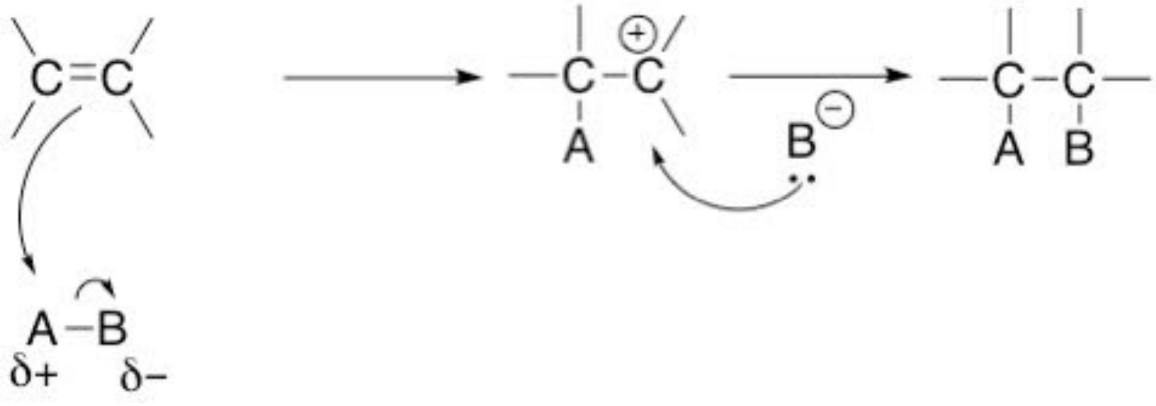
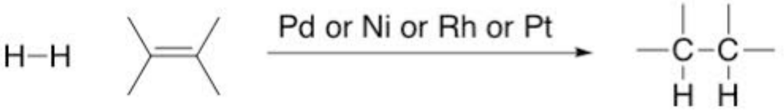
Recall:

Addition Reactions

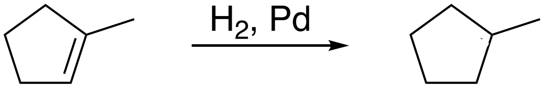
- Occurs on double bonds and triple bonds

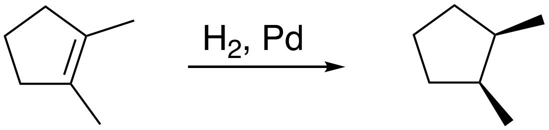


Example: Hydrogenation



- cis or syn addn
- stereospecific





Meso compound

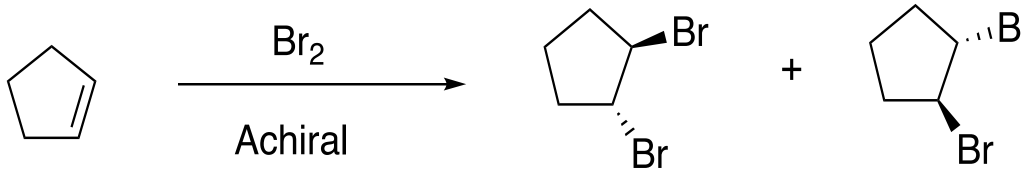
Halogenation: Addition of halogens across a double bond

X = F, Cl, Br, (I)

