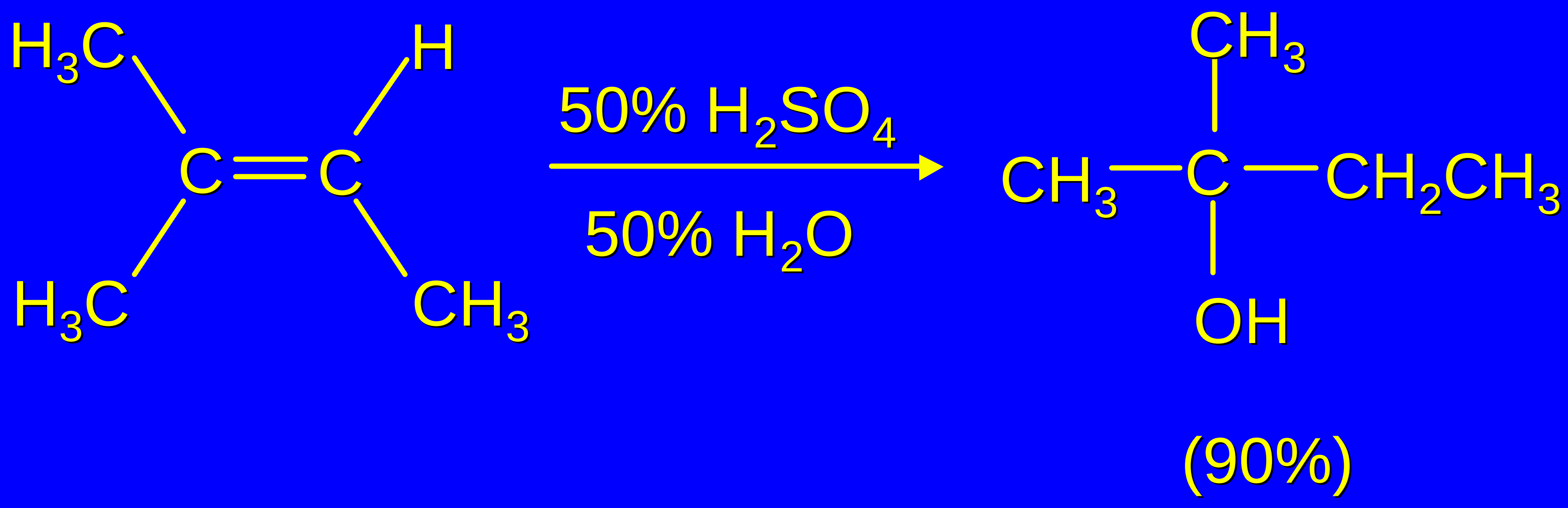
6.10
Acid-Catalyzed Hydration of Alkenes

Acid-Catalyzed Hydration of Alkenes

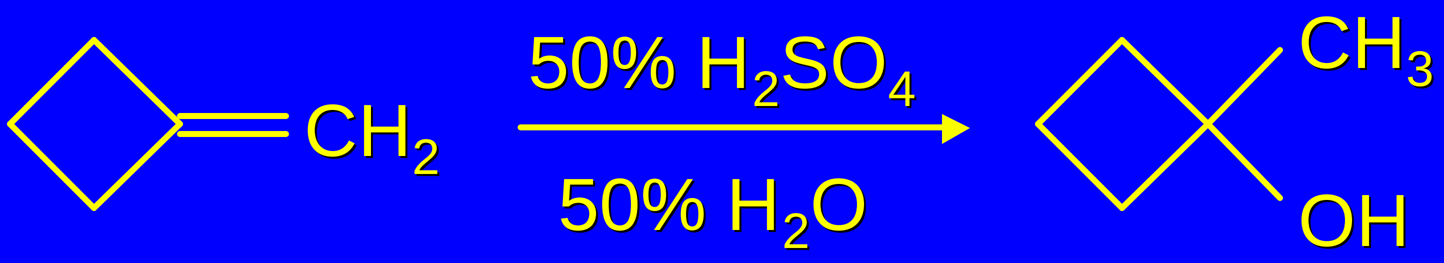


reaction is acid catalyzed; typical hydration medium is 50% H_2SO_4-50% H_2O

Follows Markovnikov's Rule



Follows Markovnikov's Rule

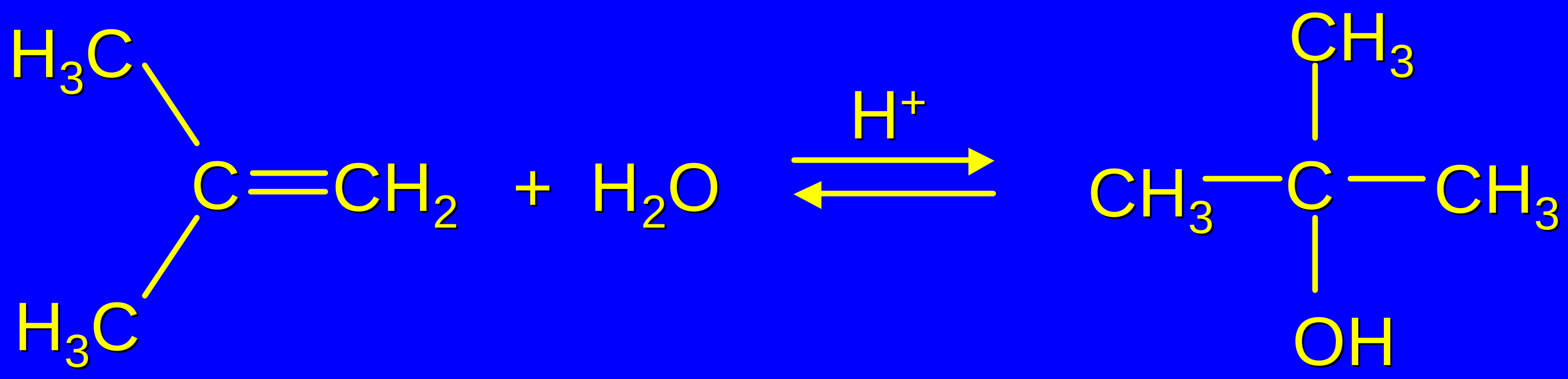


(80%)

