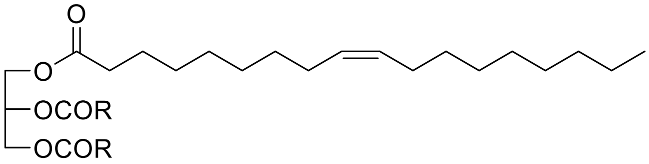
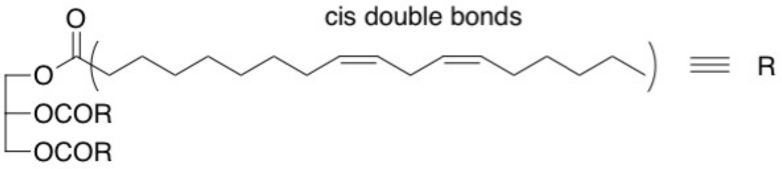
Example 3: Fats

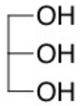
Fat



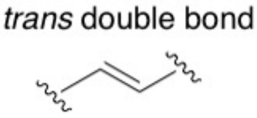
Monounsaturated triglyceride



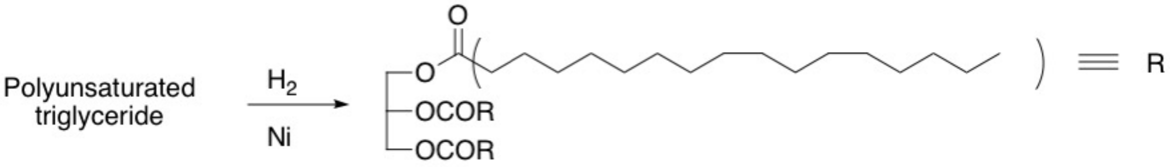
A triglyceride



Glycerol

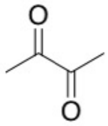


- The triglyceride is a **triester of glycerol**
- It is a polyunsaturated (>1 double bond) fats (e.g. canola oil)- unsaturation refers to the double bonds.
- Trans double bonds can also be generated in fats, which are then called trans fats.
- Hydrogenation give saturated fats (**unsaturation removed**)



Major component of margerine

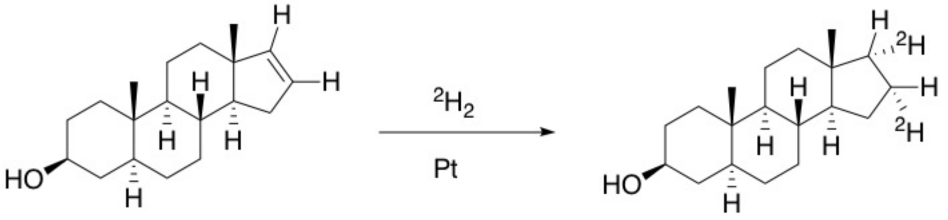
A solid saturated fat (margarine)
This molecule has greater London dispersion forces, cause it to exist as a solid



Diacetyl

Butter flavoring that adds a yellow color

Example 4: Steroid



Androstenol
(Pheromone)

