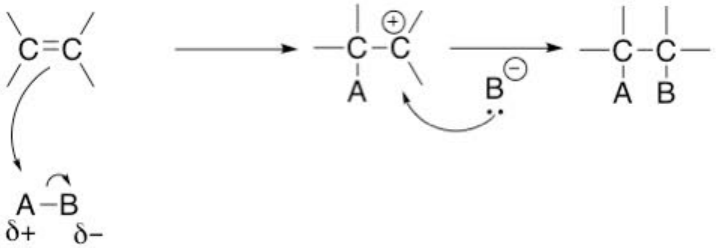
CHEM 261 November 7, 2023

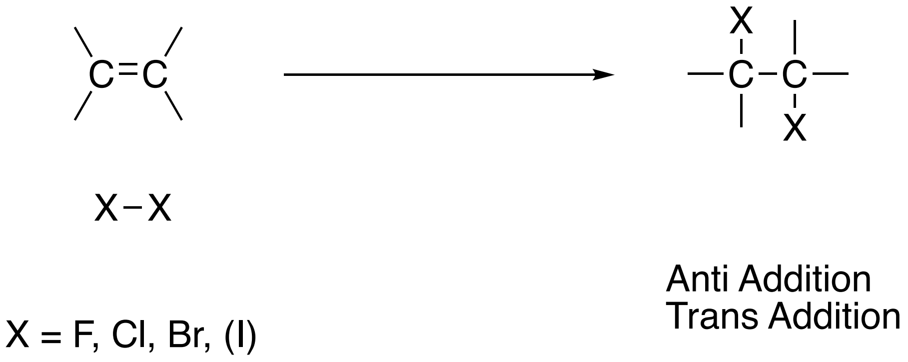
Recall:

Addition Reactions

- Occurs on double bonds and triple bonds

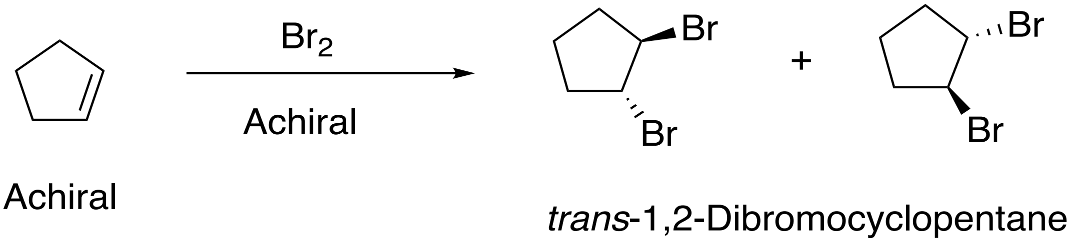


Halogenation: Addition of halogens across a double bond



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

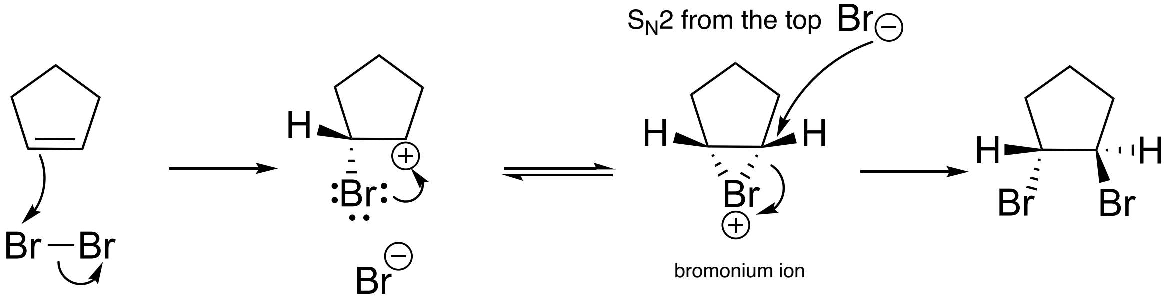
Example 1: Cyclopentene



trans-1,2-Dibromocyclopentane

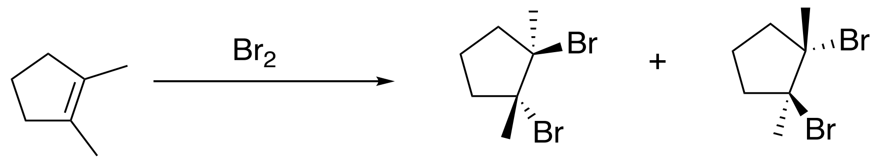
Both enantiomers formed (1:1 racemate)

Mechanism:



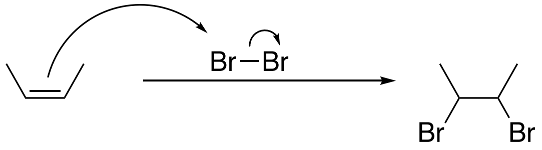
The first step can happen from the top or bottom, and the S_N2 step happens from the opposite side each time.