Mechanism

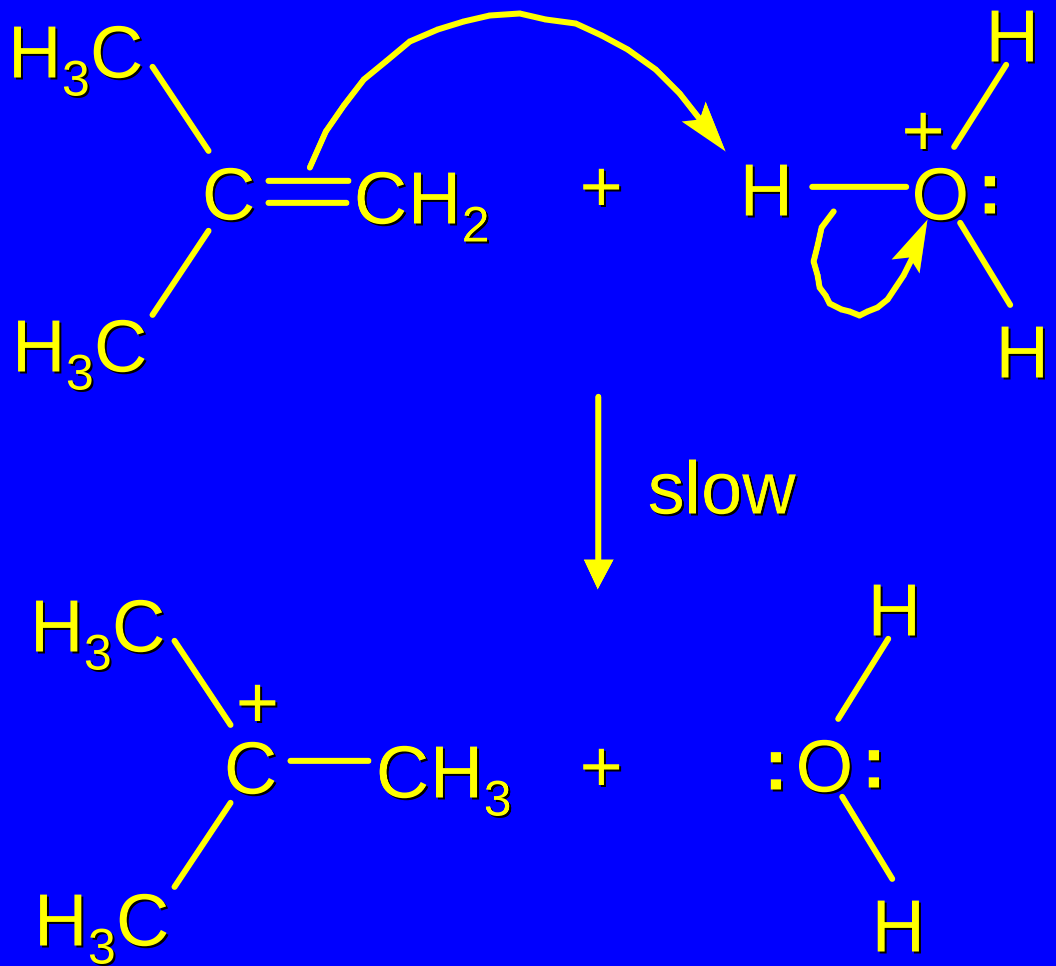
involves a carbocation intermediate

is the reverse of acid-catalyzed dehydration of alcohols to alkenes



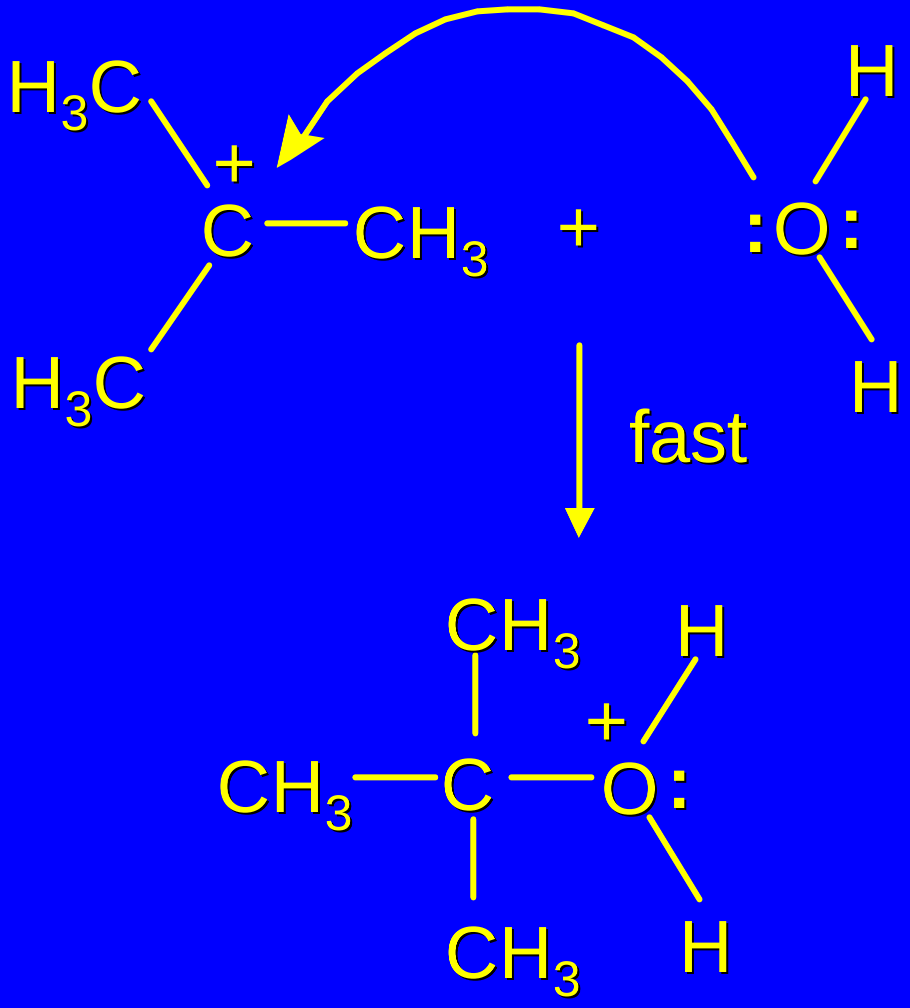
Mechanism

Step (1) Protonation of double bond



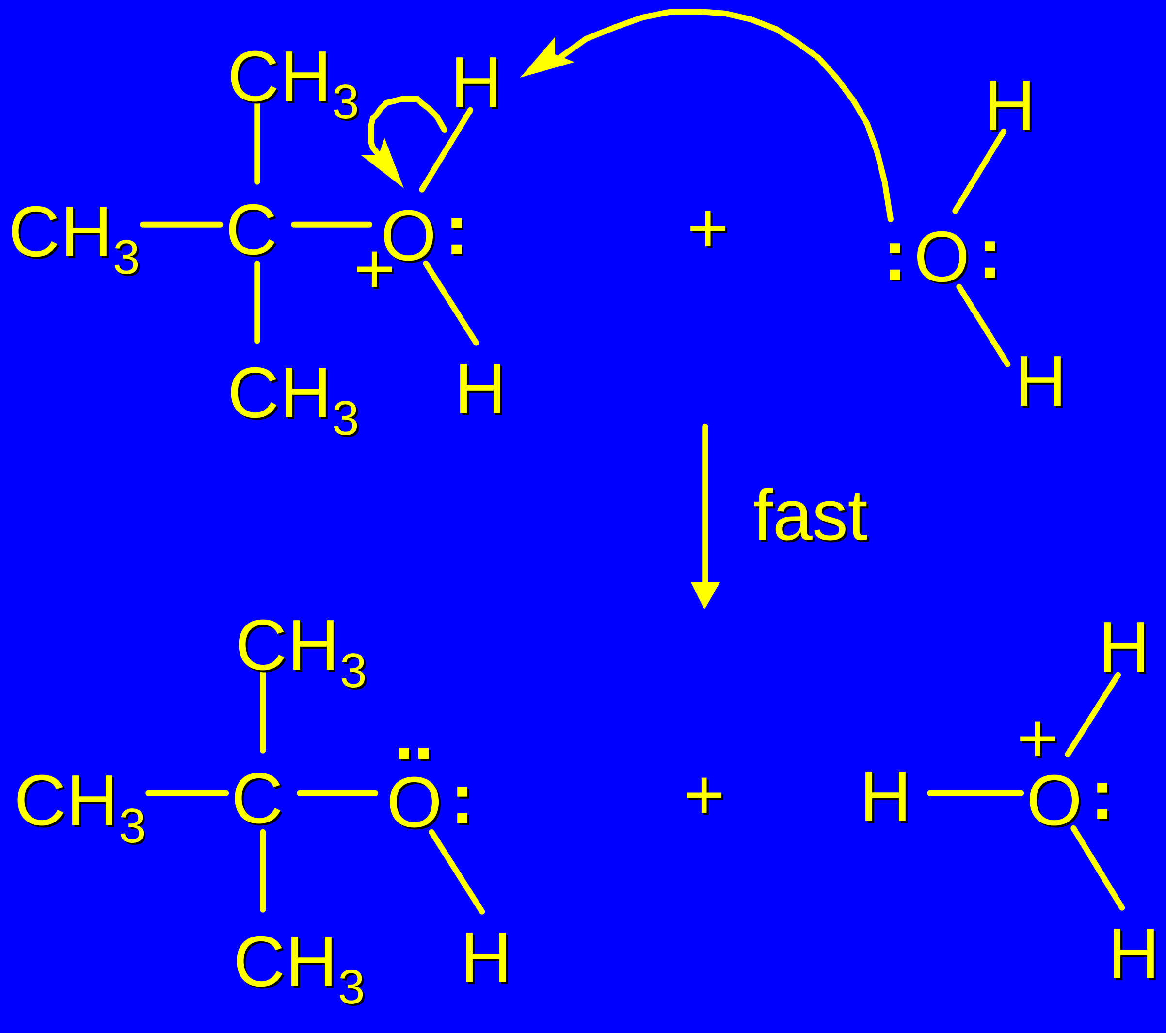
Mechanism

Step (2) Capture of carbocation by water