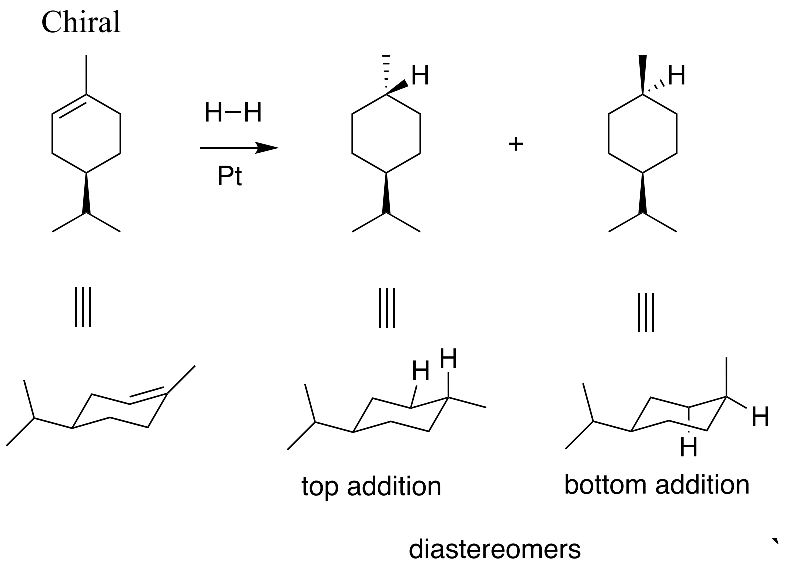
not a pheromone

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

^2H = D = deuterium

Example 5: Limonene

Limonene

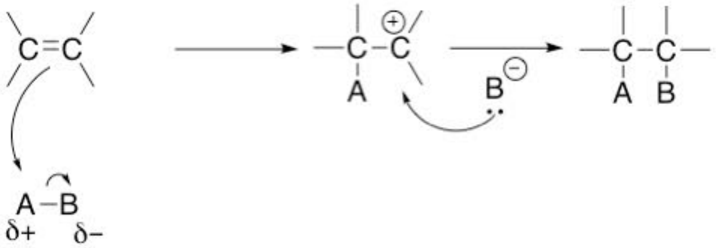


The two possible products are diastereomers and are achiral (plane of symmetry).

Recall:

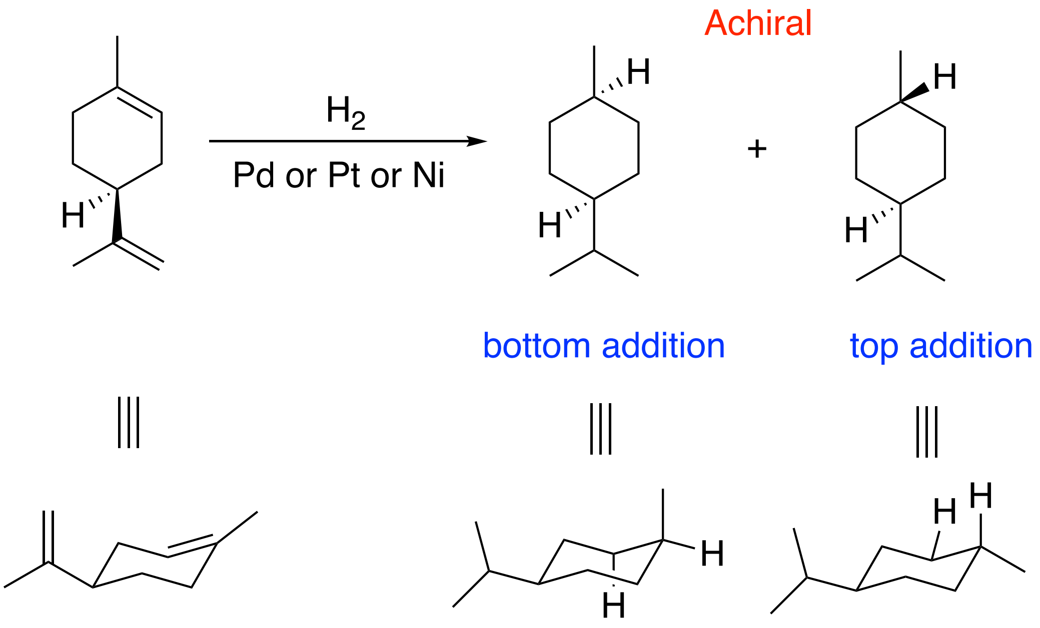
Addition Reactions

- Occurs on double bonds and triple bonds



Hydrogenation:

More example: Limonene



Diastereomers

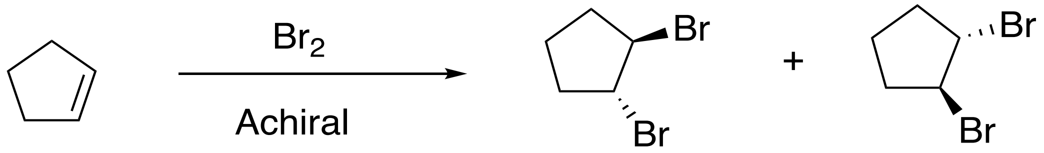
Halogenation: Addition of halogens across a double bond

X = F, Cl, Br, (I)