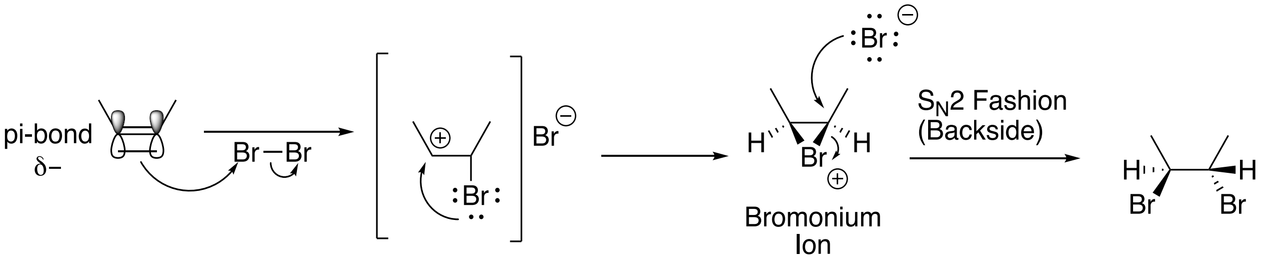
Example 2: 1,2-dimethylcyclopentene



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

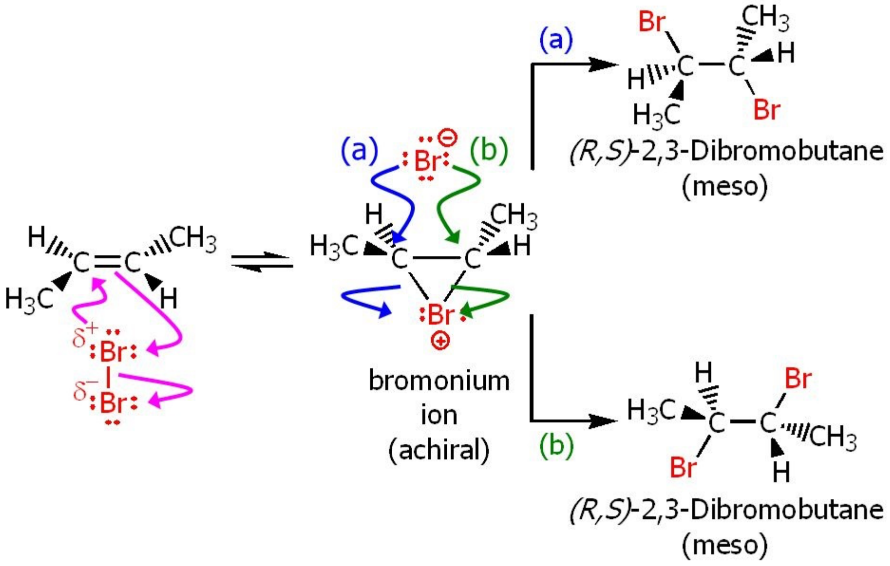
Mechanism:





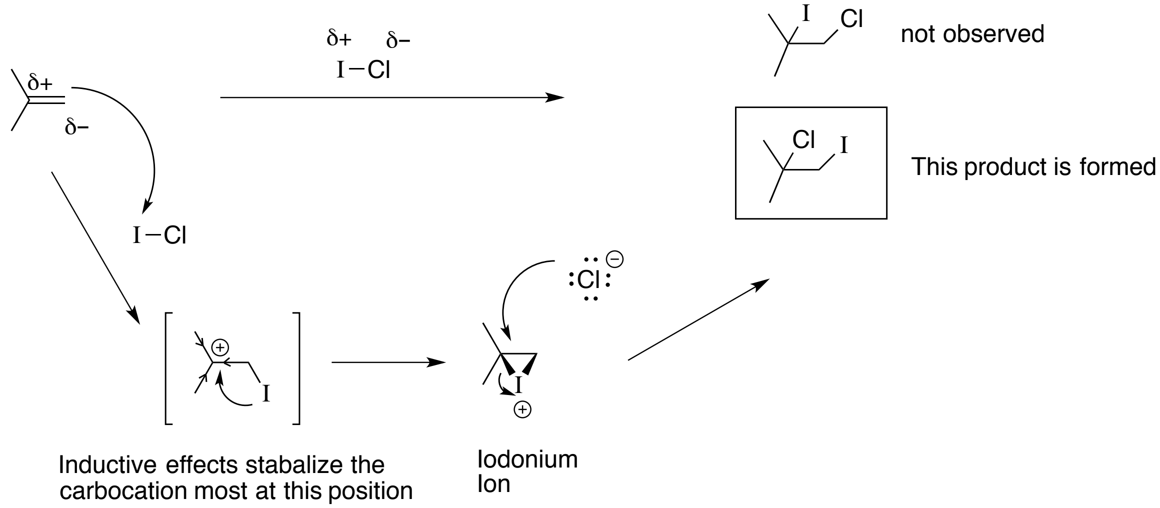
- Halogen addition to alkene is very fast at -78°C
- Attack always comes from the backside – trans product
- When the bromonium ion forms, the bond between the Br and C atom can stretch, giving more carbocation character to the C.