Anti Addition
Trans Addition

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

Ex #1) Cyclopentene

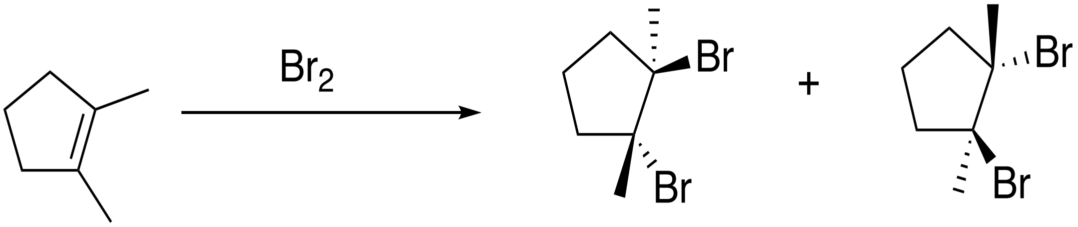


Achiral

trans-1,2-Dibromocyclopentane

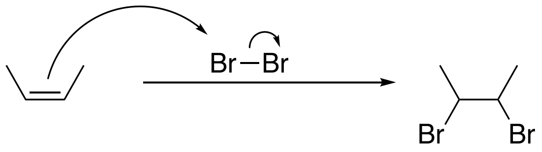
Both enantiomers formed (1:1 racemate)

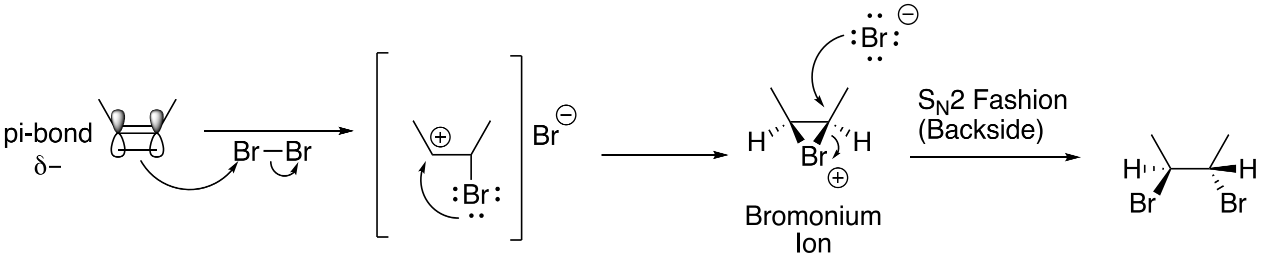
Ex #2) 1,2-dimethylcyclopentene



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

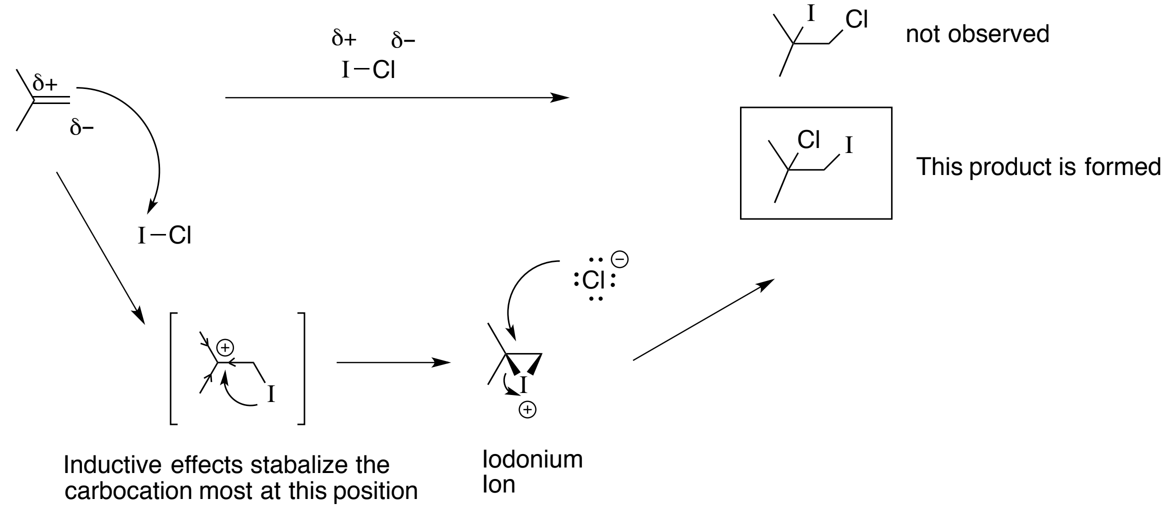
Mechanism:





- 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.

