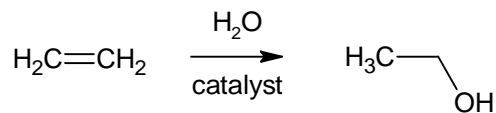
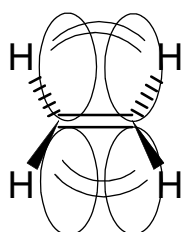


Addition to Carbon-Carbon Pi Bonds

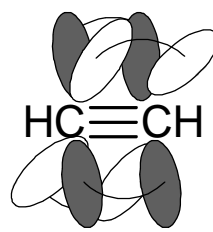


- Need a catalyst
- This is one way ethanol is manufactured
- How does this reaction proceed?

❖ Pi Bonds

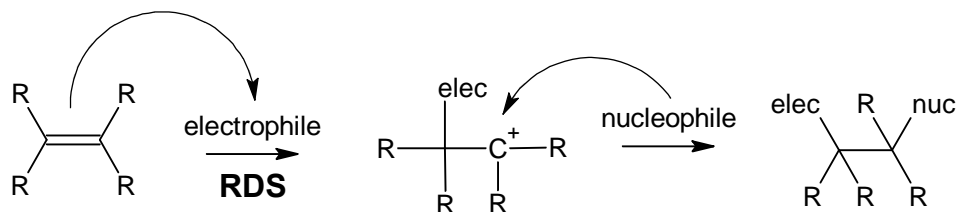


Alkene
Two electron clouds



Alkyne
Many mechanisms that apply to alkenes also apply to alkynes.

❖ Generic Addition Mechanism

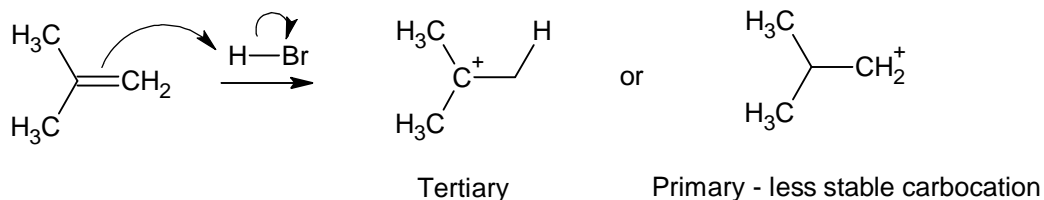


Carbocation Intermediate:

Which fate?

- ⊖ Rearrangement – nothing better than tertiary
- ⊖ Lose proton – no protons to lose
- ☺ **Capture nucleophile!**

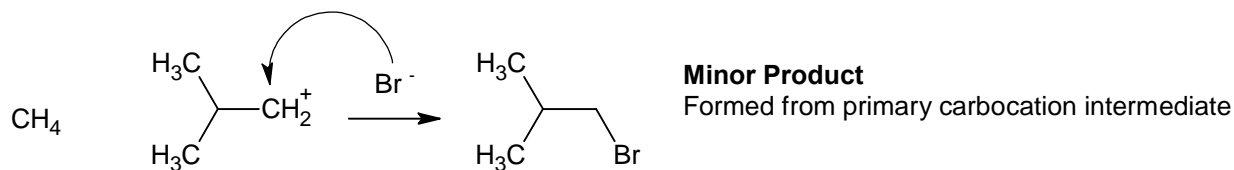
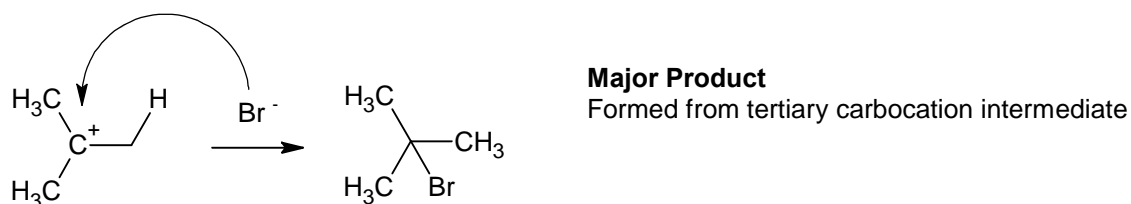
❖ Addition of H—X to a Pi Bond



3° is more stable carbocation:

Which fate?