Example 3: *trans*-2-butene



- **Stereospecific Reaction:** Stereochemistry of starting material determines the stereochemistry of product

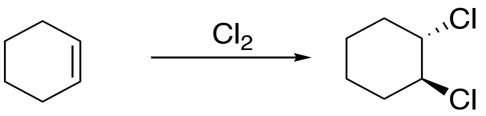
Example 4: 2-Methylpropene

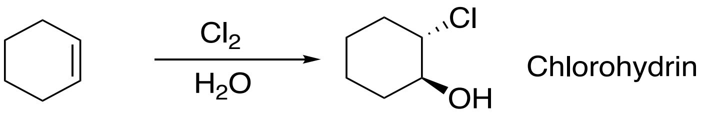


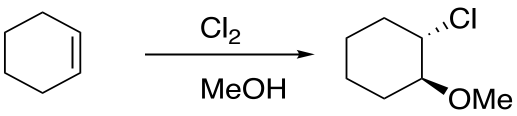
- The electrons in the π-bond attack the partially positive (δ+) I
- Cl^- will attack the more substituted C due to there being a more carbocation character (more substituted end can stabilize the positive charge better due to stabilizing effect of alkyl groups – **inductive effect**)

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 5: Cyclohexene



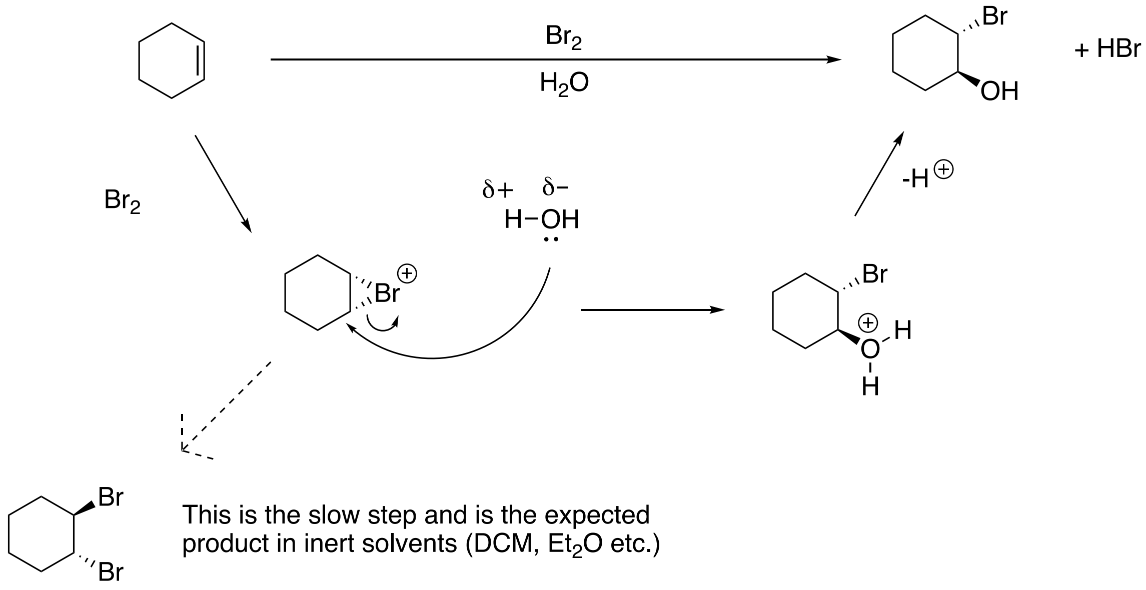




- In the presence of high concentration of H_2O (55.5 M), H_2O competes with the halide (X^-) as a nucleophile and reacts with the bromonium intermediate to form **halohydrin** – 1,2-halo alcohols.
- The same is true when using alcohols (ROH) as solvents instead of water.

