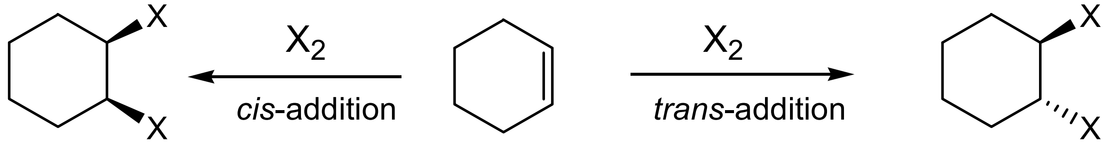
Stereochemical Possibilities

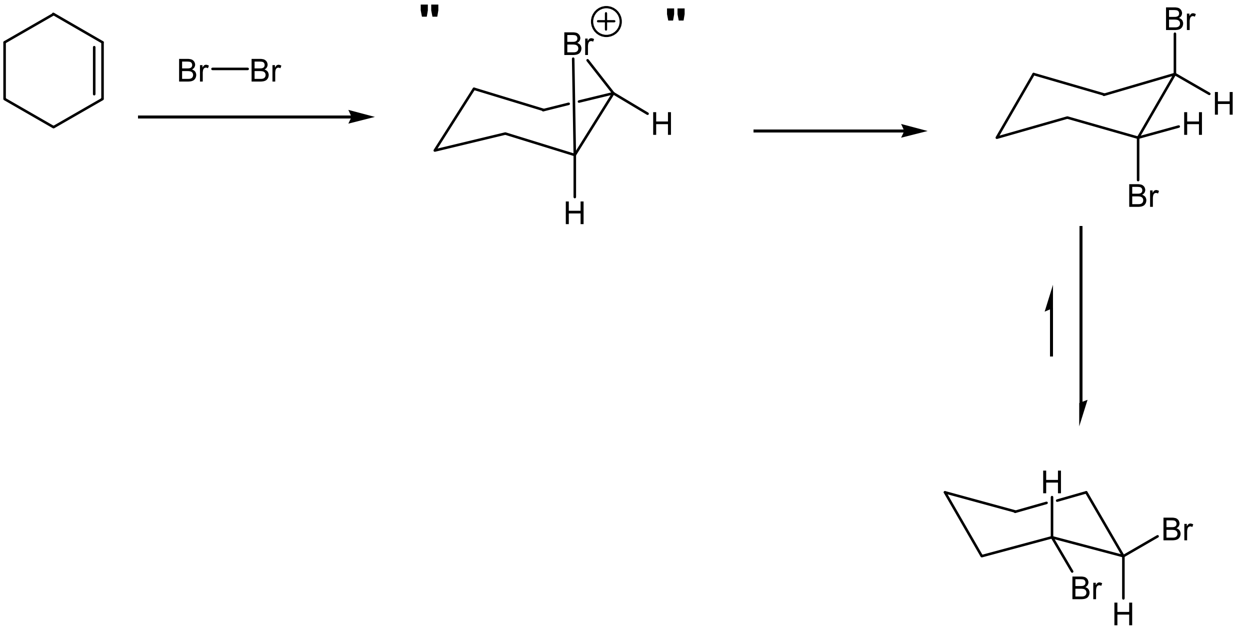
Cyclic compounds