Mechanism

Step (3) Deprotonation of oxonium ion



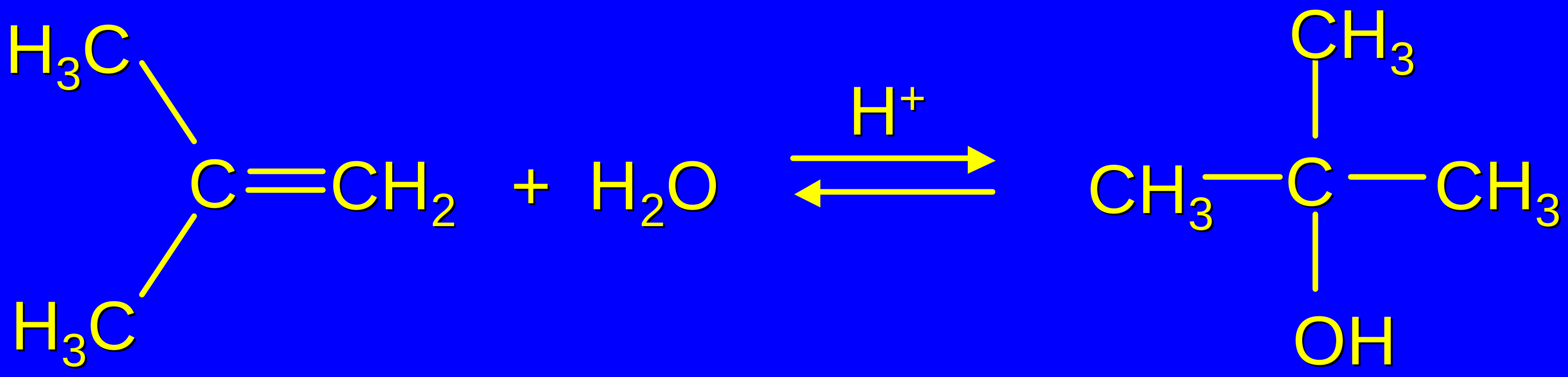
Relative Rates

Acid-catalyzed hydration

ethylene	$CH_2{=}CH_2$	1.0
propene	$CH_3CH{=}CH_2$	1.6×10^6
2-methylpropene	$(CH_3)_2C{=}CH_2$	2.5×10^{11}

The more stable the carbocation, the faster it is formed, and the faster the reaction rate.