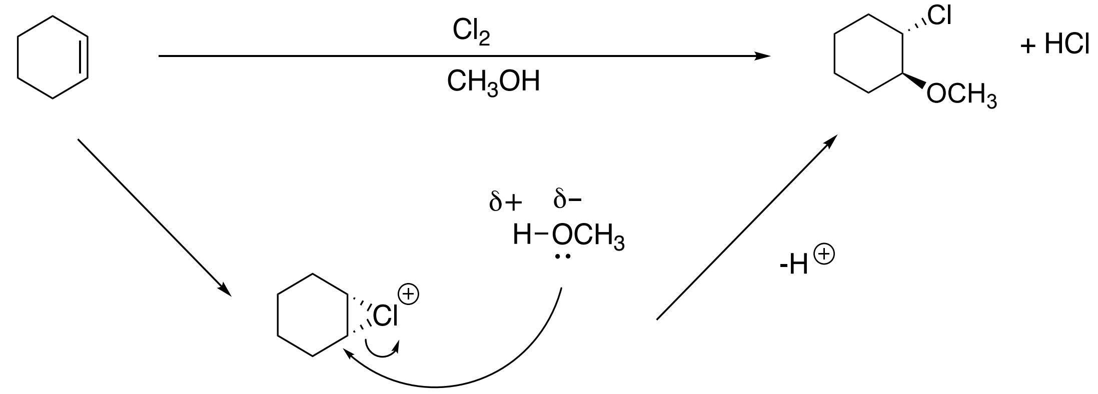
Mechanisms:

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

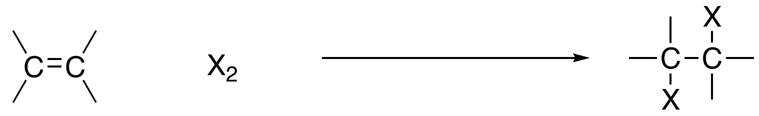


This is the slow step and is the expected product in inert solvents (DCM, Et_2O etc.)

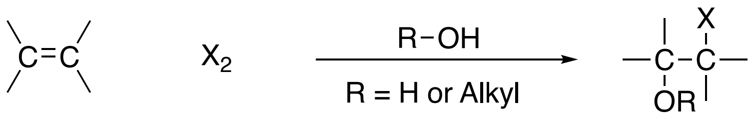
#2) Addition of an ether functional group (in CH_3OH - methanol)



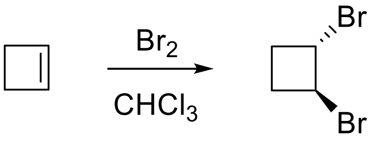
Summary:

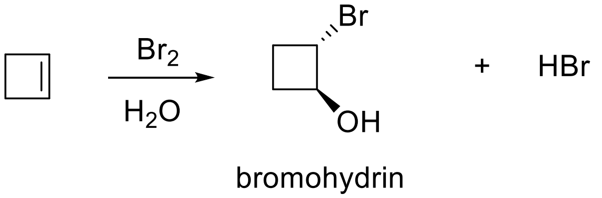


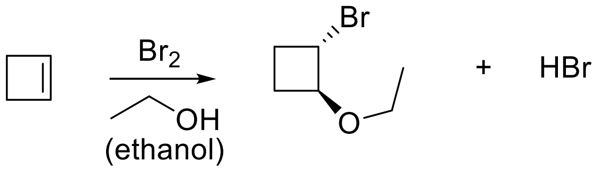
Will add in Markovnikov fashion



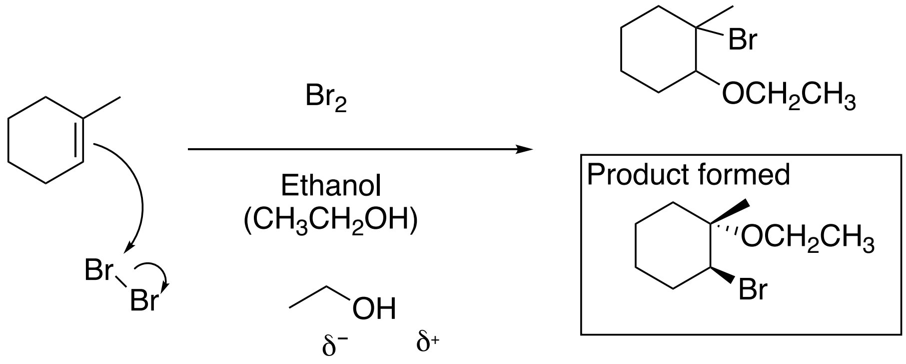
Example 5: Cyclobutene



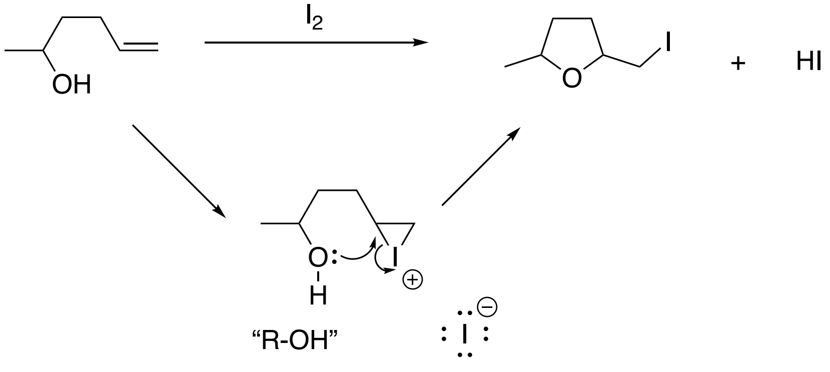




Example 6: 1-methylcyclohex-1-ene

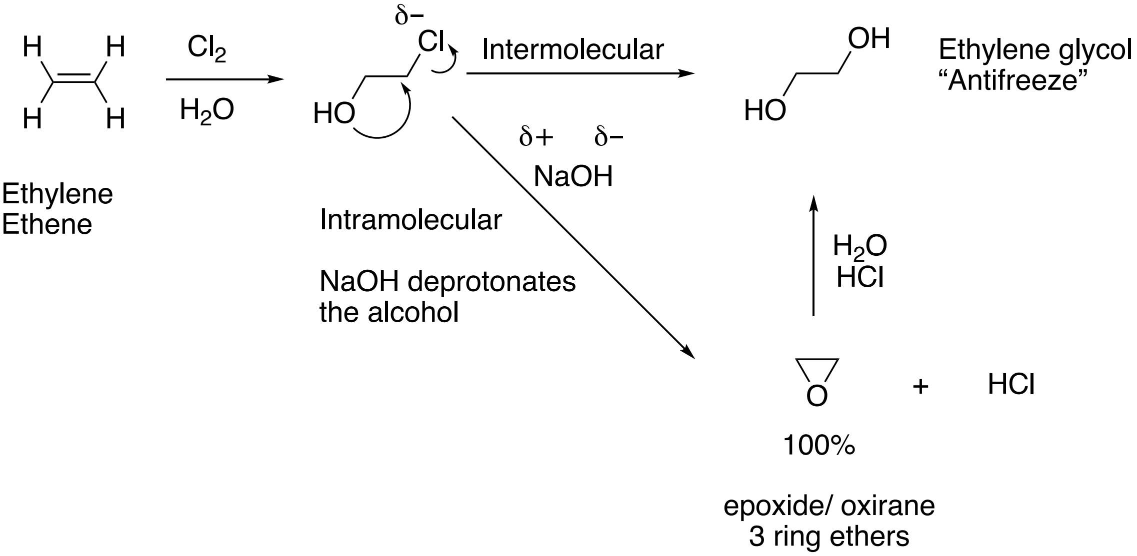


Example 7: Intramolecular



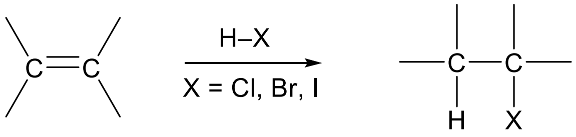
- Although iodine cannot form diiodide (I_2 cannot add to double bonds), it can form the iodinium ion.
- In the above example, the **intramolecular** reaction (meaning within the same molecule) occurs much much **<u>FASTER</u>** than the intermolecular reaction (between two or more molecules). This means 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.