Anti Addition
Trans Addition

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

Example 1: Cyclopentene

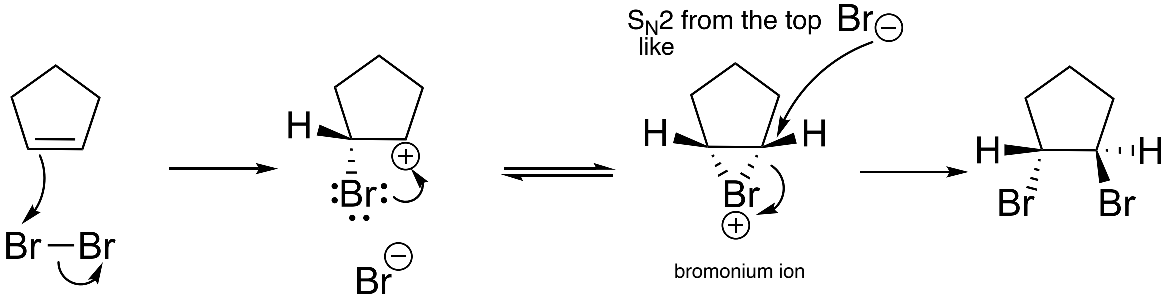


Achiral

trans-1,2-Dibromocyclopentane

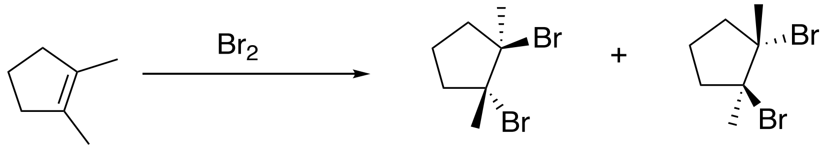
Both enantiomers formed (1:1 racemate)

Mechanism:



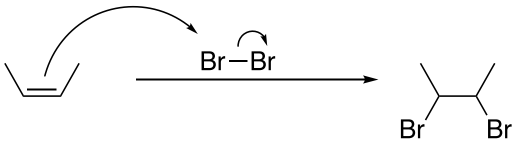
The first step can happen from the top or bottom, and the S_N2 step happens from the opposite side each time.

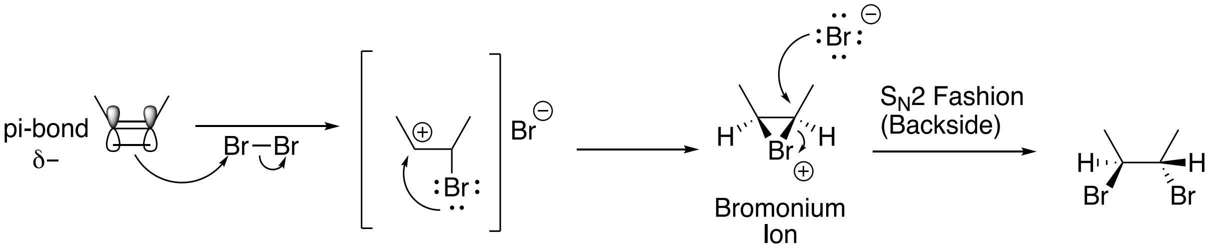
Example 2: 1,2-dimethylcyclopentene



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

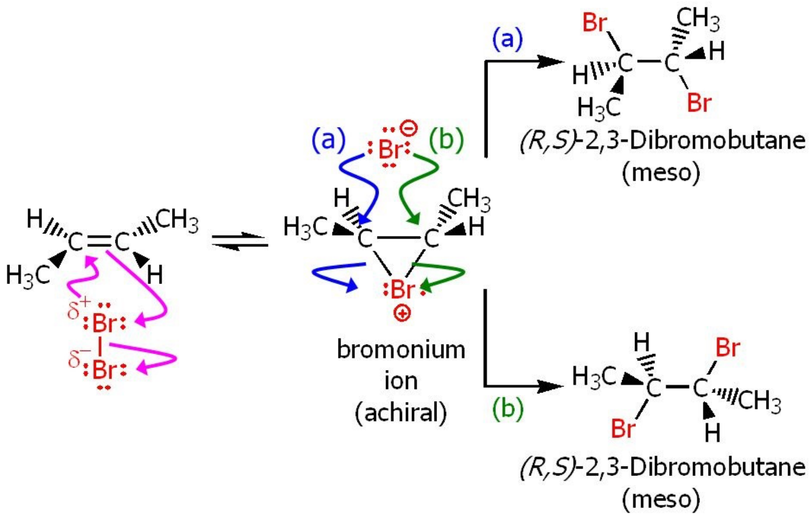
Mechanism:





- 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.