Principle of Microscopic Reversibility



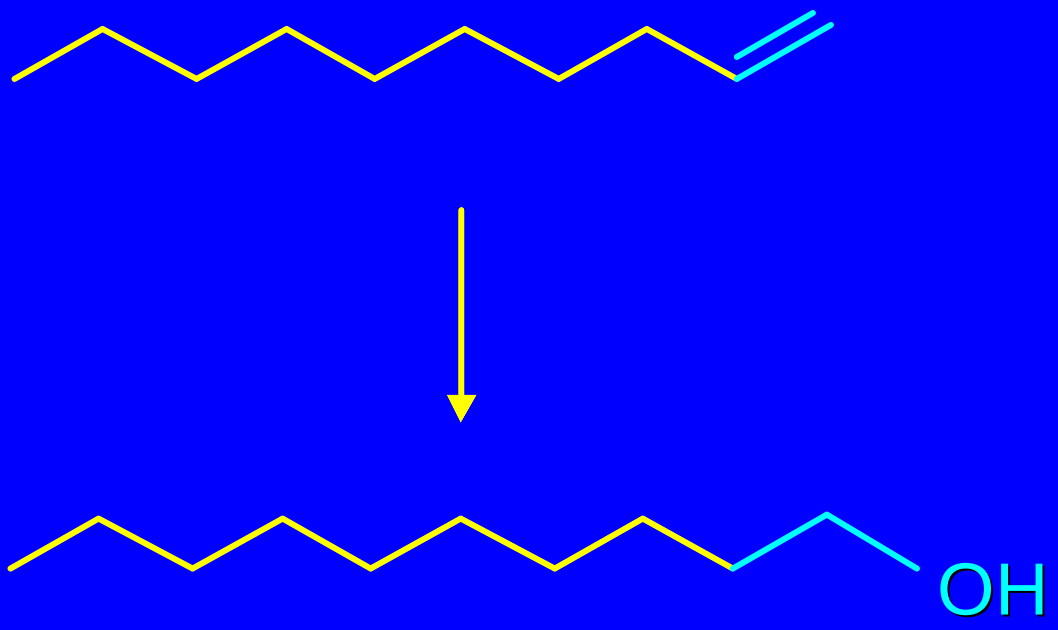
In an equilibrium process, the same intermediates and transition states are encountered in the forward direction and the reverse, but in the opposite order.

6.11

Hydroboration-Oxidation of Alkenes

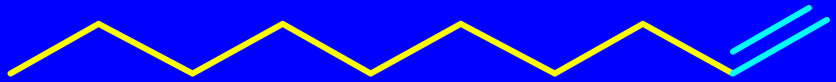
Synthesis

Suppose you wanted to prepare 1-decanol from 1-decene?

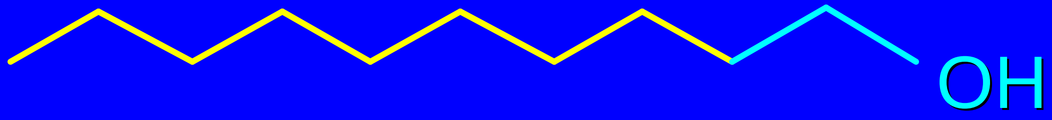


Synthesis

Suppose you wanted to prepare 1-decanol from 1-decene?

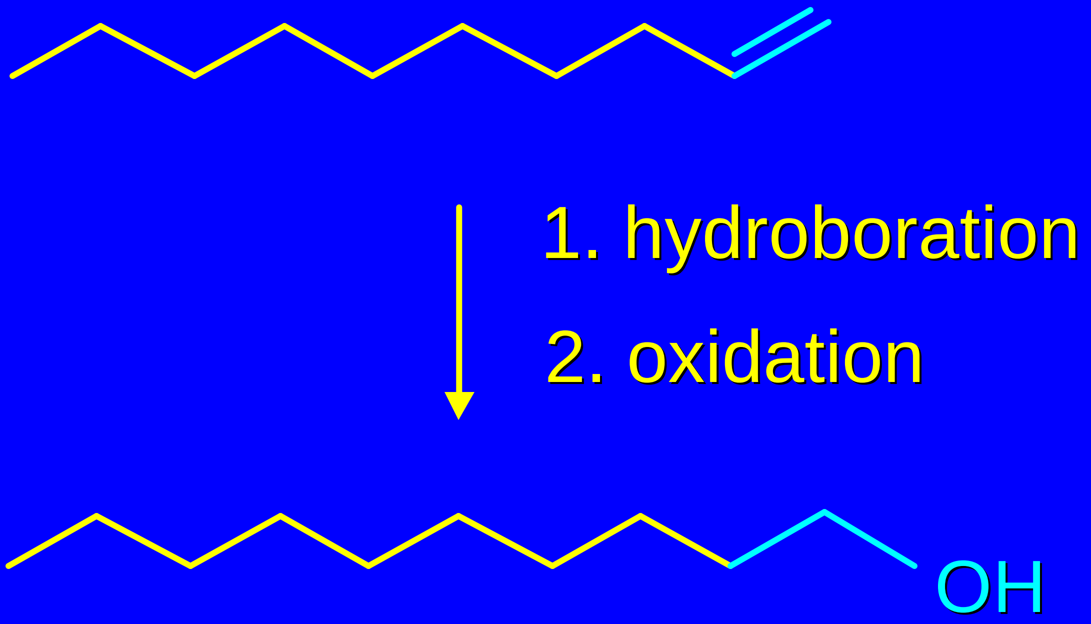


Needed: a method for hydration of alkenes with a regioselectivity opposite to Markovnikov's rule.