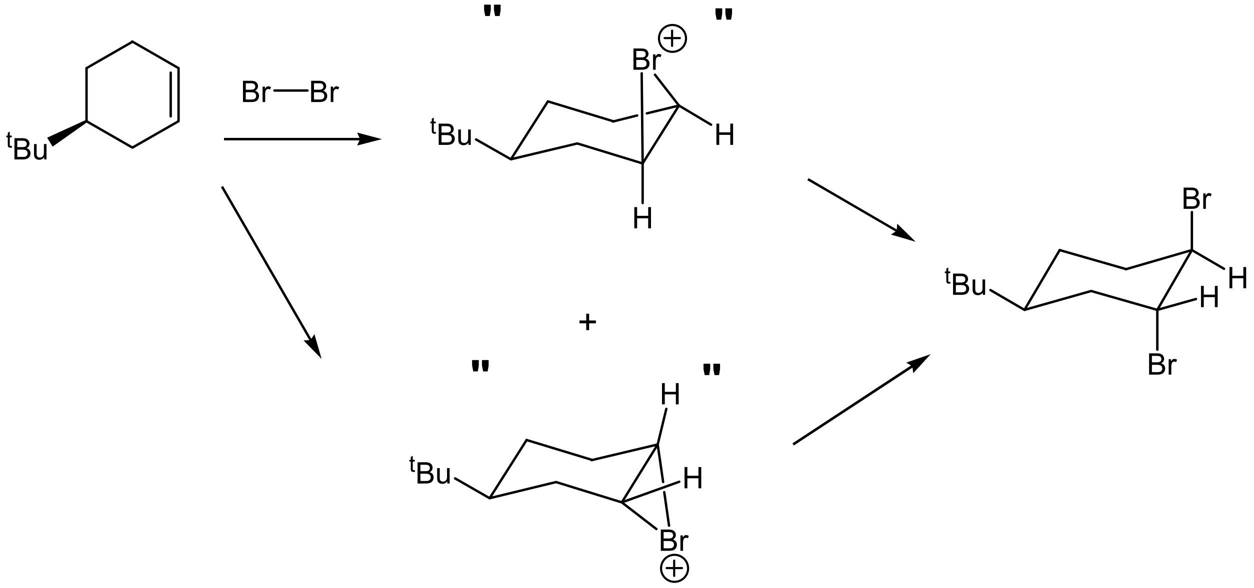
Cis and *trans* addition are defined with respect to the face of the ring:



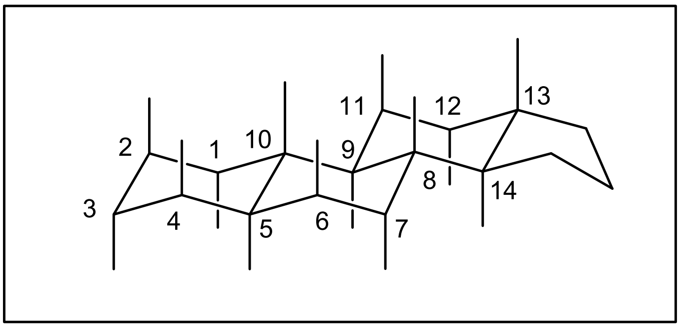
Example

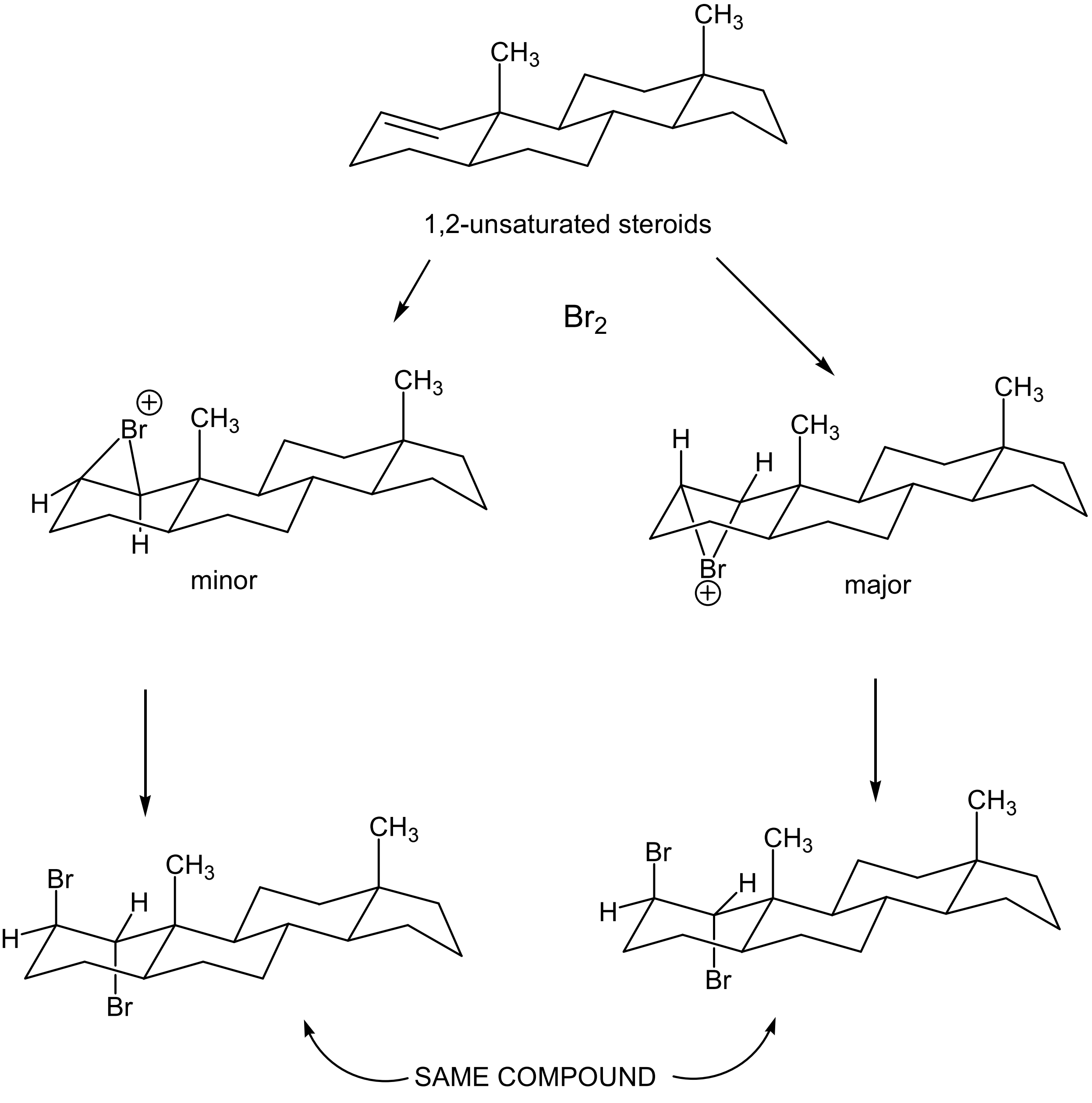
Bromination of cyclohexenes. The *anti*-periplanar requirement for S_N2 ring opening of the cyclic bromonium ion leads to (at least initially) *trans*-diaxial products (see epoxides pg 39):





Since *trans*-diaxial products are formed it is important to know which are the axial positions at the various carbons in fused ring systems. For example in the steroid ring system the β-substituents (top face) at carbons 2,4,6,8,10,11,13 and 13 are axial, while the α-substituents (bottom face) at carbons 1,3,5,7,9,12 and 14 are axial.

