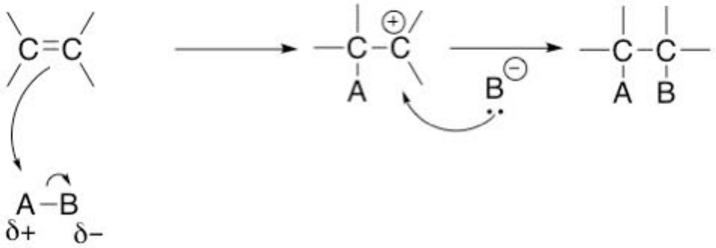
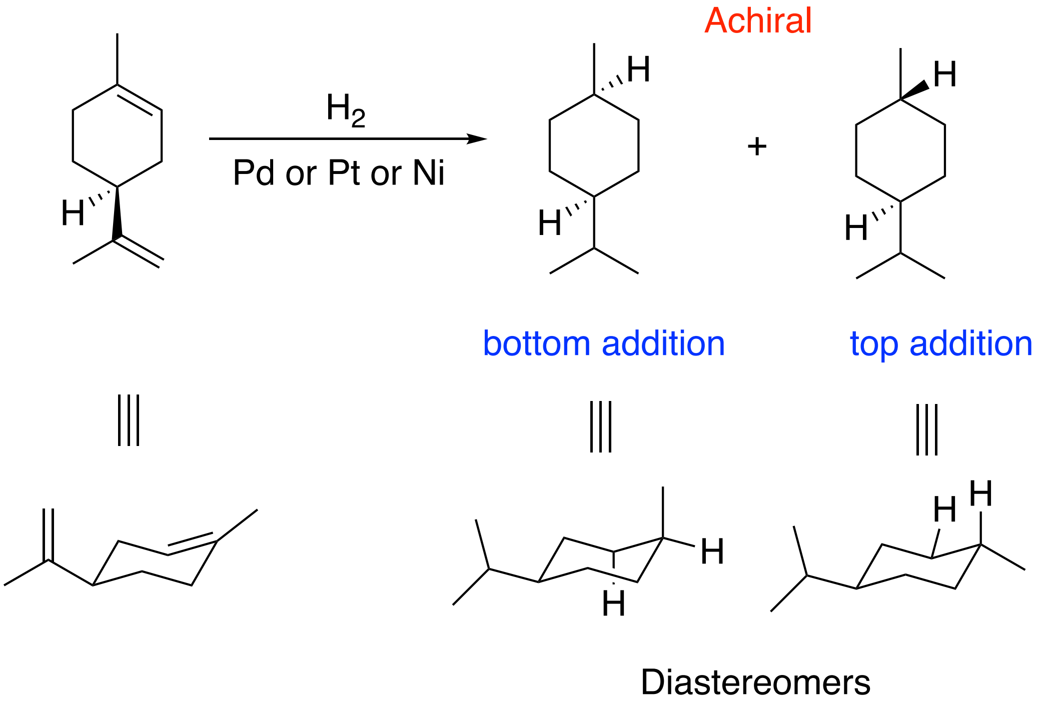
Addition Reactions

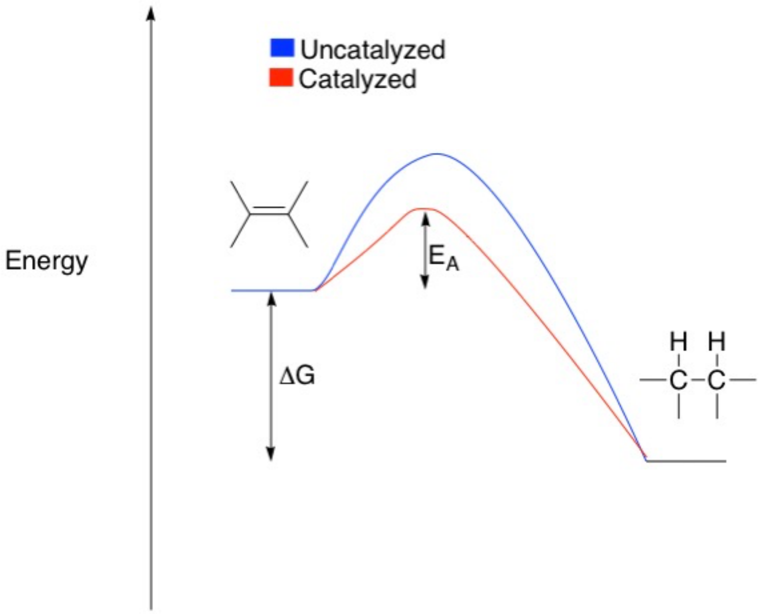
- Occurs on double bonds and triple bonds



Hydrogenation:

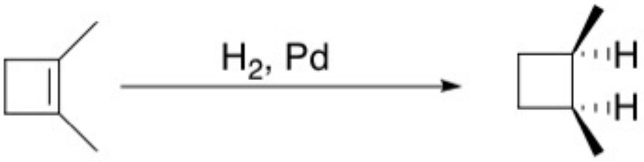
Limonene





Hydrogenation examples

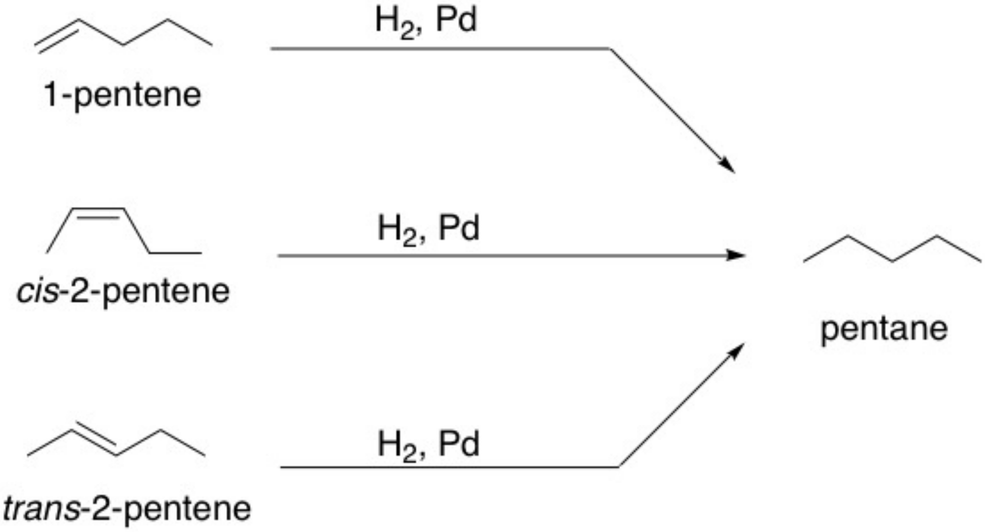
Example 1: 1,2-dimethylcyclobutene



1,2-dimethylcyclobutene *cis*-1,2-dimethylcyclobutane

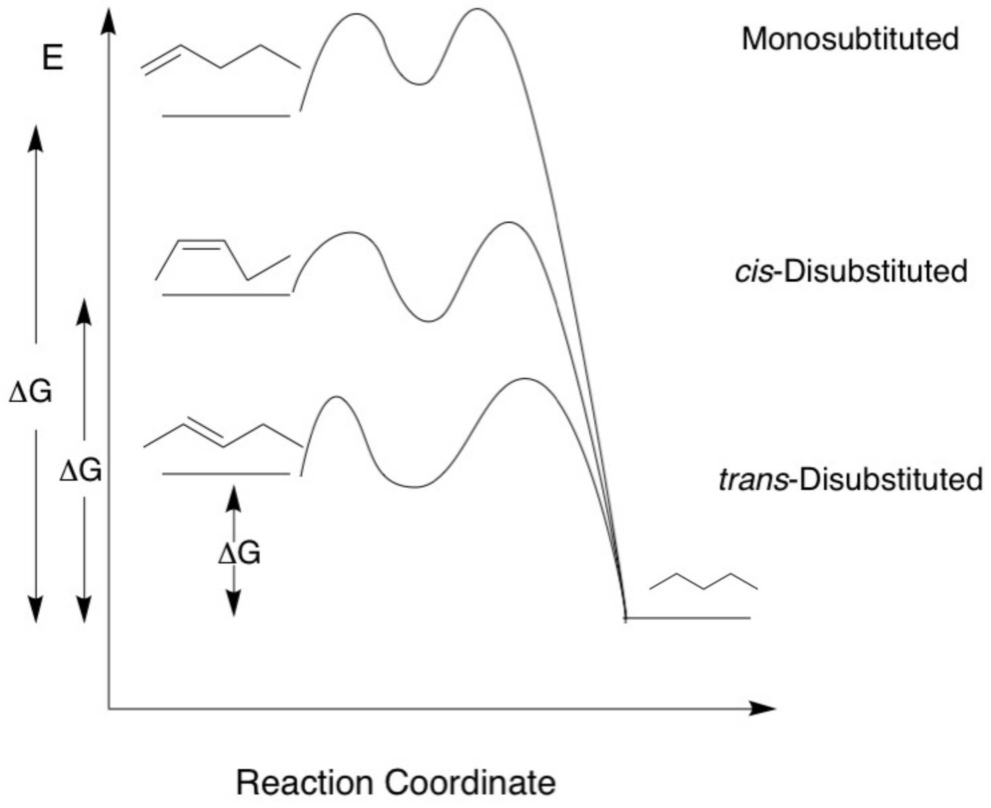
The hydrogenation can occur from the top or the bottom, which in this case produces the same product (cis isomer of 1,2-dimethylcyclobutane). The starting material is achiral, and the product is a **meso compound** (two stereogenic centers, but a plane of symmetry)

Example 2: Pentene



Energy is released in each of these reactions, the energy released implies stabilization caused from transforming the starting material into the product

