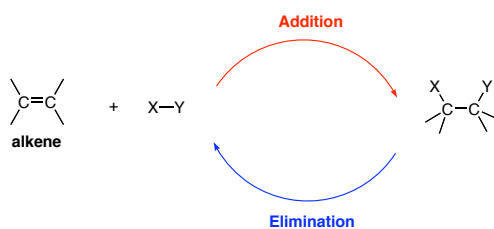
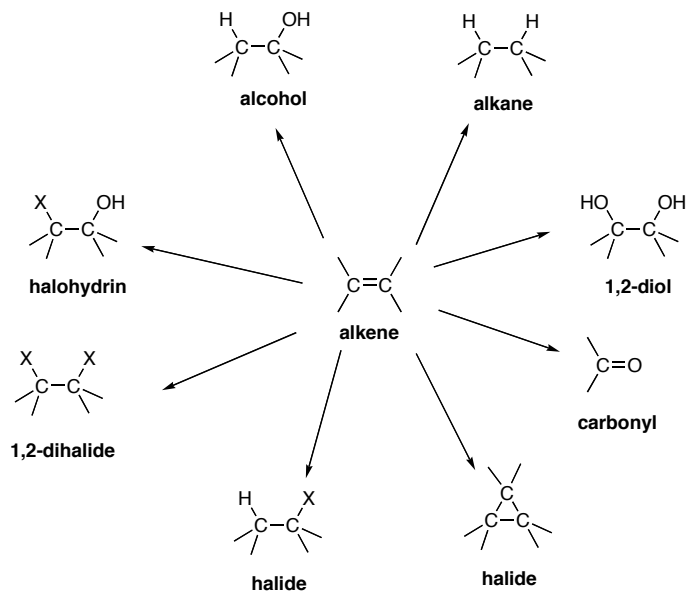
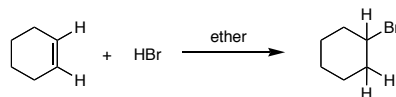


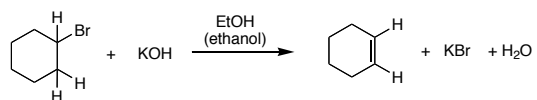
Chapter 7: Alkenes: Reactions and Synthesis



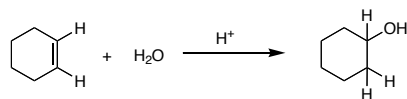
Electrophilic Addition



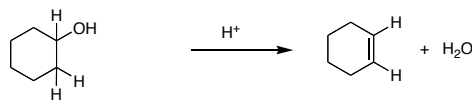
Dehydrohalogenation: loss of HX from an alkyl halide to form an alkene



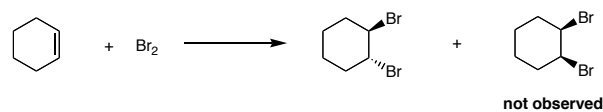
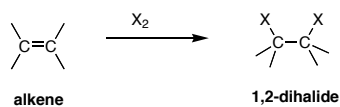
Hydration: addition of water (H-OH) across a double bond to give an alcohol



Dehydration: Loss of water (H-OH) from an alcohol to give an alkene



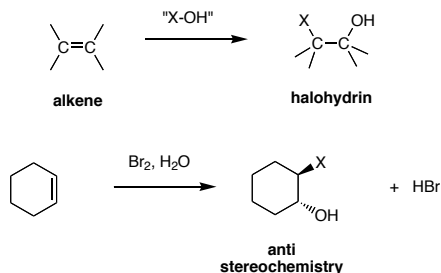
Addition of Halogens (X₂) to Alkenes: 1,2-dihalides



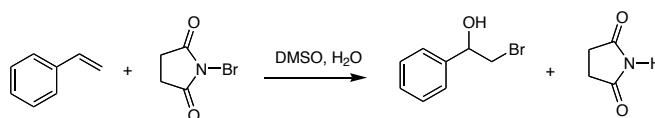
1,2-dibromide has the anti stereochemistry

Bromonium ion intermediate controls the stereochemistry

Halohydrin Formation

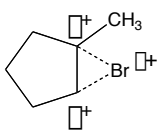


Organic molecules are sparingly soluble in water as solvent. The reaction is often done in a mix of organic solvent and water using N-bromosuccinimide (NBS) as the electrophilic bromine source.



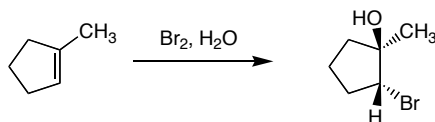
Note that the aryl ring does not react!!!