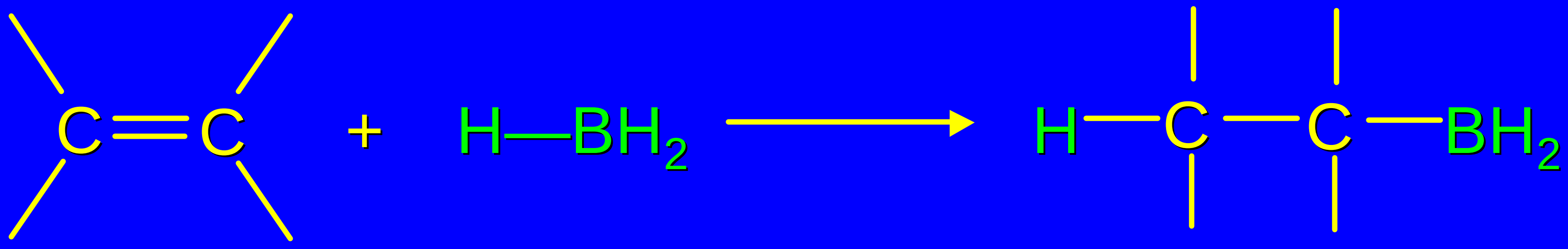


Synthesis

Two-step reaction sequence called hydroboration-oxidation converts alkenes to alcohols with a regiochemistry opposite to Markovnikov's rule.

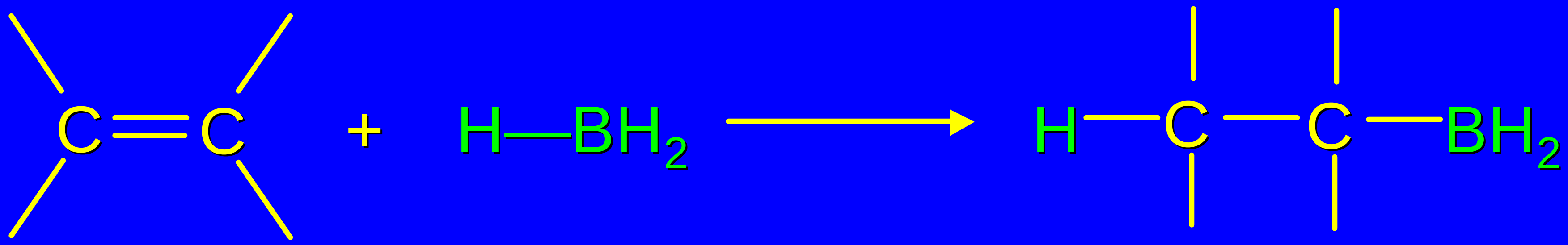


Hydroboration Step

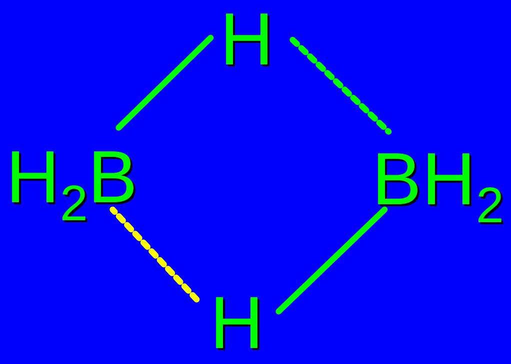


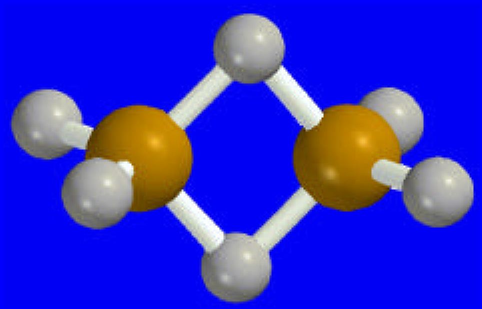
Hydroboration can be viewed as the addition of borane (BH_3) to the double bond. But BH_3 is not the reagent actually used.

Hydroboration Step



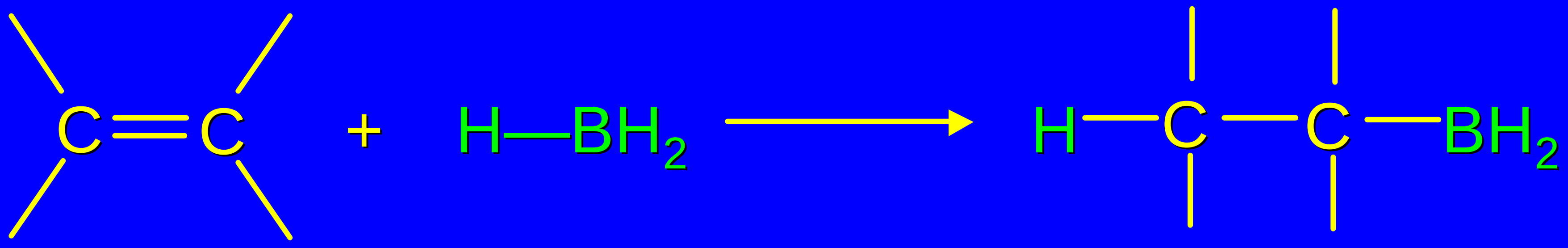
Hydroboration reagents:



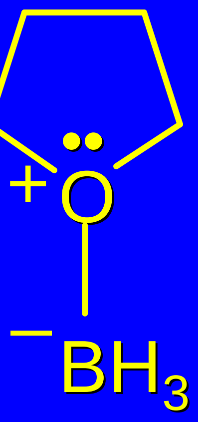


Diborane (B_2H_6) normally used in an ether- like solvent called "diglyme"

Hydroboration Step

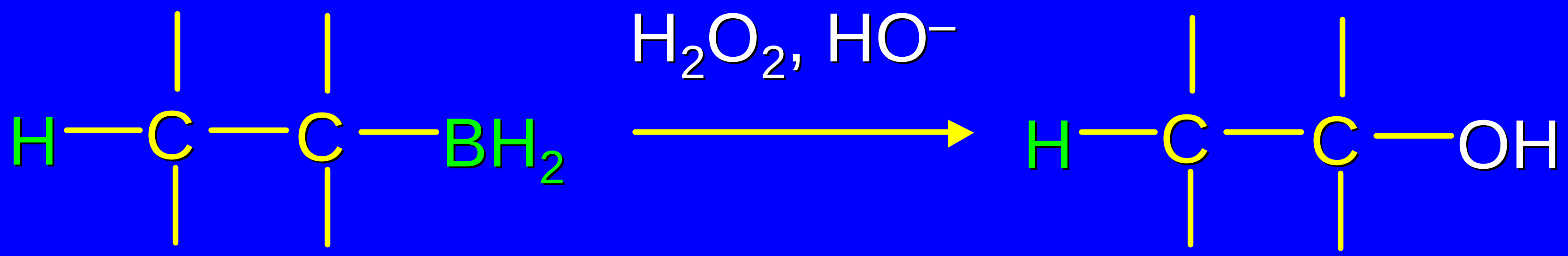


Hydroboration reagents:



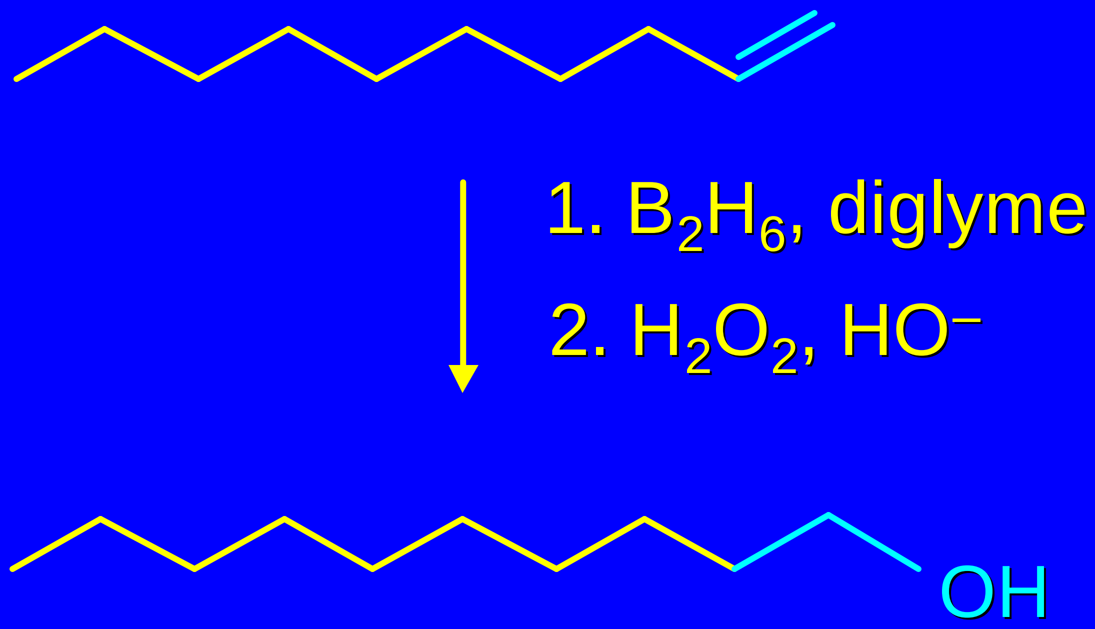
Borane-tetrahydrofuran complex (H_3B-THF)

Oxidation Step



Organoborane formed in the hydroboration step is oxidized with hydrogen peroxide.

Example

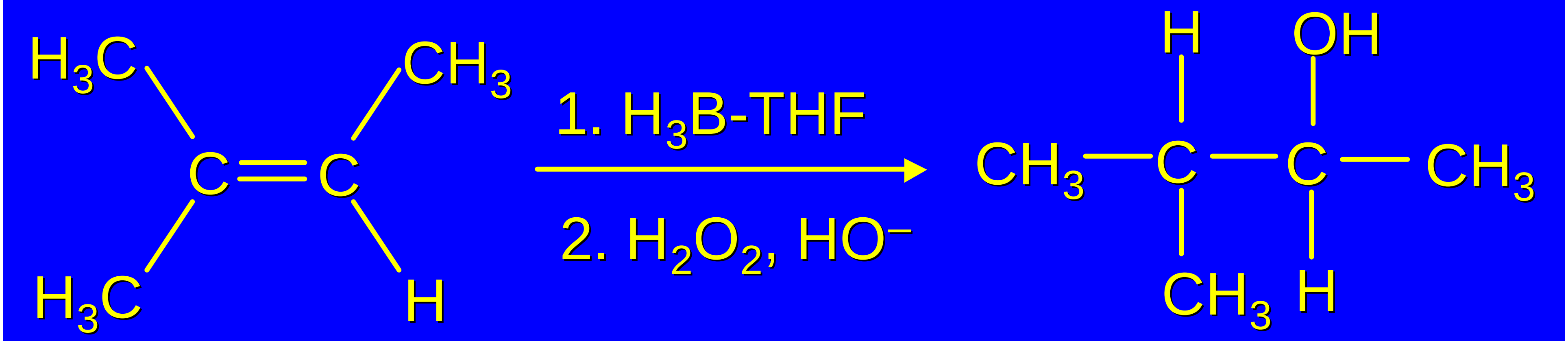


1. B_2H_6, diglyme

2. H_2O_2, HO^-

(93%)

Example



(98%)

Features of Hydroboration-Oxidation

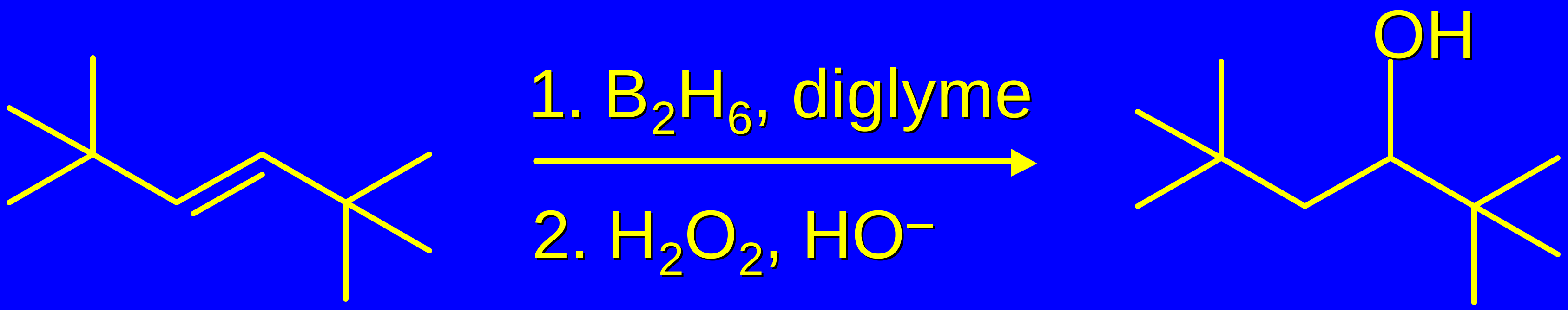
hydration of alkenes

regioselectivity opposite to Markovnikov's rule

no rearrangement

stereospecific *syn* addition

Example



1. B_2H_6, diglyme

2. H_2O_2, HO^-

(82%)