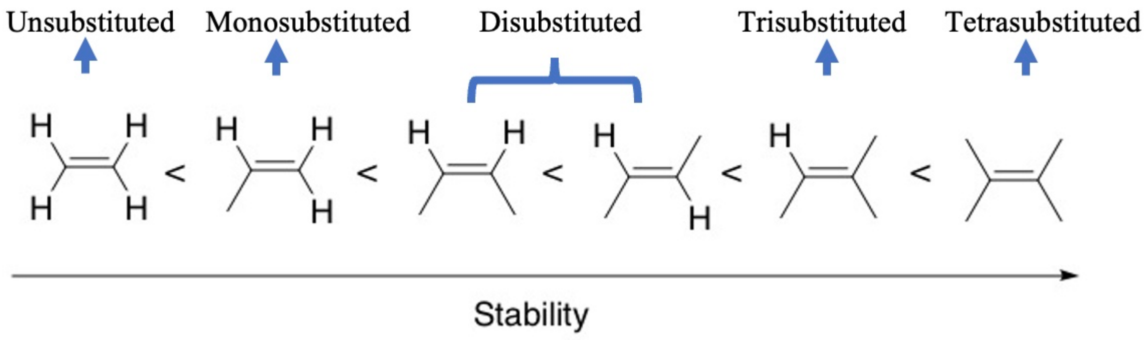
Energy diagram



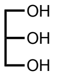
ΔG *trans*-isomer < ΔG *cis*-isomer < ΔG 1-pentene isomer

Alkenes with more substituents are more stable. Carbons in a double bond have a $\delta+$ (electron-deficient), this is stabilized by the **electron donating effects** of alkyl groups. Hydrogens are less electron-donating and so less substituted alkenes are less stable.

Cis alkenes are less stable than trans alkenes as they have methyl groups facing the same direction, which causes unfavourable steric interactions.

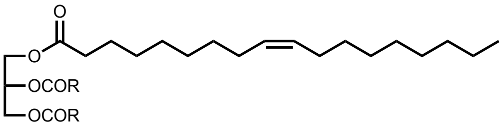


Example 3: Fats

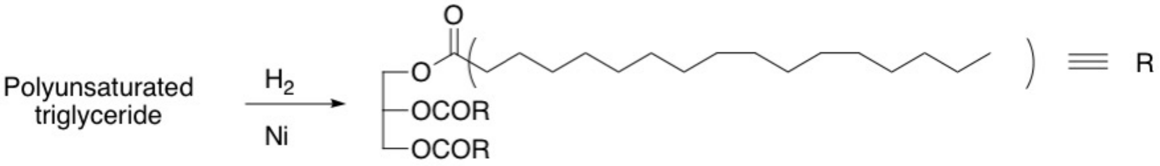


Glycerol

Basic component used to make fatty acids.

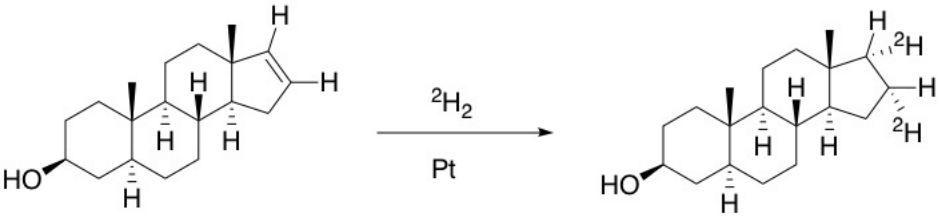


mono-unsaturated fat (oil)



Major component of margerine

Example 4: Steroids



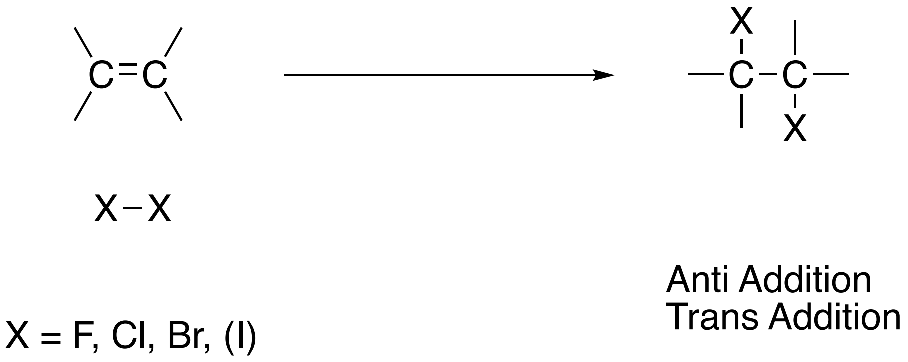
Androstenol
(Pheromone)

not a pheromone

The deuteriums add to the bottom because of the steric hindrance of the nearby methyl group.