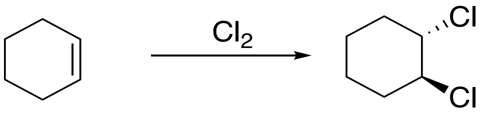
Ex #3) 2-Methylpropene

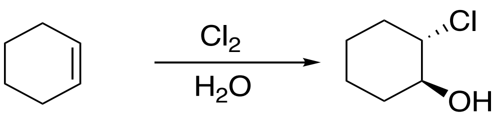


- The electrons in the π-bond attack the partially positive (δ+) I
- Cl^- will attack the more substituted C due to there being a more carbocation character (more substituted end can stabilize the positive charge better due to stabilizing effect of alkyl groups – **inductive effect**)

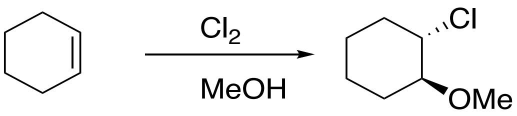
Markovnikov's Rule: In an addition reaction, the positive end of an A–B system (e.g. I–Cl) adds to the least substituted end of the double bond to make the more stable carbocation.

Ex #4) Cyclohexene





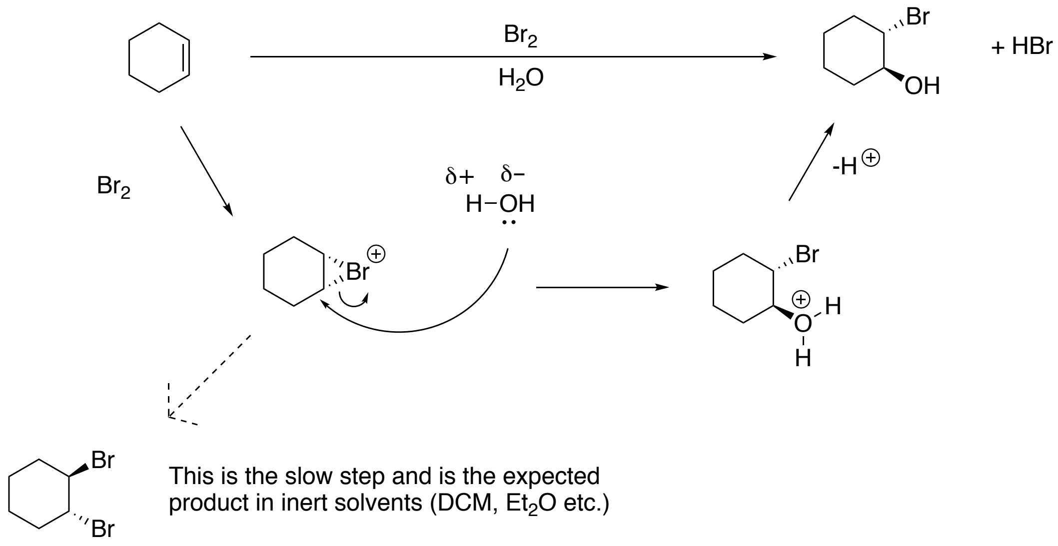
Chlorohydrin



- 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.

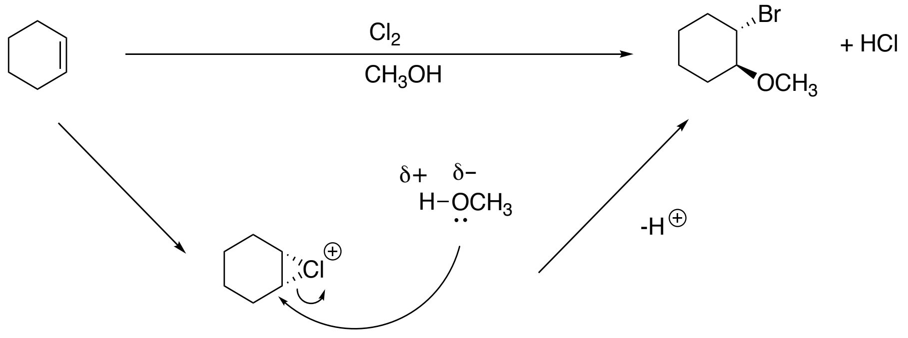
Mechanisms:

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

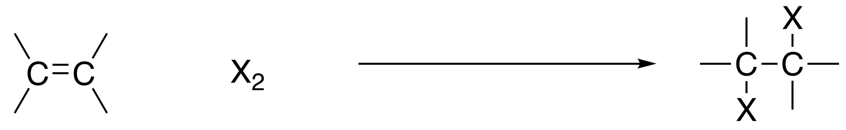


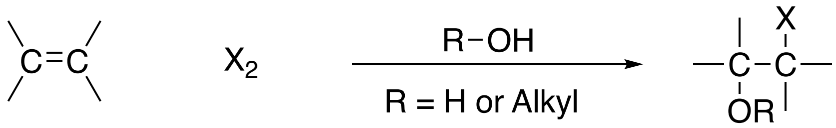
This is the slow step and is the expected product in inert solvents (DCM, Et_2O etc.)

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



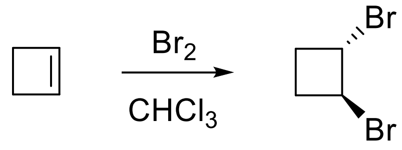
Summary:

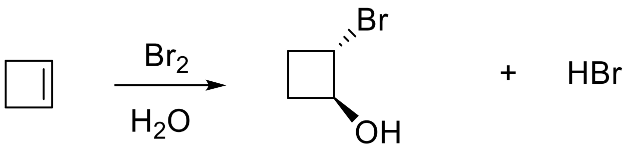




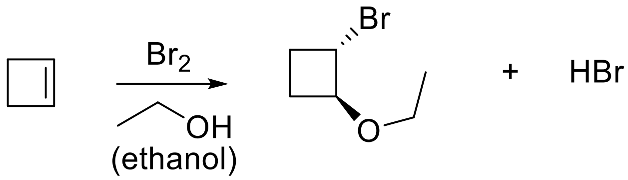
Will add in Markovnikov fashion

Ex #5) Cyclobutene

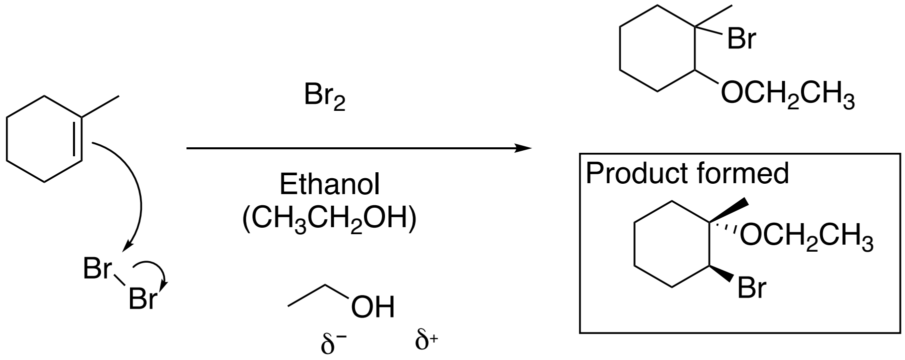




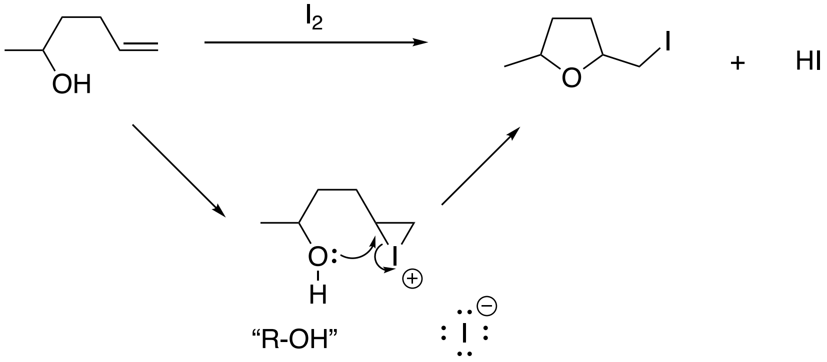
bromohydrin



Example #6) 1-methylcyclohex-1-ene

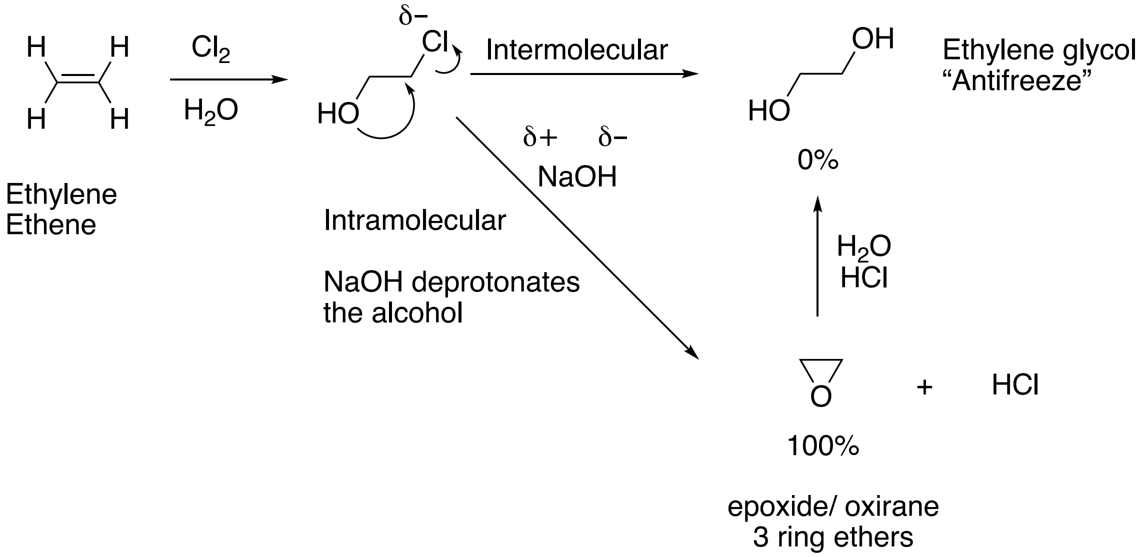


Ex #6)



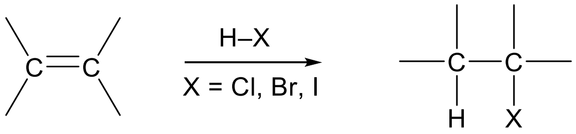
- Although iodine cannot form diiodide (cannot add to double bonds), it can form the iodinium ion.
- In the above example, the intramolecular reaction (meaning within the same molecule) occurs much much FASTER than the intermolecular reaction (between two or more molecules). This means that the –OH group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

Ex #7) Ethylene



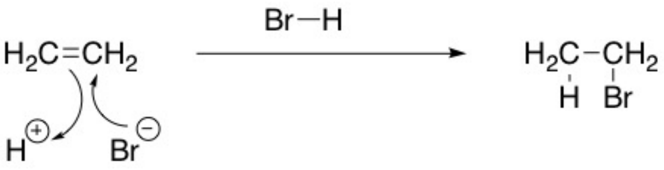
- NaOH – good nucleophile and can attack a primary alkyl halide (intermolecular)
- NaOH – can act as a base and deprotonate the -OH group. The deprotonated -OH group would then attack the primary alkyl chloride to form an ethylene oxide via an Sn2 reaction (**intramolecular reaction** – within one molecule)
- 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