6.12
Stereochemistry of Hydroboration-Oxidation

Features of Hydroboration-Oxidation

hydration of alkenes

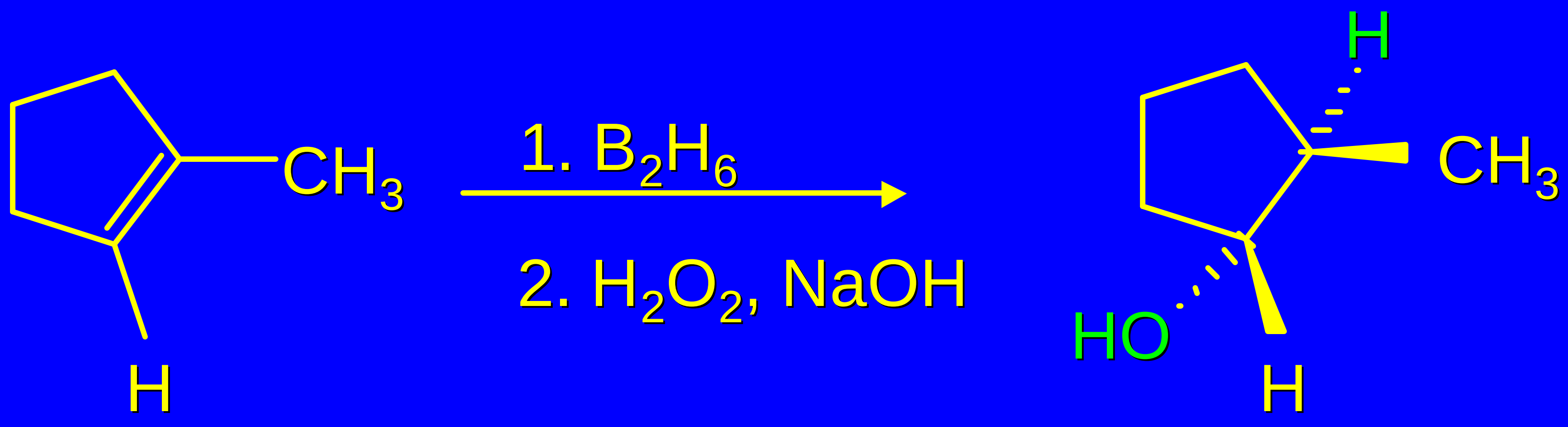
regioselectivity opposite to Markovnikov's rule