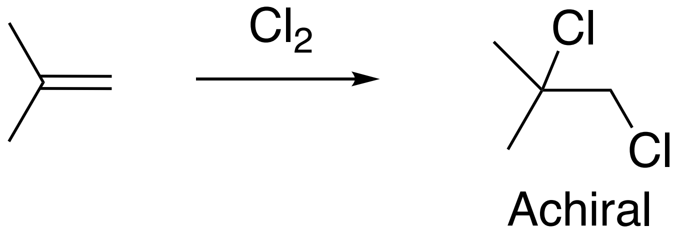
^2H = D = deuterium

Halogenation: Addition of halogens across a double bond

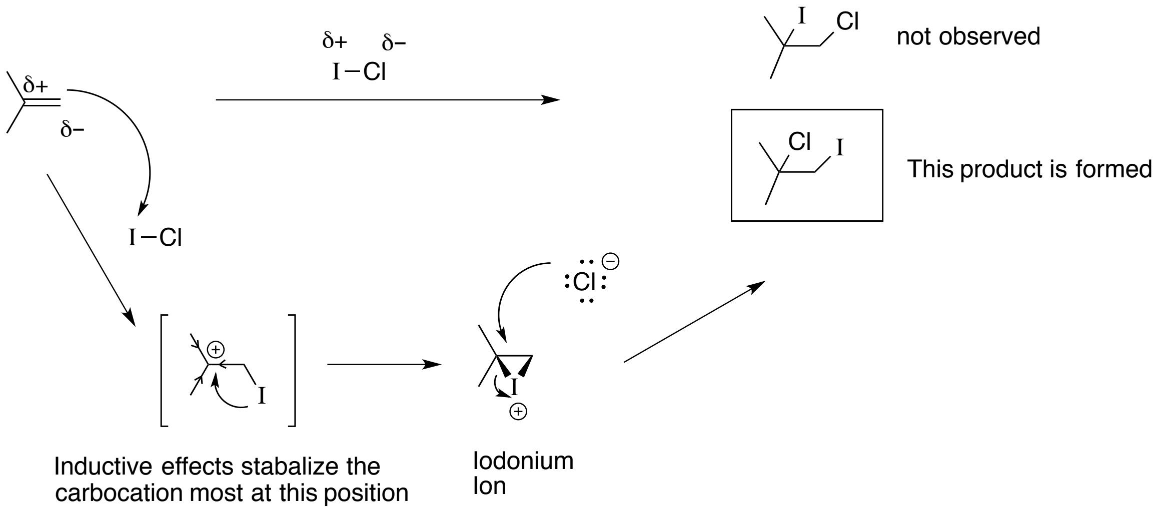


Note: Iodine (I_2) does not react with most alkenes (i.e., won't add across the double bond).

Example: 2-Methylpropene



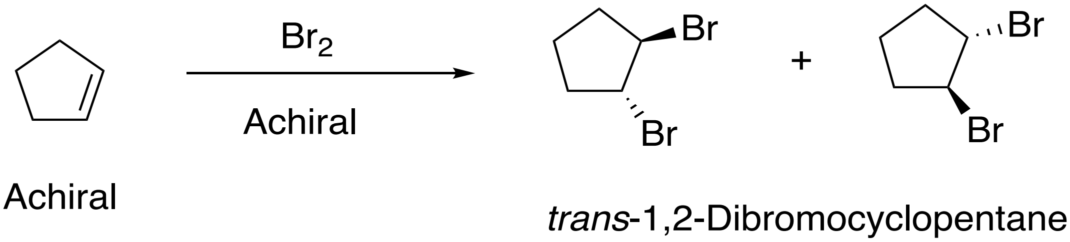
Example: 2-Methylpropene



- The electrons in the π-bond attack the partially positive (δ+) I
- Cl^- will attack the more substituted C due to there being a more carbocation character (more substituted end can stabilize the positive charge better due to stabilizing effect of alkyl groups – **inductive effect**)

Markovnikov's Rule: In an addition reaction, the positive end of an A–B system (e.g. I–Cl) adds to the least substituted end of the double bond to make the more stable carbocation.

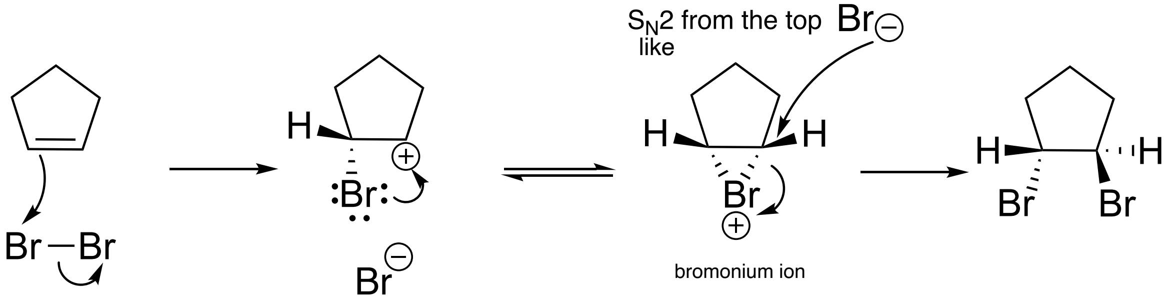
Example 1: Cyclopentene



trans-1,2-Dibromocyclopentane

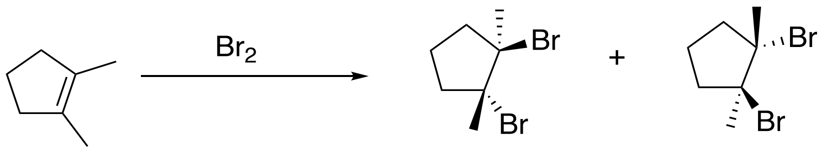
Both enantiomers formed (1:1 racemate)

Mechanism:



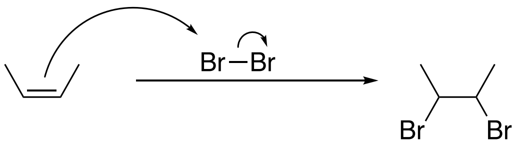
The first step can happen from the top or bottom, and the S_N2 step happens from the opposite side each time.