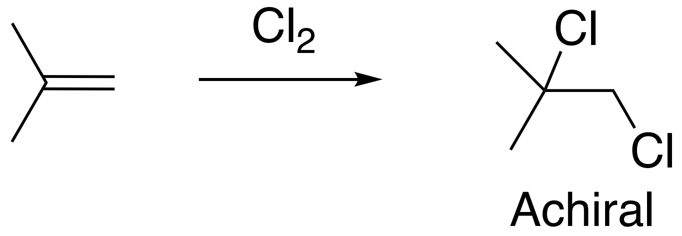
Example 3: *trans*-2-butene



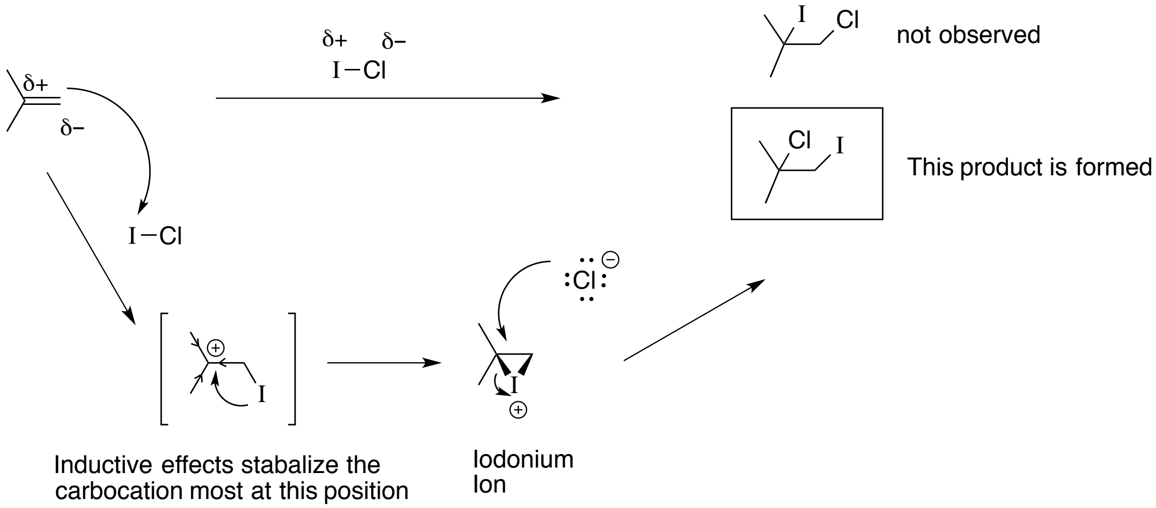
- Stereochemistry of starting material determines the stereochemistry of product - identical in this case

-

Example 4A: 2-Methylpropene



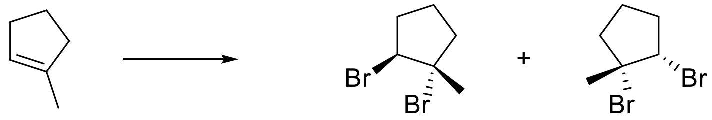
Example 4B: 2-Methylpropene



- 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 4C:** 1-methylcyclopentene



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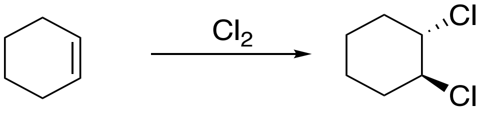
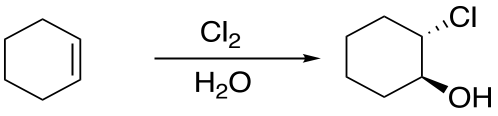
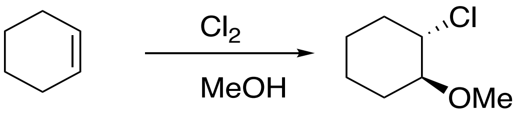
Example 5: Cyclohexene





Chlorohydrin
(Halohydrin)