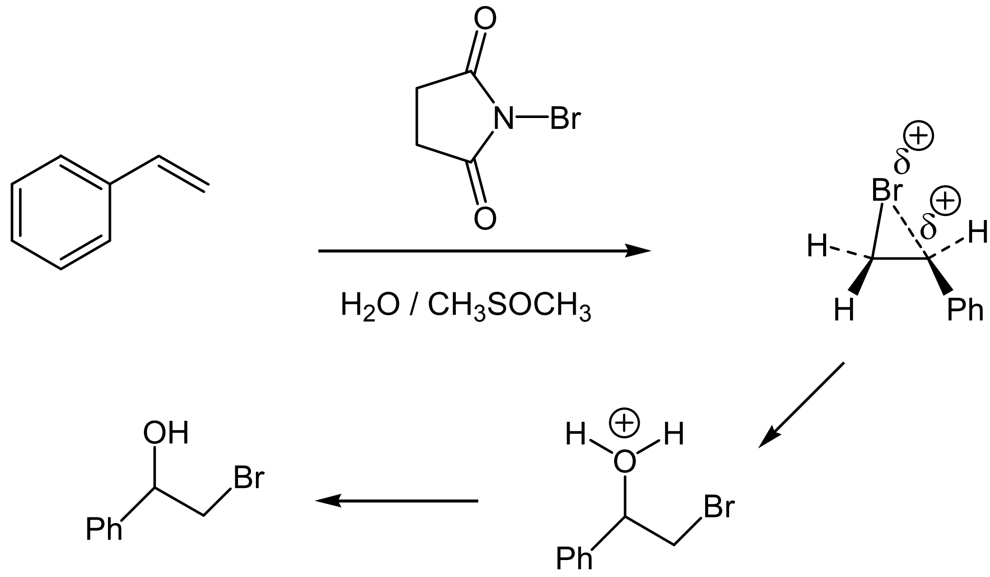


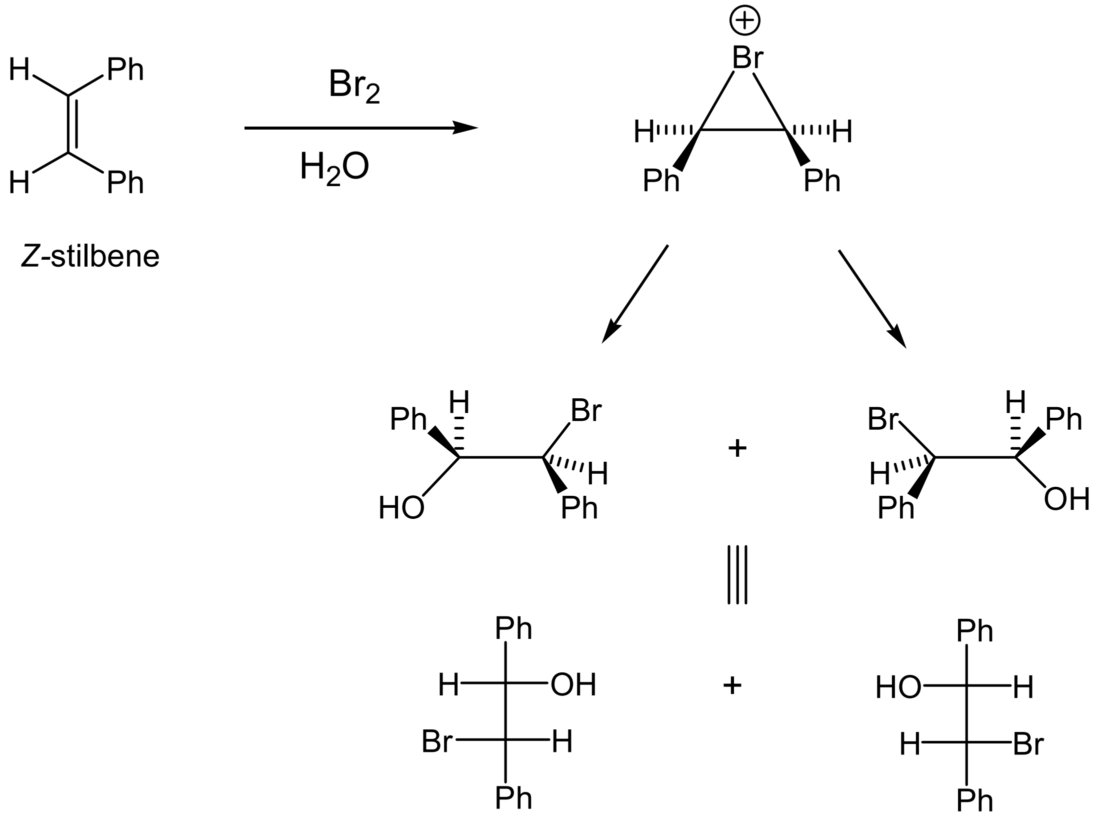


Other Addition Reactions

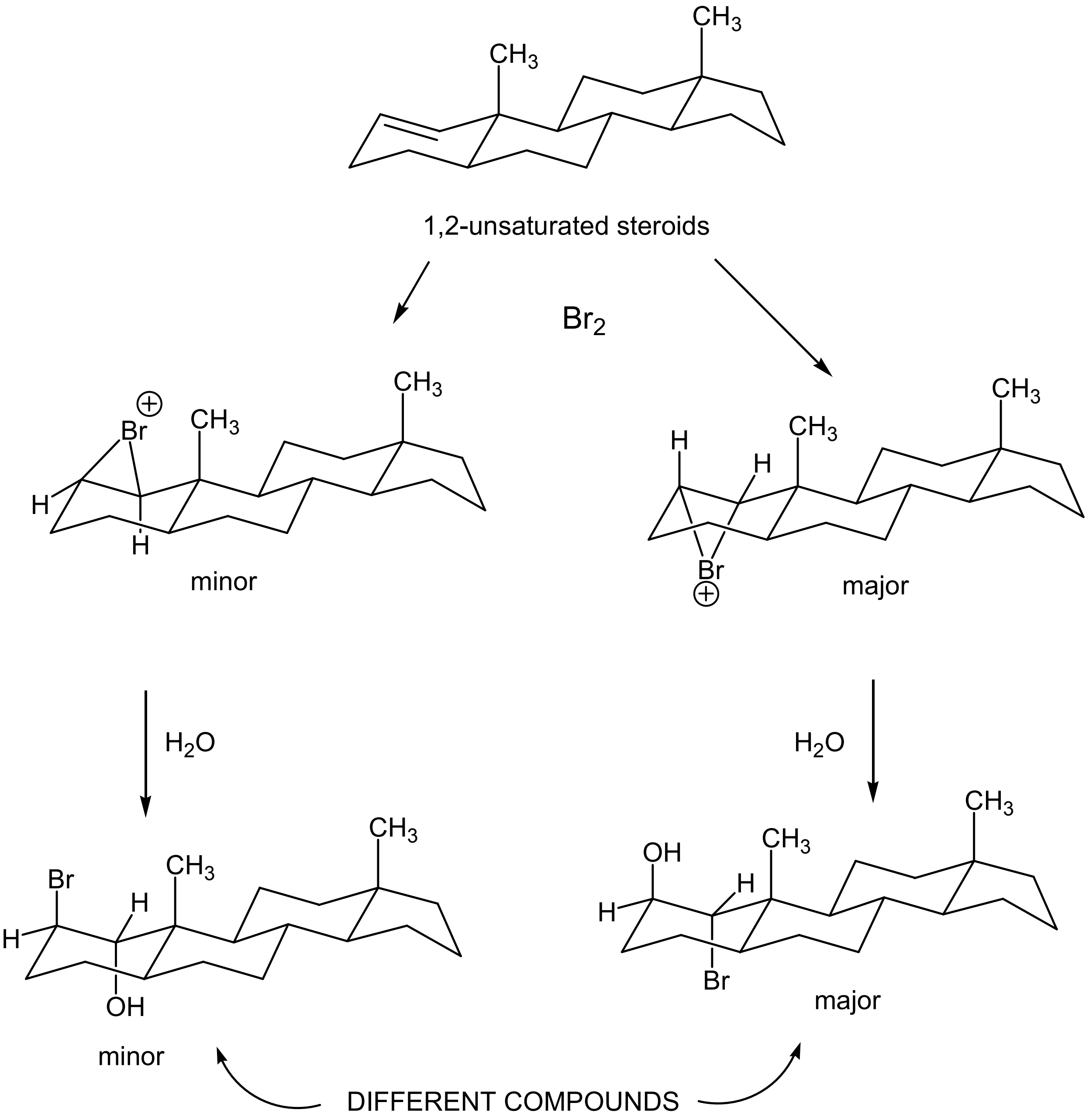
Bromohydrin Formation

Regiochemistry and Stereochemistry – more substituted carbon of bromonium ion intermediate is attacked in an S_N2 fashion by water (compare acid-catalysed epoxide ring opening – pg. 38).





threo diastereoisomer (racemic)


CH3
CH3
1,2-unsaturated steroids
Br2
Br
CH3
CH3
H
H
minor
H
H
CH3
CH3
Br
major
H2O
H2O
Br
H
CH3
CH3
H
OH
minor
OH
H
CH3
CH3
H
Br
major
DIFFERENT COMPOUNDS