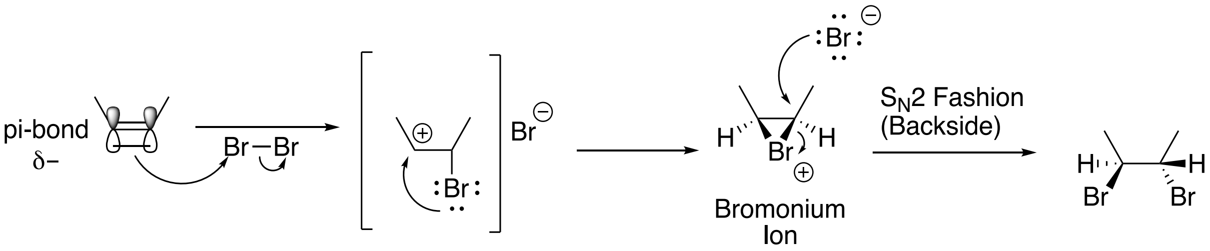
Example 2: 1,2-dimethylcyclopentene



trans-1,2-Dibromo-1,2-dimethylcyclopentane

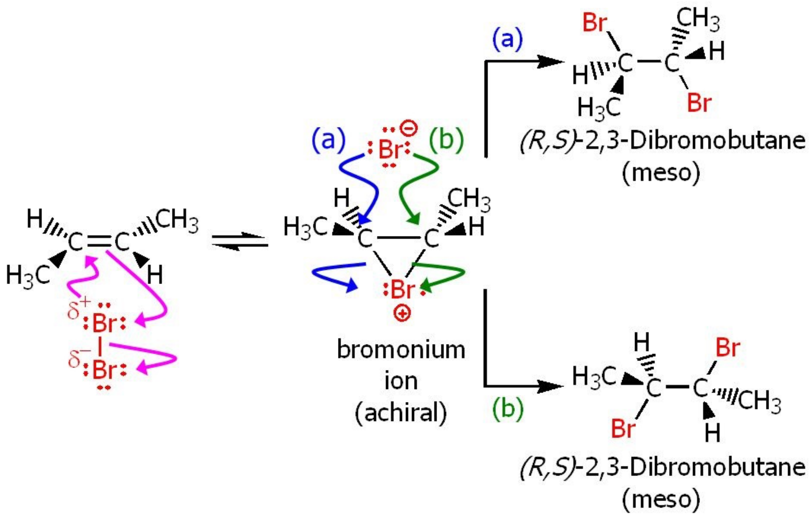
Mechanism:





- Halogen addition to alkene is very fast at -78℃
- Attack always comes from the backside – trans product
- When the bromonium ion forms, the bond between the Br and C atom can stretch, giving more carbocation character to the C.