no rearrangement

stereospecific *syn* addition

syn-Addition

H and OH become attached to same face of double bond

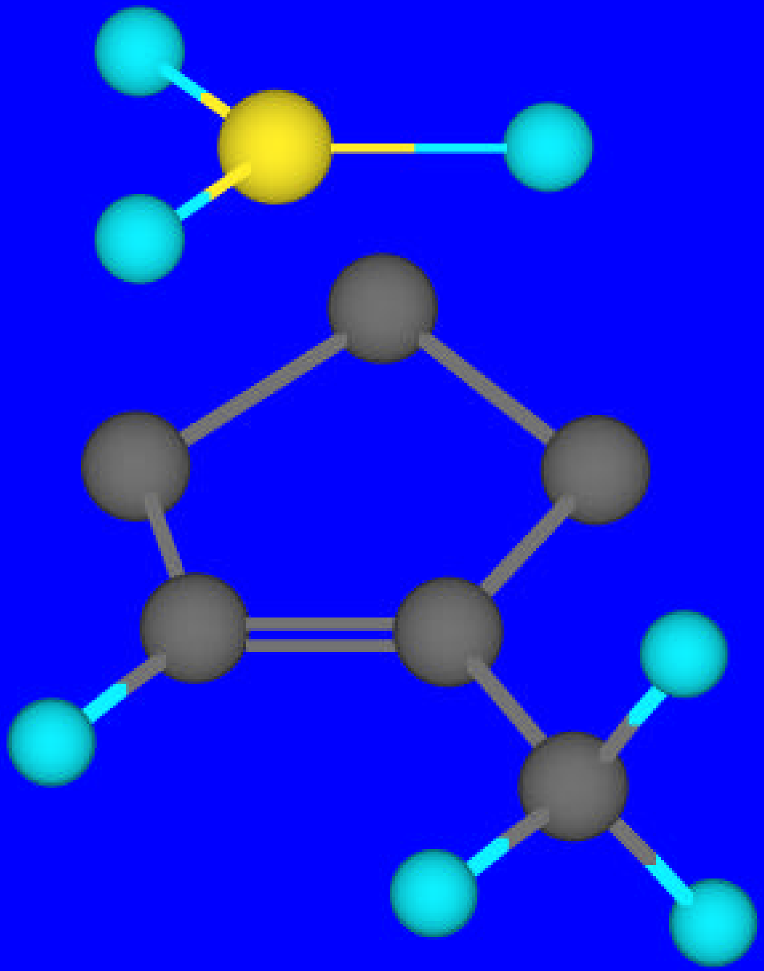


only product is *trans*-2-methylcyclopentanol (86%) yield

6.13

Mechanism of Hydroboration-Oxidation

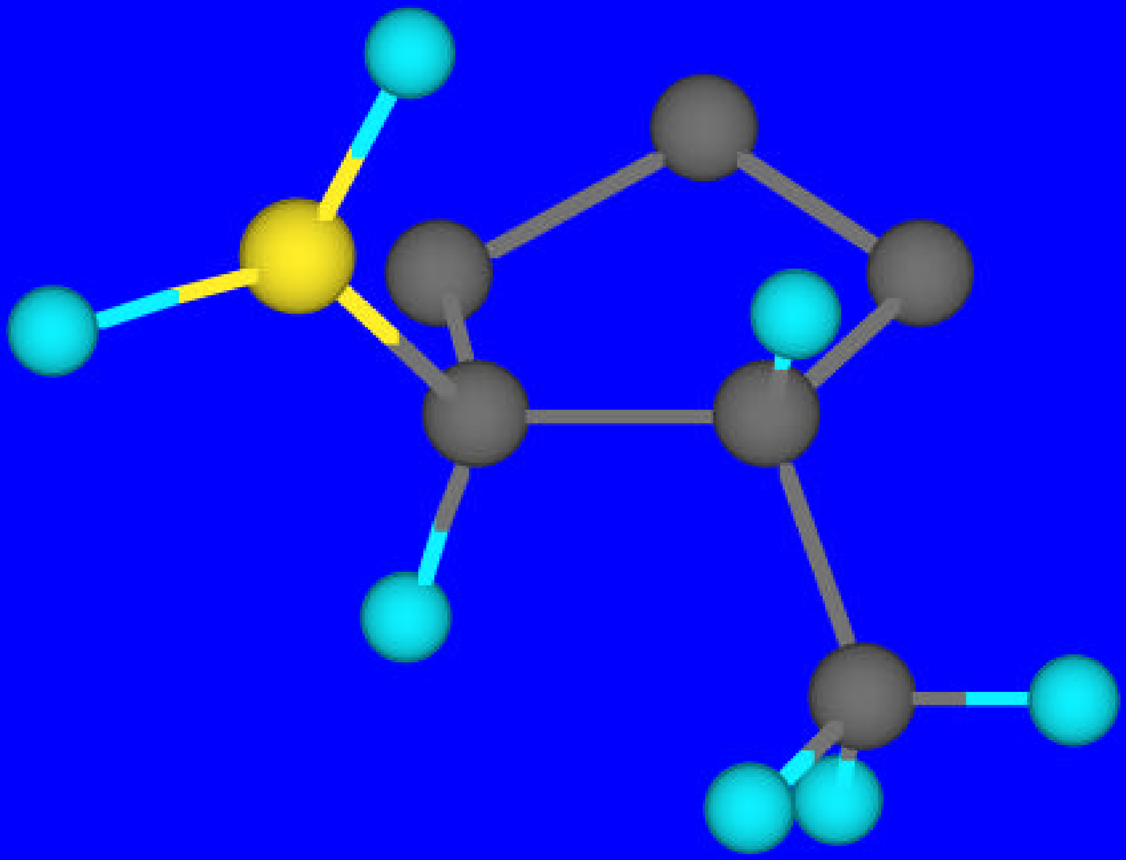
1-Methylcyclopentene + BH_3



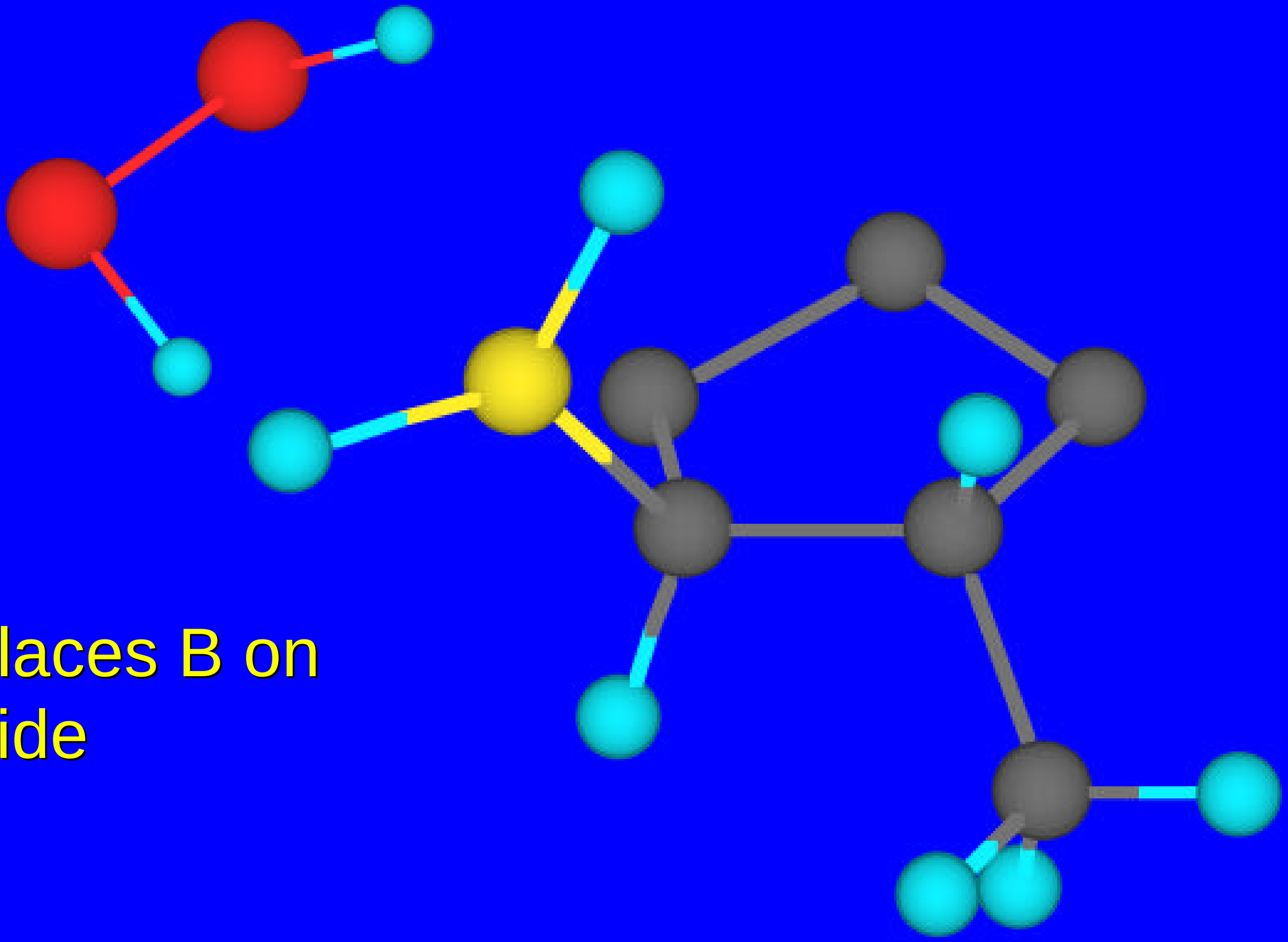
syn addition of H and B to double bond

B adds to less substituted carbon

Organoborane intermediate



Add hydrogen peroxide



OH replaces B on
same side

trans-2-*Methylcyclopentanol*