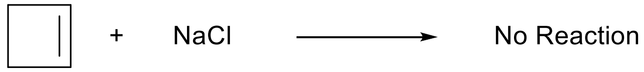


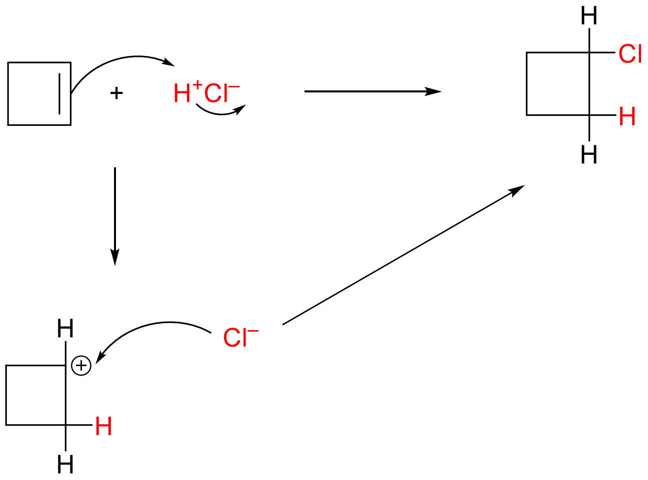
  - Reaction generally leads to syn/cis addition

Example 1: Ethylene



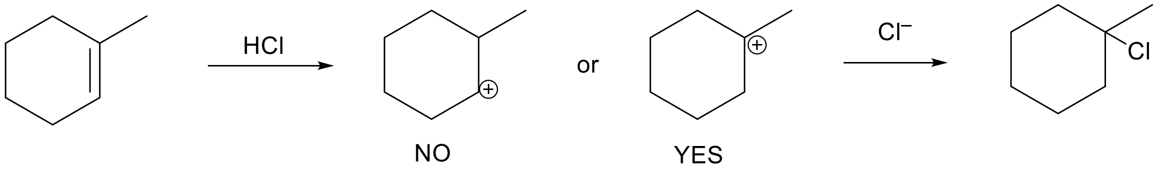
Example 2: Cyclobutene





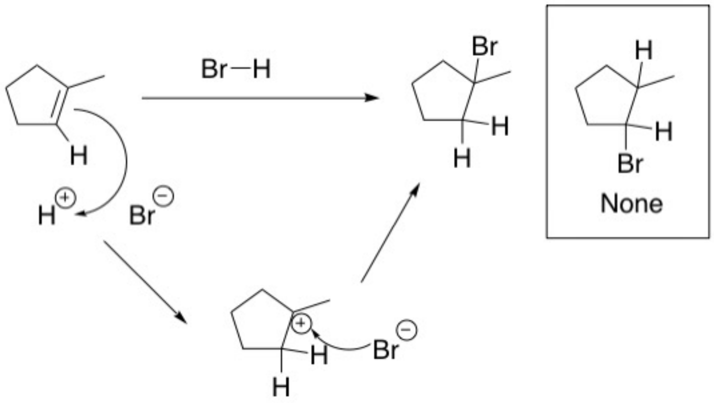
Note: Need an acid (H^+) to pull out the electrons from the double bond

Example 3: 1-Methylcyclohex-1-ene



<u>**RECALL:**</u> Carbocation stability 3° > 2° > 1° > CH_3^+

Example 4: 1-Methylcyclopent-1-ene



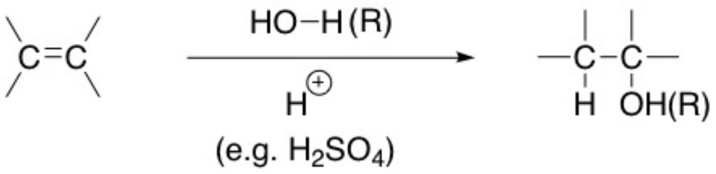
- Markovnikov addition

- 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)