Example 8: Ethylene (intramolecular)



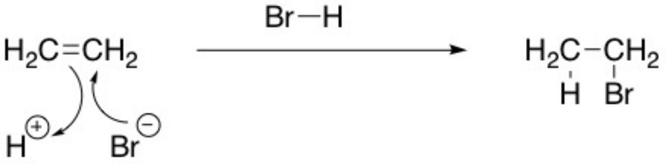
- NaOH – good nucleophile and can attack a primary alkyl halide (intermolecular)
- NaOH – can act as a base and deprotonate the -OH group. The deprotonated -OH group would then attack the primary alkyl chloride to form an ethylene oxide via an Sn2 reaction (**intramolecular reaction** – within one molecule)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

Hydrogen Halide (HX) Addition

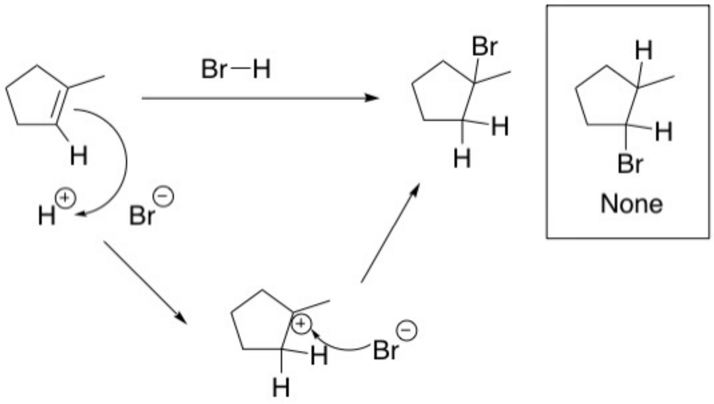


- Reaction generally leads to syn/cis addition

Example 1: Ethylene

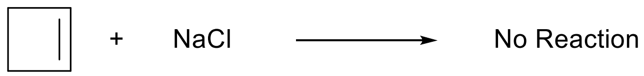


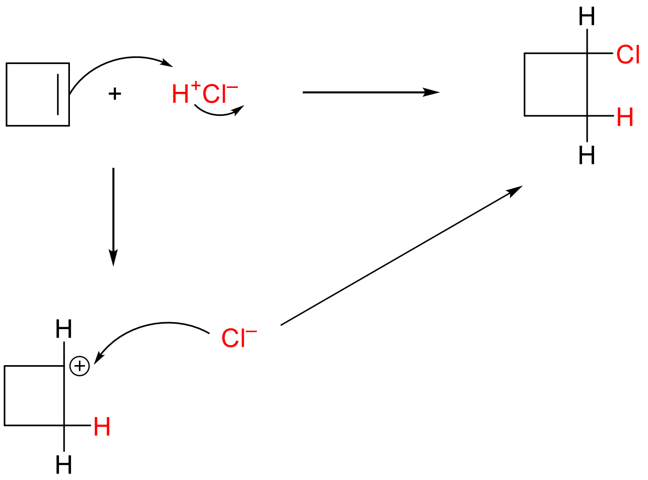
Example 2: 1-Methylcyclopent-1-ene



- Markovnikov addition
- H^+ would add to the less substituted C in the double bond to form the 3° carbocation (more stable due to alkyl stabilization – inductive effect)

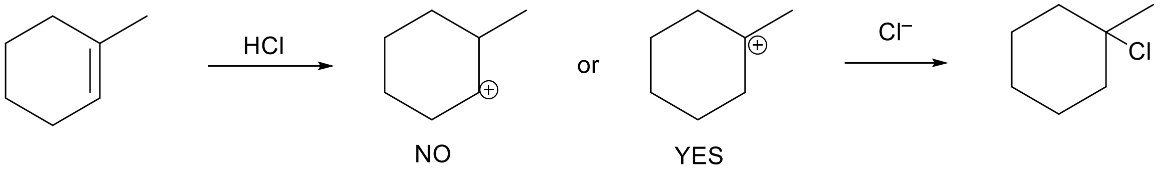
Example 3: Cyclobutene





Note: Need an acid (H^+) to pull out the electrons from the double bond

Example 4: 1-Methylcyclohex-1-ene

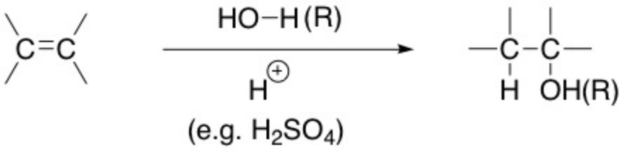


RECALL: Carbocation stability 3° > 2° > 1° > CH_3^+

Addition of H_2O and ROH (Hydration and Ether Formation)