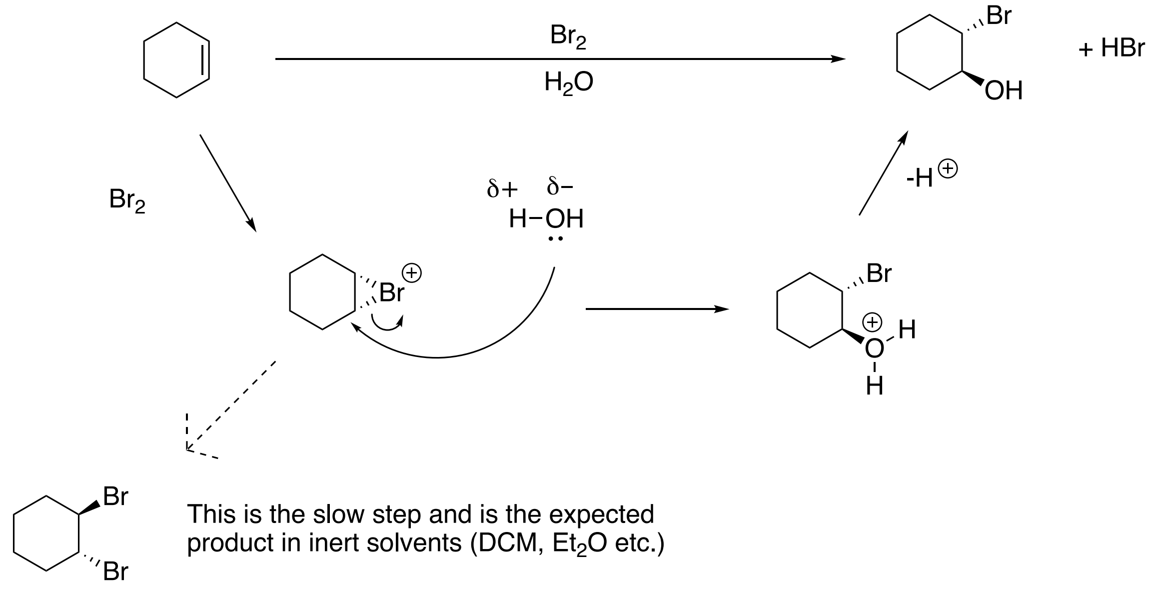


- In the presence of high concentration of H_2O (55.5 M), H_2O competes with the halide (X^-) as a nucleophile and reacts with the bromonium intermediate to form **halohydrin** – 1,2-halo alcohols.
- The same is true when using alcohols (ROH) as solvents instead of water.

Mechanisms:

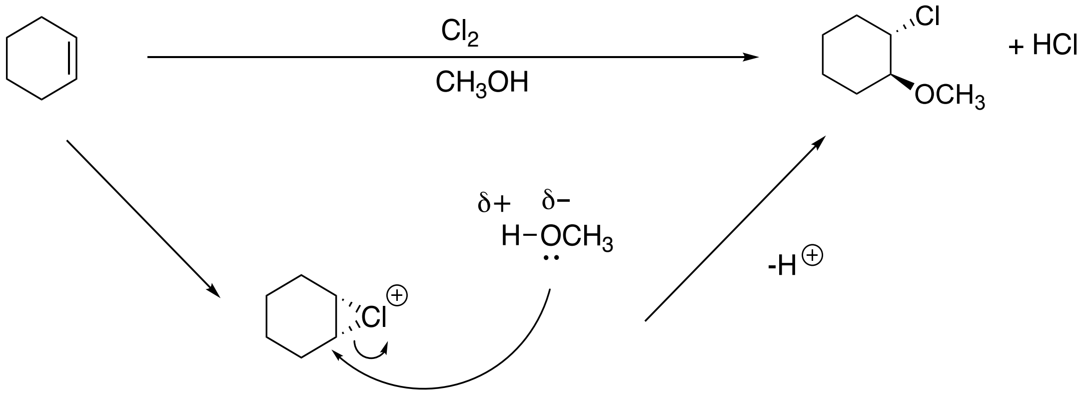
#1) Addition of an alcohol functional group (in H_2O)

Bromohydrin

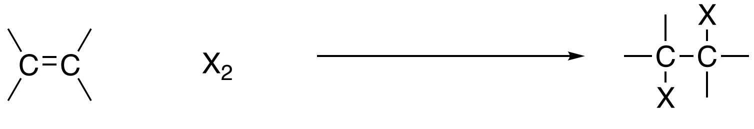


This is the slow step and is the expected product in inert solvents (DCM, Et_2O etc.)

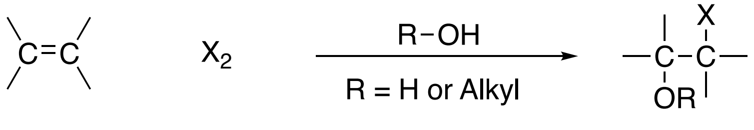
#2) Addition of an ether functional group (in CH_3OH - methanol)



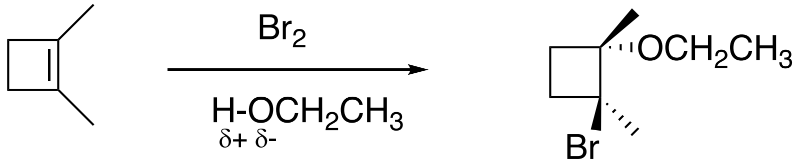
Summary:



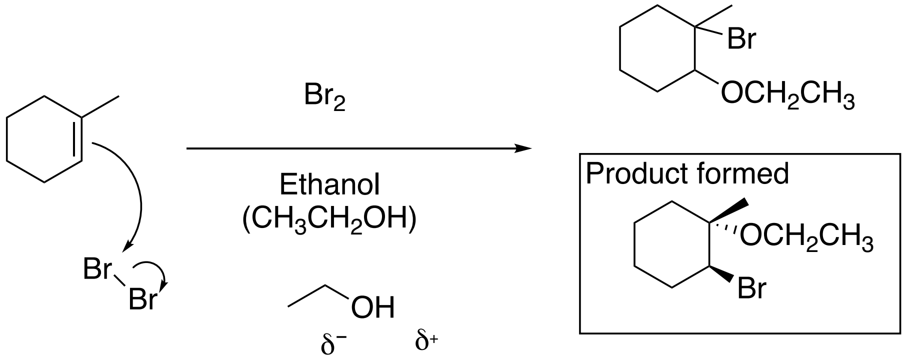
Will add in Markovnikov fashion



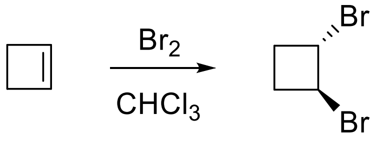
Example 6: 1,2-dimethylcyclobutene

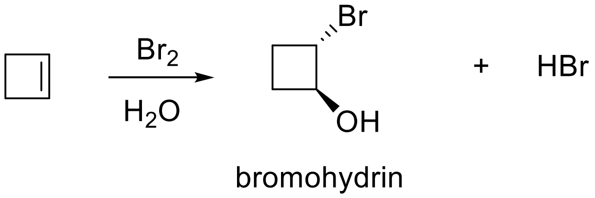


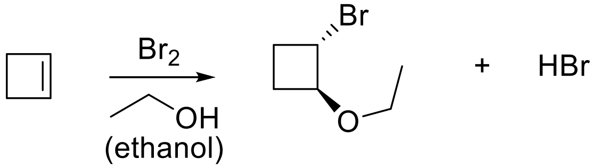
Example 7: 1-methylcyclohex-1-ene



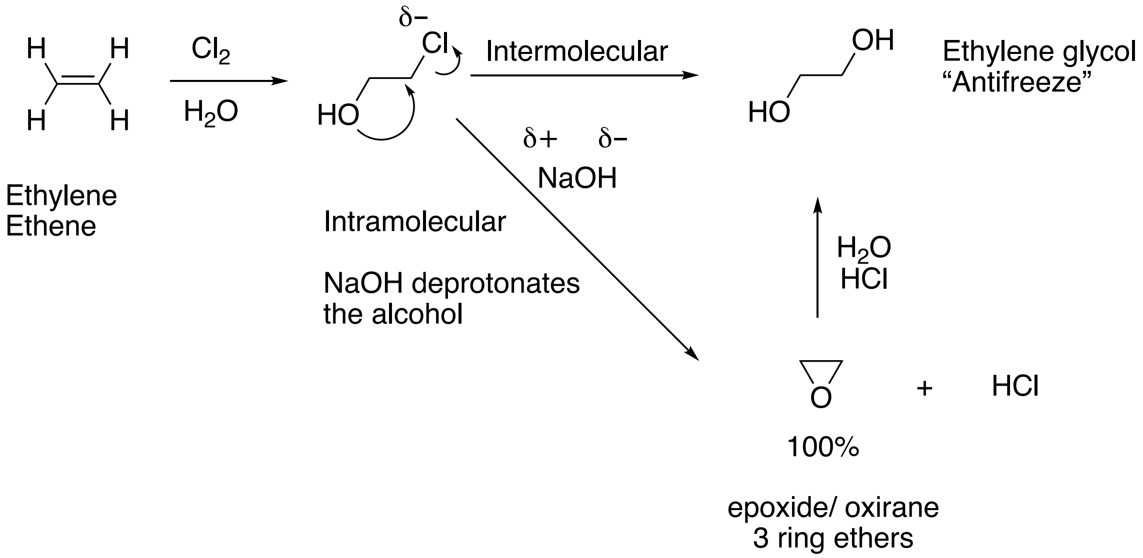
Example 8: Cyclobutene





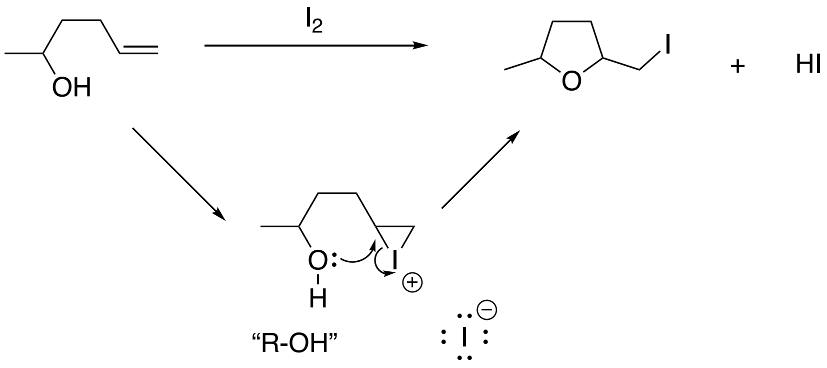


Example 9: Ethylene (intramolecular)



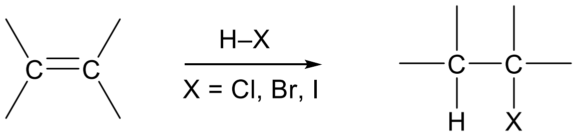
- NaOH – good nucleophile and can attack a primary alkyl halide (intermolecular)
- NaOH – can act as a base and deprotonate the -OH group. The deprotonated -OH group would then attack the primary alkyl chloride to form an ethylene
- oxide via an Sn2 reaction (**intramolecular reaction** – within one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