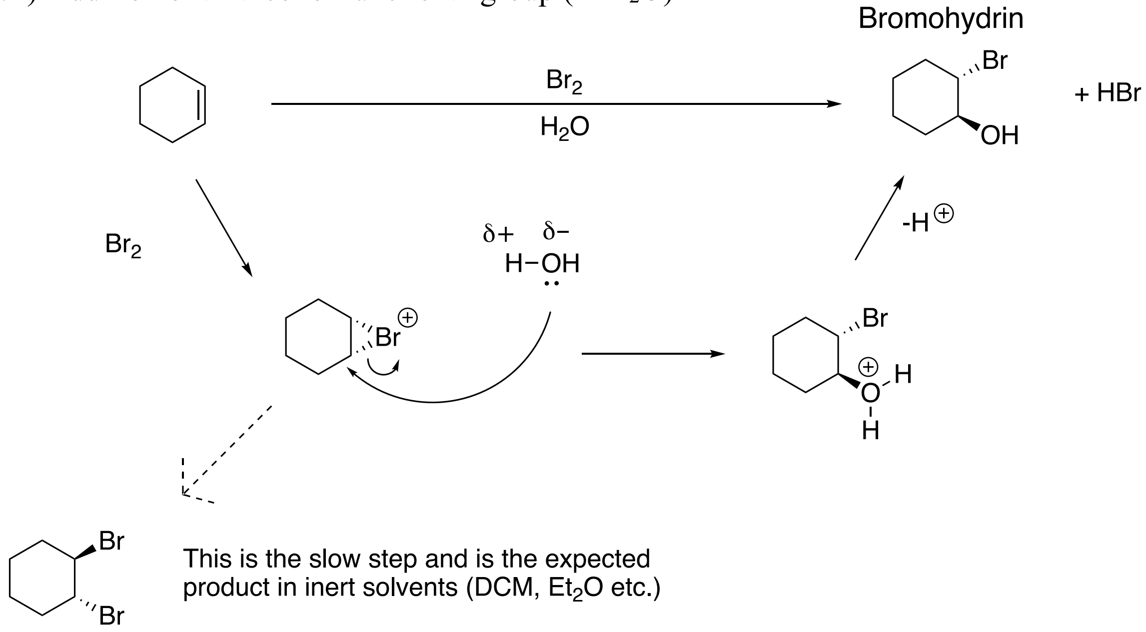
Example: *trans*-2-butene



- Stereochemistry of starting material determines the stereochemistry of product

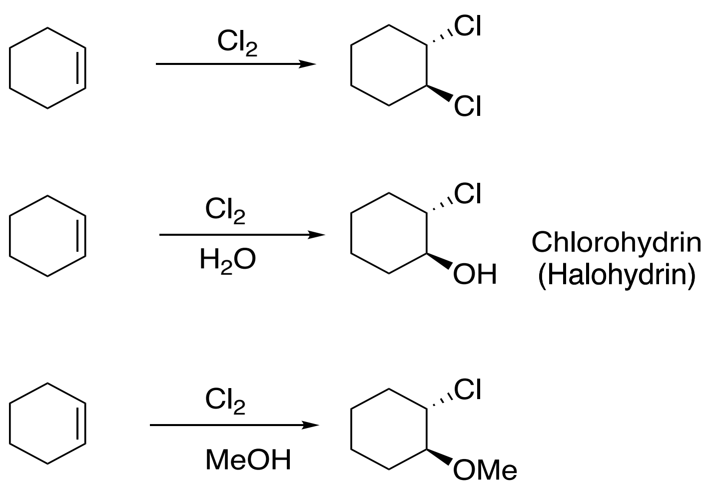
Mechanisms:

#1) Addition of an alcohol functional group (in H_2O)



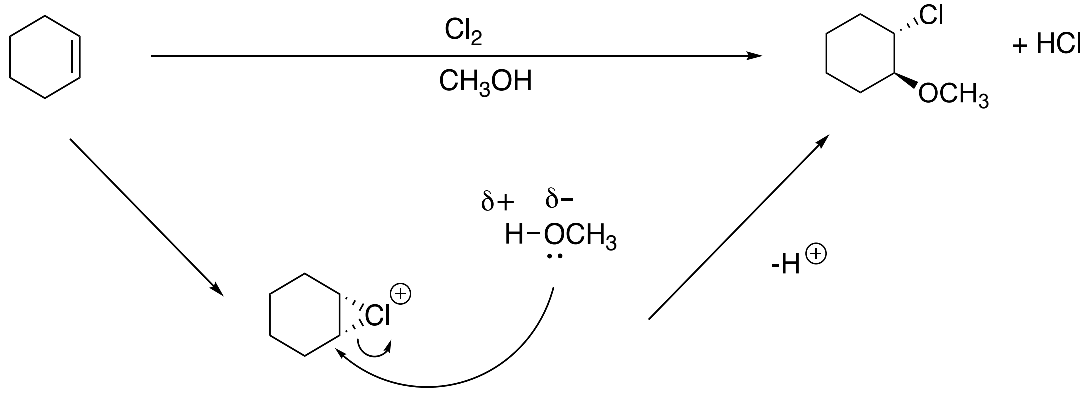
This is the slow step and is the expected product in inert solvents (DCM, Et_2O etc.)

Example: Cyclohexene

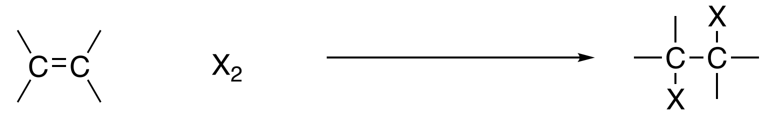


- In the presence of high concentration of H_2O (55.5 M), H_2O competes with the halide (X^-) as a nucleophile and reacts with the bromonium intermediate to form **halohydrin** – 1,2-halo alcohols.
- The same is true when using alcohols (ROH) as solvents instead of water.

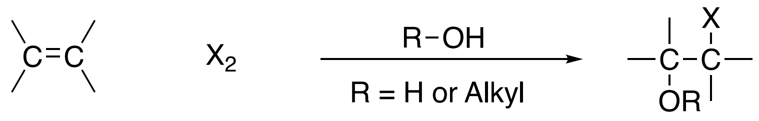
#2) Addition of an ether functional group (in CH_3OH - methanol)



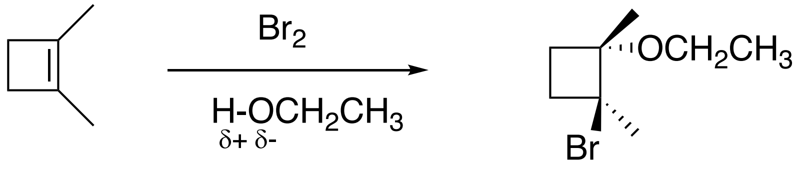
Summary:



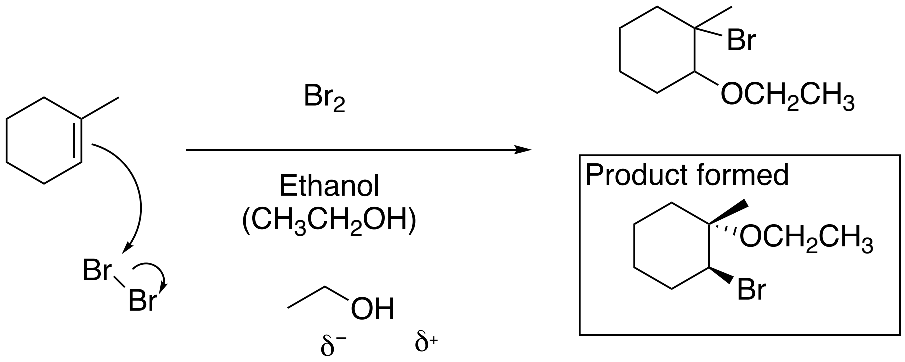
Will add in Markovnikov fashion



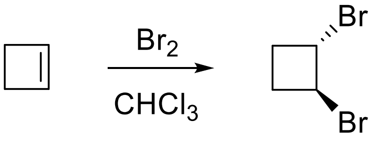
Example: 1,2-dimethylcyclobutene

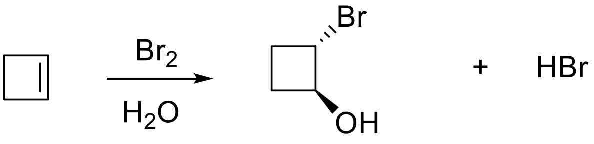


Example: 1-methylcyclohex-1-ene

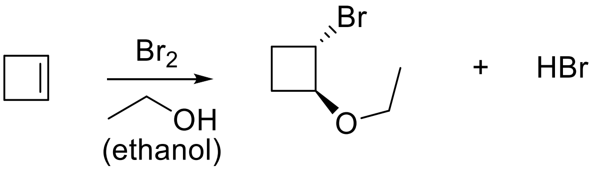


Example: Cyclobutene

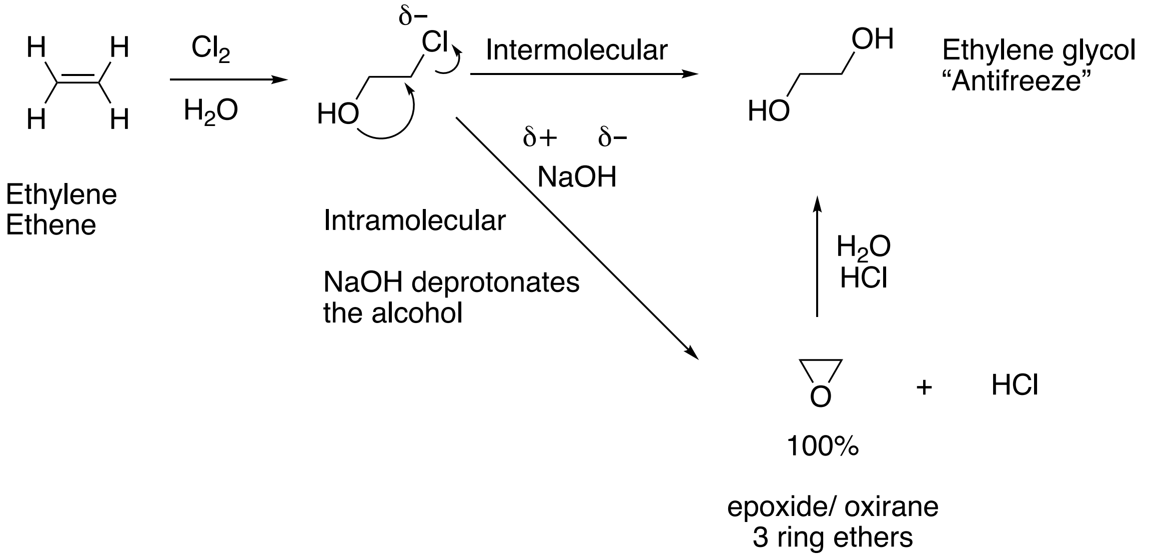




bromohydrin

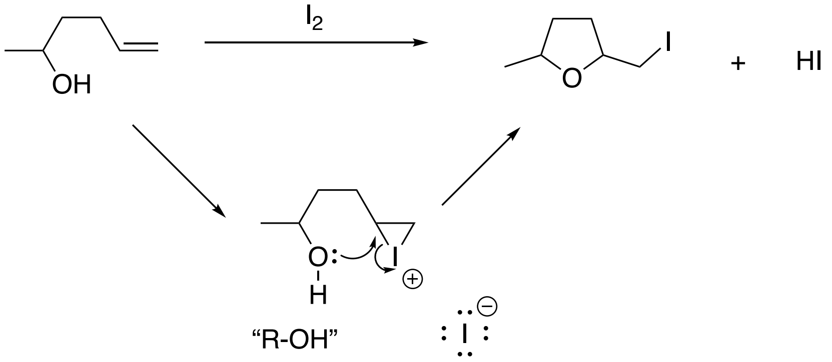


Example: Ethylene (intramolecular)



- NaOH – good nucleophile and can attack a primary alkyl halide (intermolecular)
- NaOH – can act as a base and deprotonate the -OH group. The deprotonated -OH group would then attack the primary alkyl chloride to form an ethylene
- oxide via an Sn2 reaction (**intramolecular reaction** – within one molecule)
- **Intramolecular reaction is faster than intermolecular reactions**
- OH bonds break fairly easily so proton transfer reactions happen at a faster rate

Example 10: Intramolecular

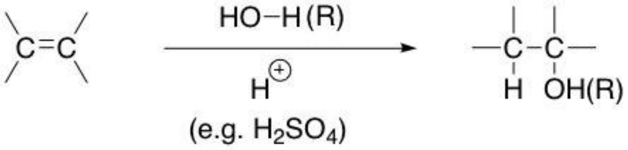


- Although iodine cannot form diiodide (I_2 cannot add to double bonds), it can form the iodinium ion.
- In the above example, the intramolecular reaction (meaning within the same molecule) occurs much much FASTER than the intermolecular reaction (between two or more molecules). This means that the –OH group will attack the iodonium ion much faster than the I^- group because it is an intramolecular reaction.
- Intramolecular reaction almost always beats intermolecular reactions.
- 5-membered rings form much faster than 6-membered rings.