HO−H or RO−H

Addition R = Alkyl

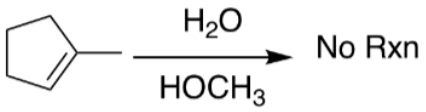


Not Stereospecific

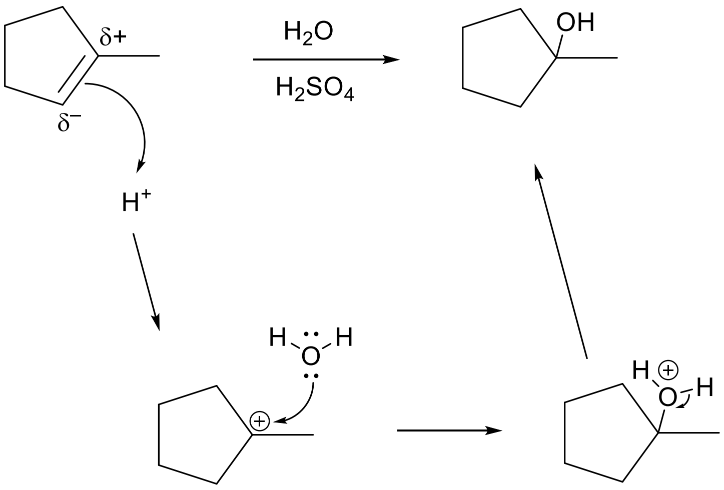
Hydration formation

- 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.

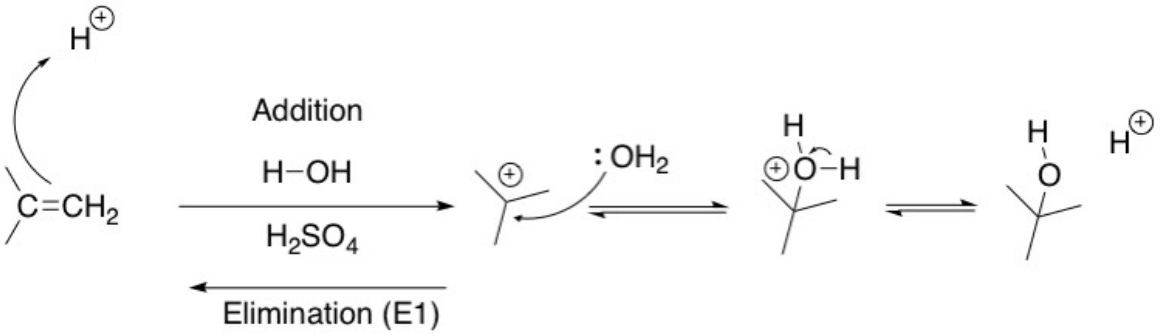
Example 1:



No reaction if no strong acid present

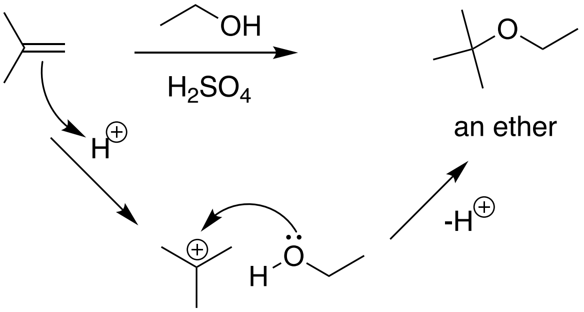


Example 2:

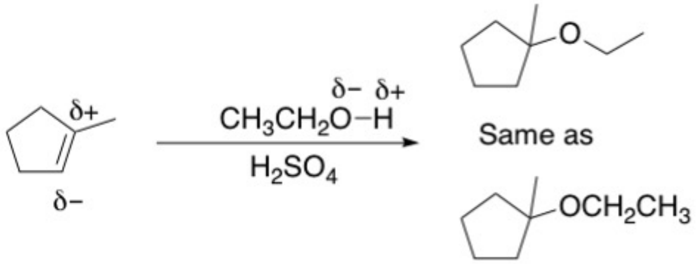


Ether formation

Example 1:

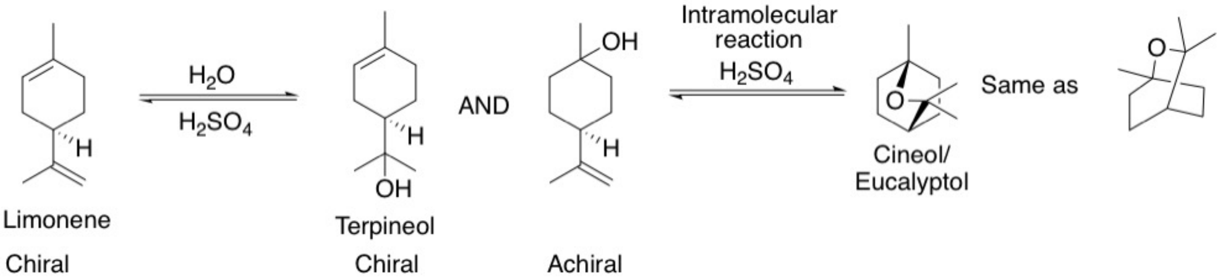


Example 2:

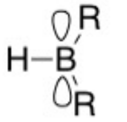


Rxn will not proceed without cat. H_2SO_4

Example 3:



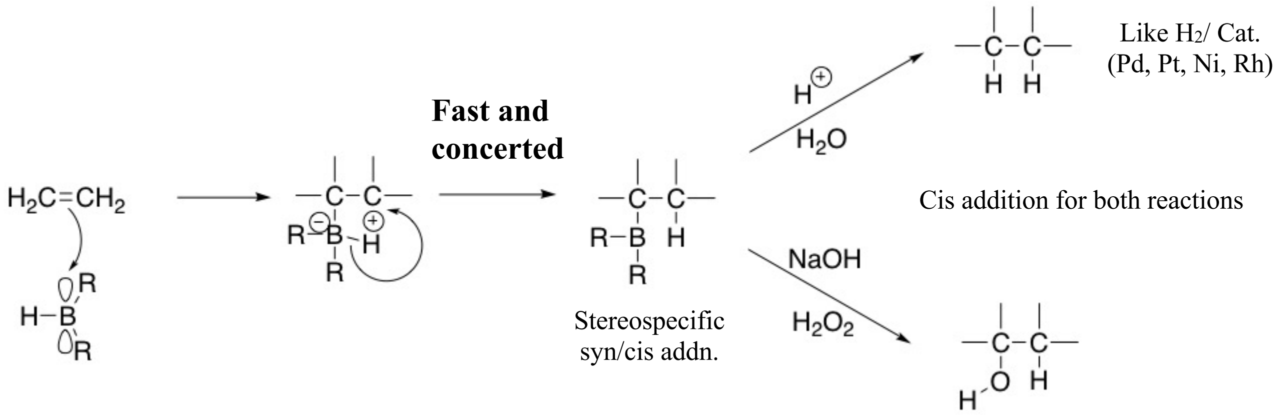
Hydroboration



R = H Borane

Lewis acid
Empty orbitals allow it to accept a pair of e⁻

- B when stable and uncharged has 3 bonds and no lone pairs
- Borane forms partial bonds with another borane molecule to form B_2H_6 (diborane)
- Borane is a hydride (H^-) donor



Fast and concerted

Stereospecific syn/cis addn.

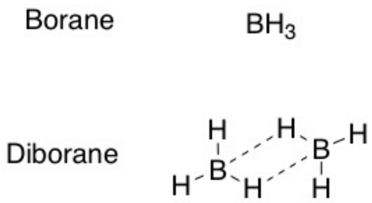
Like H_2/ Cat. (Pd, Pt, Ni, Rh)

Cis addition for both reactions

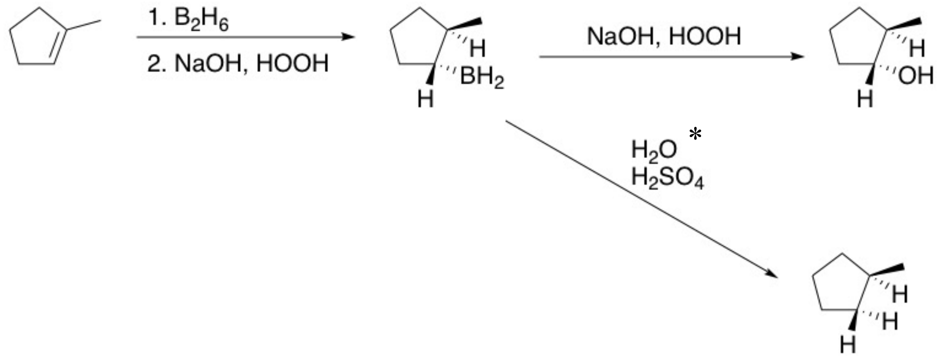
Concerted reaction: bond breaking and bond formation happens in a single step
Anti-Markovnikov: the hydrogen ends up on the more substituted C in a double bond. It is SYN.

Structure of borane

Exists as Diborane (B_2H_6), but behaves like BH_3



Example



Syn addition, but anti-Markovnikov addition of OH

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