For unsymmetrical alkenes, halohydrin formation is Markovnikov-like in that the orientation of the addition of X-OH can be predicted by considering carbocation stability



more δ⁺ charge on the more substituted carbon

H₂O adds in the second step and adds to the carbon that has the most δ⁺ charge and ends up on the more substituted end of the double bond

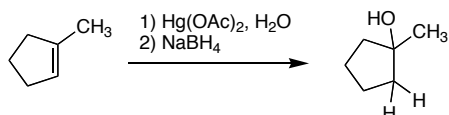


Br adds to the double bond first (formation of bromonium ion) and is on the least substituted end of the double bond

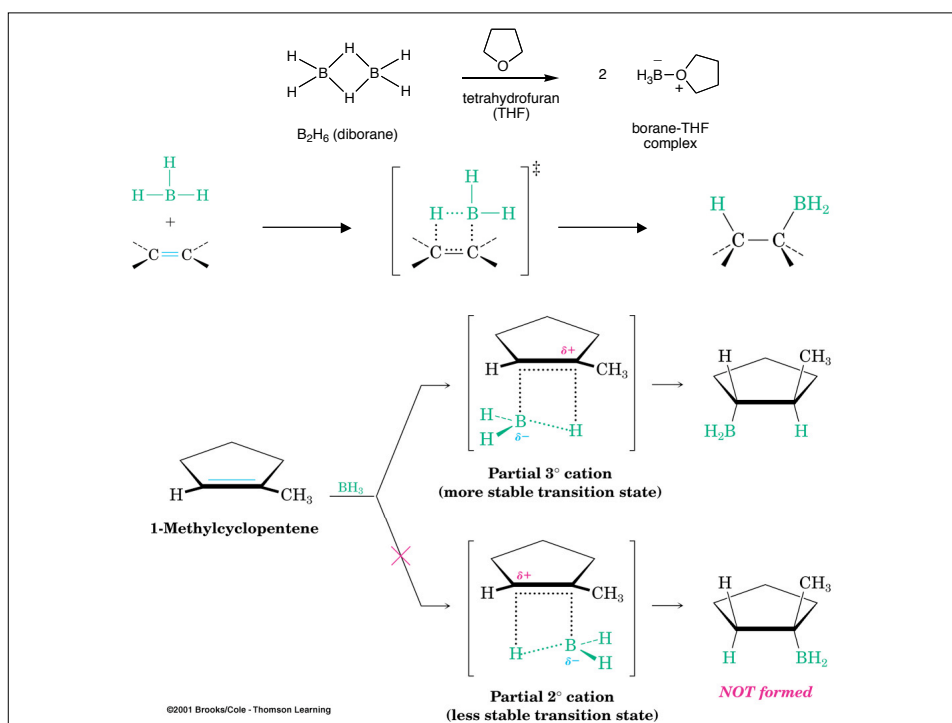
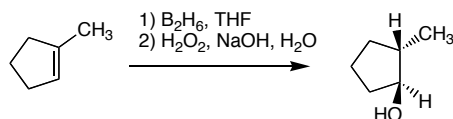
Hydration of Alkenes: addition of water (H-OH) across the π -bond of an alkene to give an alcohol.

1. Acid catalyzed hydration- Markovnikov addition of H-OH
Not a good method for hydration of an alkene

2. Oxymercuration- Markovnikov addition H-OH

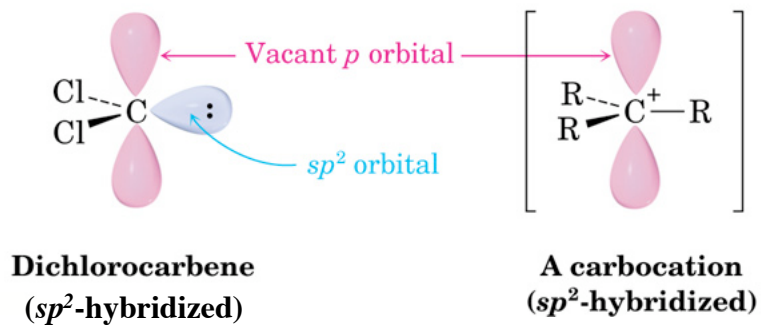


3. Hydroboration- Anti-Markovnikov addition of H-OH,
Syn addition of H-OH

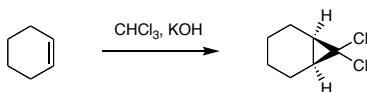
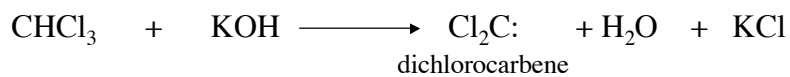


Reaction of Alkenes with Carbenes to give Cyclopropanes

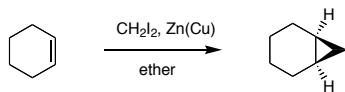
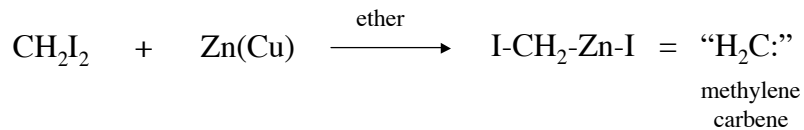
Carbene: highly reactive, 6-electron species.



Generation and Reaction of Carbenes:

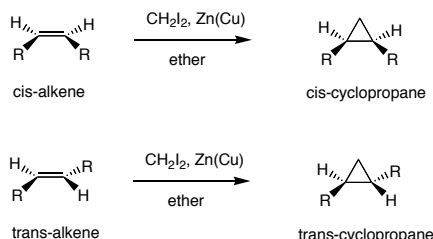


Simmons-Smith Reaction (cyclopropanation)

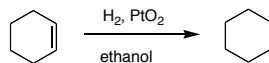


The cyclopropanation reaction of an alkene with a carbene takes place in a single step. There is NO intermediate.