Addition of H_2O and ROH (Hydration and Ether Formation)

HO–H or RO–H

Addition R = Alkyl

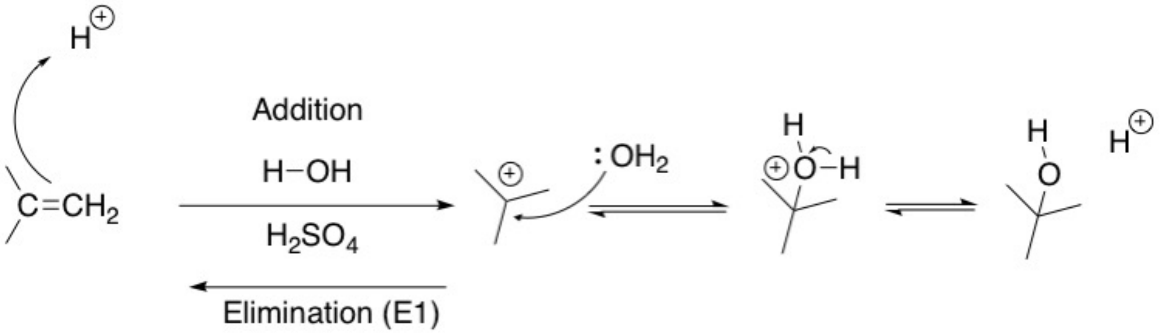


Not Stereospecific

Examples

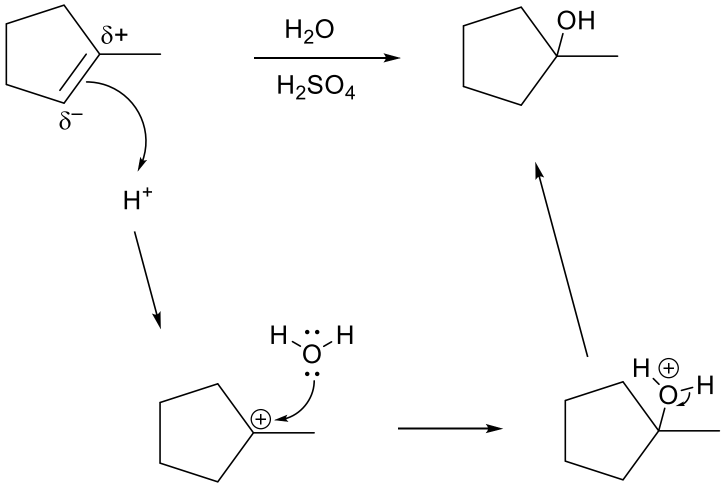
Hydration formation

Ex #1)



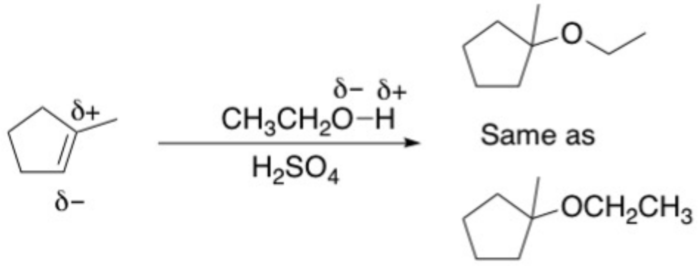
- H_2O or ROH by itself cannot add to the double bond. Need an acid (H^+) to pull the electrons from the double bond.
- H_2SO_4 (H^+) is a catalyst, meaning that it is not transformed or used up in the reaction but is present to lower the activation energy.

Ex #2)



Ether formation

Ex #1)



Rxn will not proceed without cat. H_2SO_4

Ex #2)