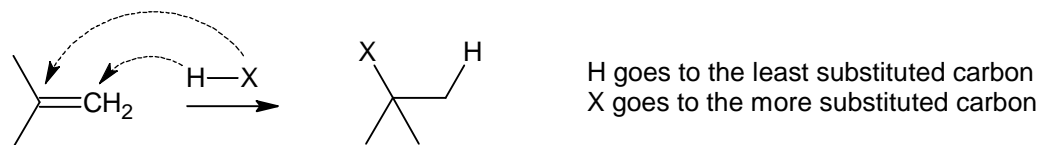
- ⊗ Rearrangement – won't stabilize charge
- ⊗ Lose proton – reaction will go backwards
- ⊙ **Capture nucleophile – Br⁻!**



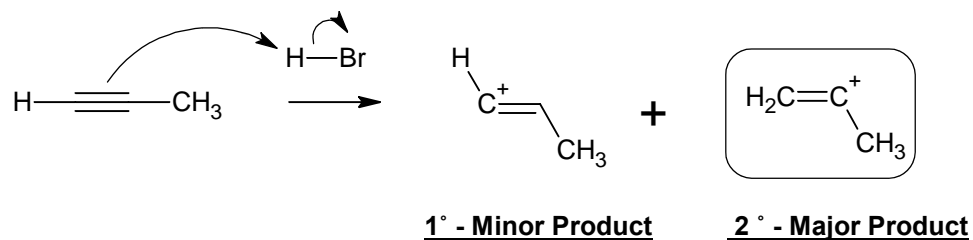
- This noted addition of Br to the more substituted end of the alkene was discovered by **Markovnikov**

Markovnikov's Rule:

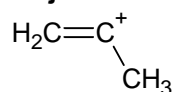
When a hydrogen halide adds to an alkene, *the hydrogen is added to the carbon bearing the most hydrogen substituents (least substituted carbon), and the halide is added to the end of the alkene with the least number of hydrogens.*



❖ Addition of H—Br to a Triple Bond

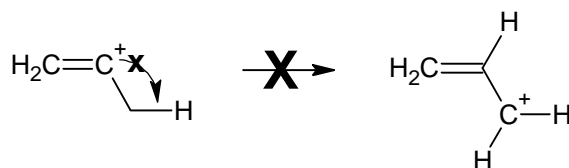


Major Product:

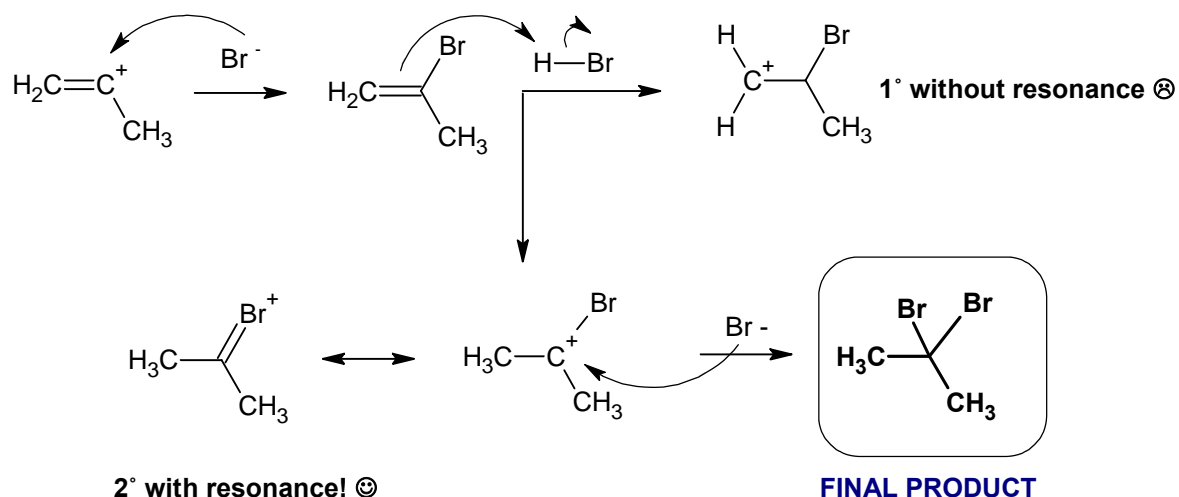


Carbocation fate?

- ⊗ Lose a proton → unproductive, would move reaction backwards
- ⊗ Rearrangement → **Vinyl carbocations CANNOT rearrange!**

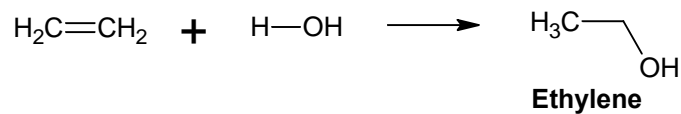


☺ **Capture a nucleophile!**

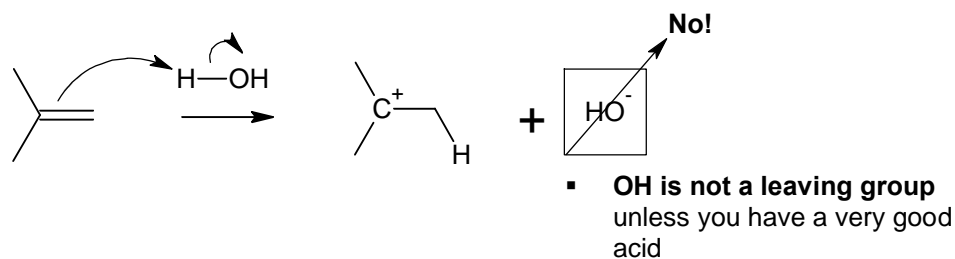


2° with resonance! ☺
One contributor with complete octets!