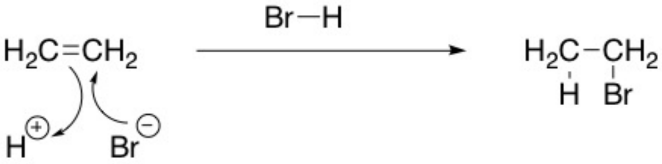
- Although iodine cannot form diiodide (I_2 cannot add to double bonds), it can form the iodinium ion.
- In the above example, the intramolecular reaction (meaning within the same molecule) occurs much much FASTER than the intermolecular reaction (between two or more molecules). This means that the –OH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

Hydrogen Halide (HX) Addition

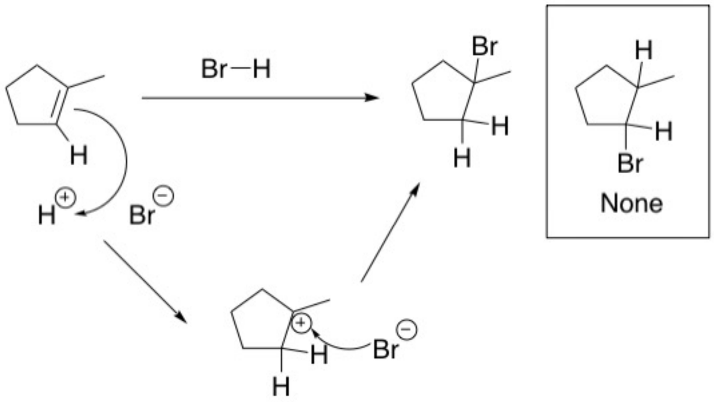


- Reaction generally leads to syn/cis addition

Example 1: Ethylene

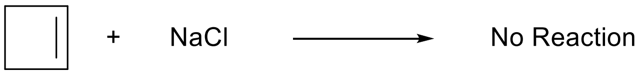


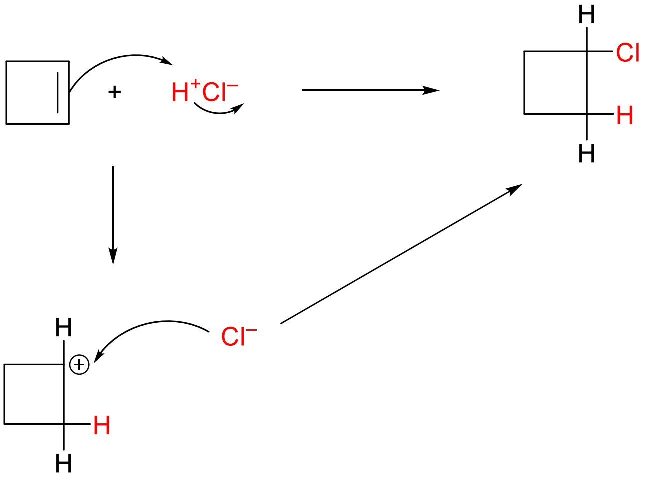
Example 2: 1-Methylcyclopent-1-ene



- 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)