As such, the geometry of the alkene is preserved in the product. *Groups that are trans on the alkene will end up trans on the cyclopropane product. Groups that are cis on the alkene will end up cis on the cyclopropane product.*



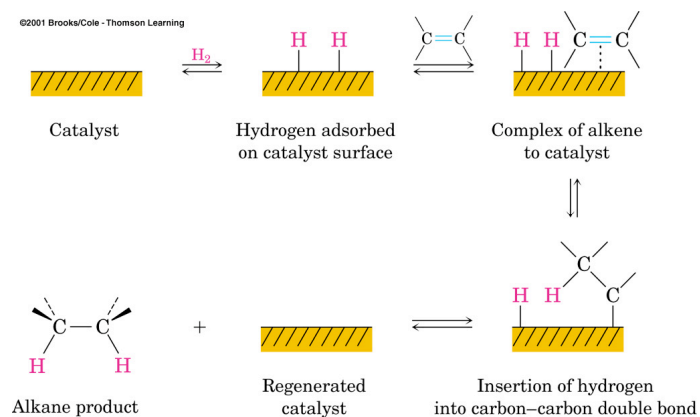
Hydrogenation: Addition of H_2 across the π -bond of an alkene to give an alkane. This is a reduction.



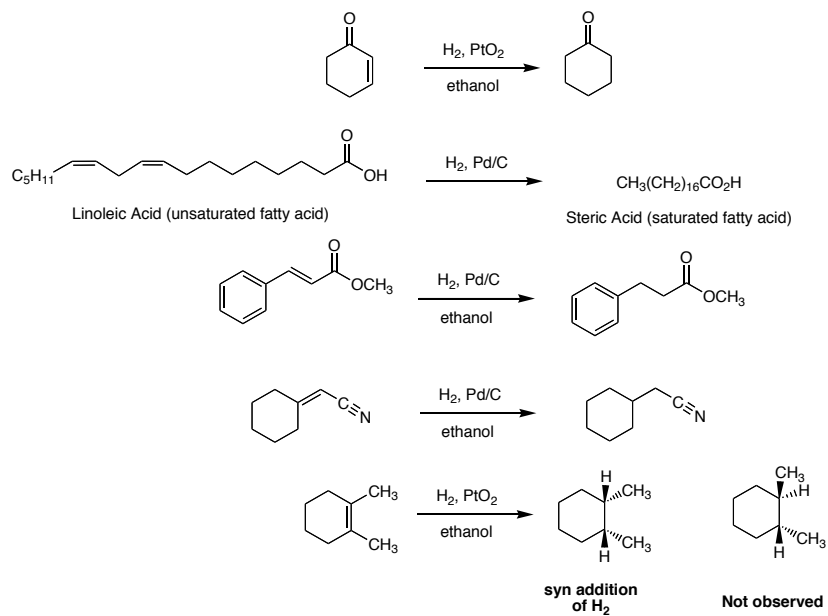
- The reaction uses H_2 and a precious metal catalyst.
- The catalyst is not soluble in the reaction media, thus this process is referred to as a *heterogenous* catalysis.
- The catalyst assists in breaking the π -bond of the alkene and the H-H σ -bond.
- The reaction takes place on the surface of the catalyst. Thus, the rate of the reaction is proportional to the surface area of the catalyst.
- To increase the surface area of the catalyst it is finely dispersed on an inert support such as charcoal (carbon, C)
- Carbon-carbon π -bond of alkenes and alkynes can be reduced to the corresponding saturated C-C bond. Other π -bond bonds such as C=O (carbonyl) and $\text{C}\equiv\text{N}$ are not easily reduced by catalytic hydrogenation. The C=C bonds of aryl rings are not easily reduced.

Catalysts: Pt_2O (Adam's catalyst) or Pd/C

mechanism:

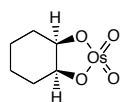
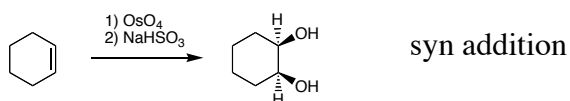


The addition of H_2 across the $\text{C}=\text{C}$ bond is syn



Oxidation of Alkenes to 1,2-Diols and Carbonyl

Hydroxylation: formal addition of HO-OH across the π -bond of an alkene to give a 1,2-diol. This is an overall oxidation.



osmate ester intermediate

- not usually isolate
- NaHSO_3 breaks down the osmate ester to the product

Ozonolysis: oxidative cleavage of an alkene to carbonyl compounds.

The π - and σ -bonds of the alkene are broken and replaced with $\text{C}=\text{O}$ double bonds.

$\text{C}=\text{C}$ of aryl rings, $\text{C}\equiv\text{N}$ and $\text{C}=\text{O}$ do not react with ozone,
 $\text{C}\equiv\text{C}$ react very slowly with ozone