Addition of H_2O and ROH (Hydration and Ether Formation)

HO−H or RO−H

Addition R = Alkyl

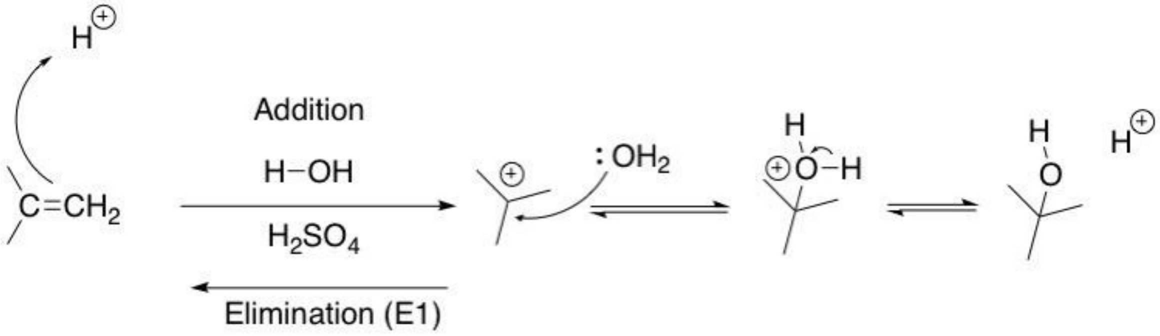


Not Stereospecific

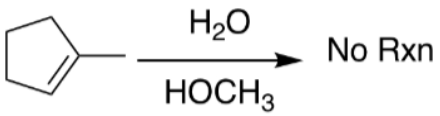
Hydration formation

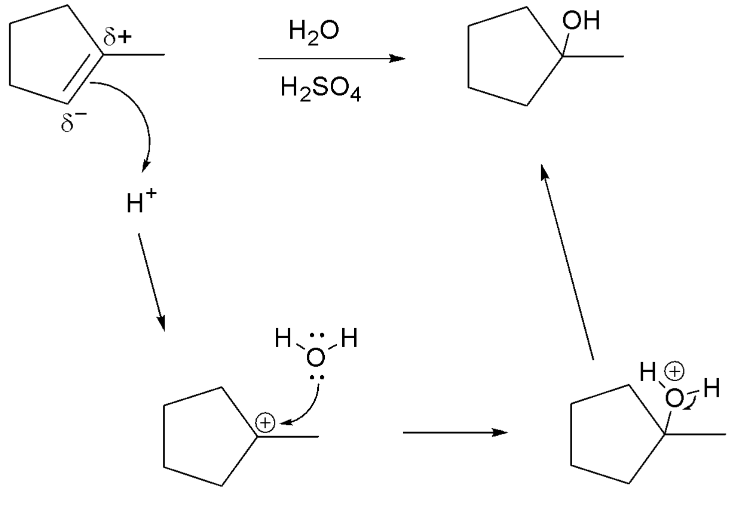
- H_2O or ROH by itself cannot add to the double bond. Need an acid (H^+) to pull the electrons from the double bond.
- H_2SO_4 (H^+) is a catalyst, meaning that it is not transformed or used up in the reaction but is present to lower the activation energy.
- Follows Markovnikov rules

Example 1:



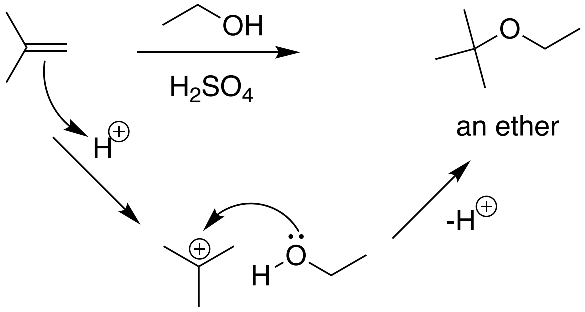
Example 2:



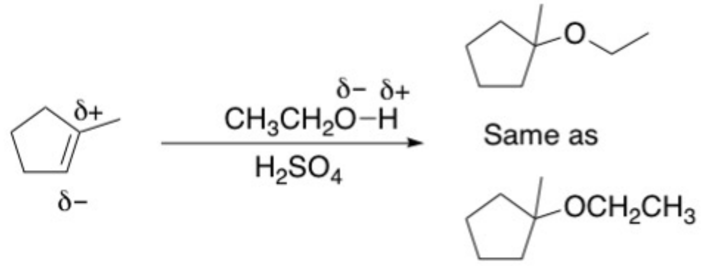


Ether formation

Example 1:



Example 2:



Rxn will not proceed without cat. H_2SO_4