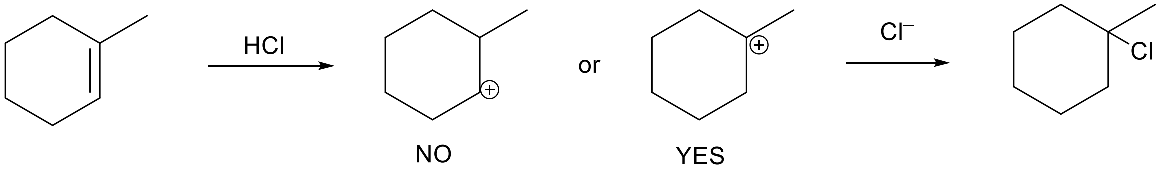
Example 3: Cyclobutene





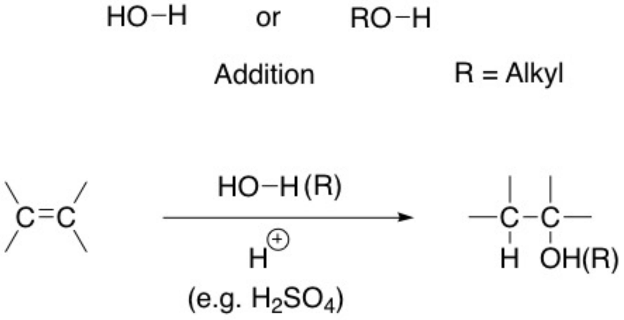
Note: Need an acid (H^+) to pull out the electrons from the double bond

Example 4: 1-Methylcyclohex-1-ene



<u>RECALL:</u> Carbocation stability $3^\circ > 2^\circ > 1^\circ > CH_3^+$

Addition of H_2O and ROH (Hydration and Ether Formation)

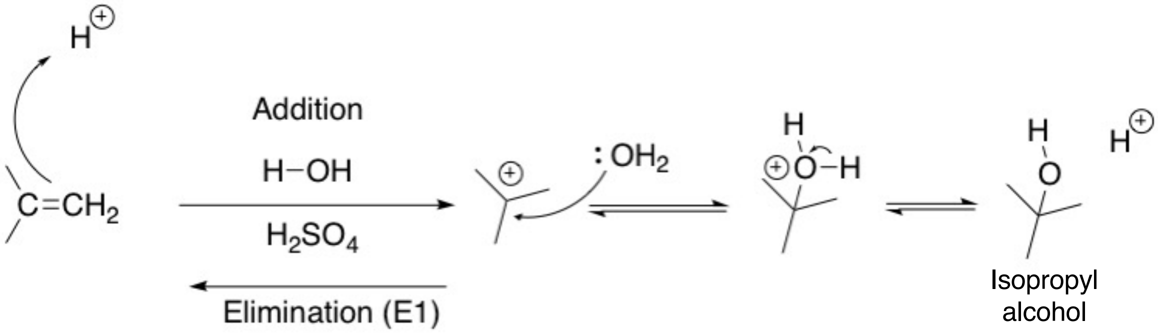


Not Stereospecific

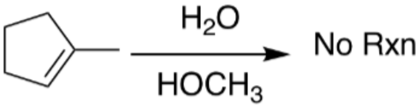
Hydration formation

- 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

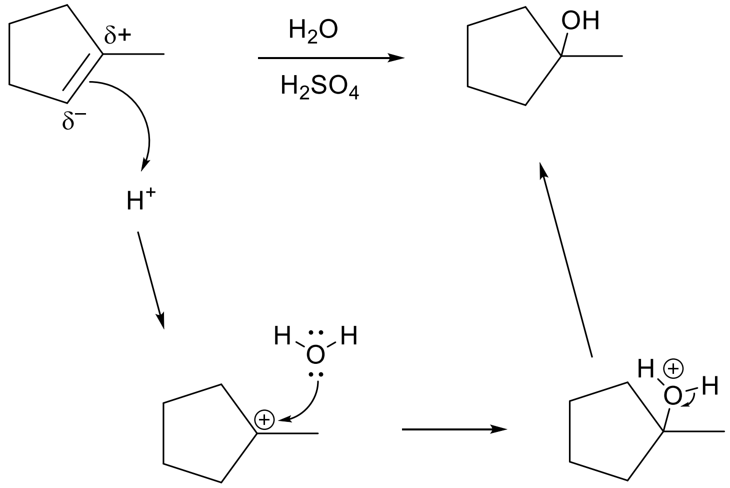
Example 1:



Example 2:



Need Acid to break into double bond



Example 3