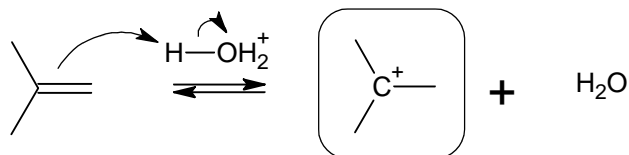
❖ Addition of H₂O



Example:

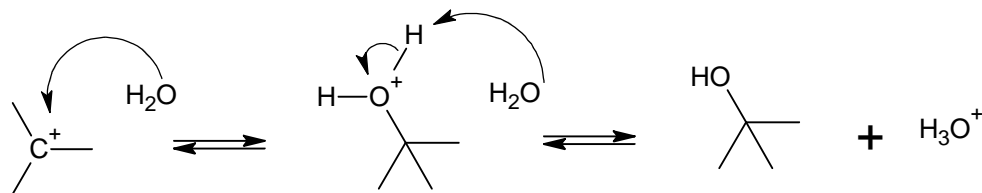


Mechanism:

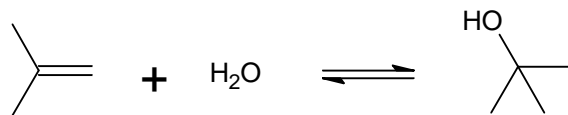


Carbocation Intermediate:

- ⊗ Rearrangement is unproductive
- ⊗ Lose proton → reaction goes backwards
- ⊙ **Capture nucleophile: H₂O**

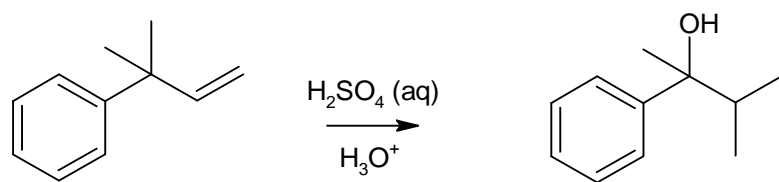


- This reaction is reversible
- It is in **EQUILIBRIUM!**

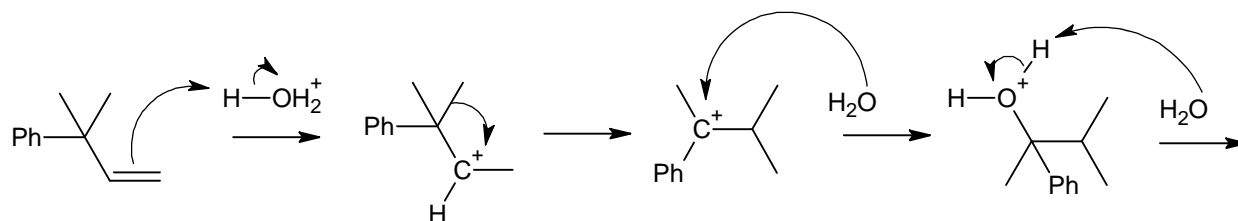


- Favors alkene just a *little*
- How do you control the direction of equilibrium? Think of Le Chatelier's Principle: increase the concentration on one side (reactants or products) to shift the equilibrium to the other side.

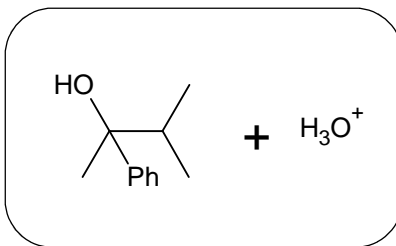
❖ **Addition of H₂O**



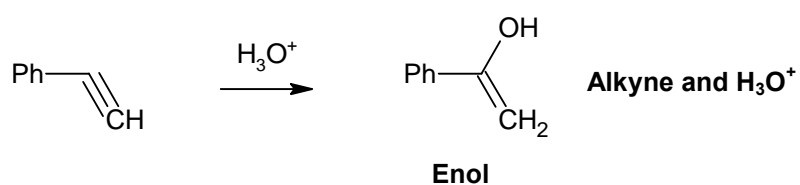
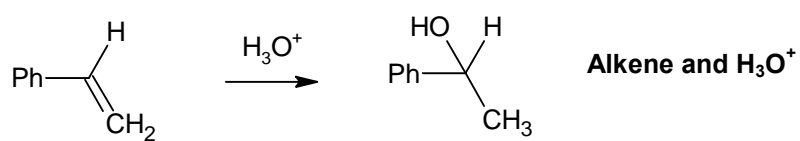
Ph = Phenyl = C₆H₅



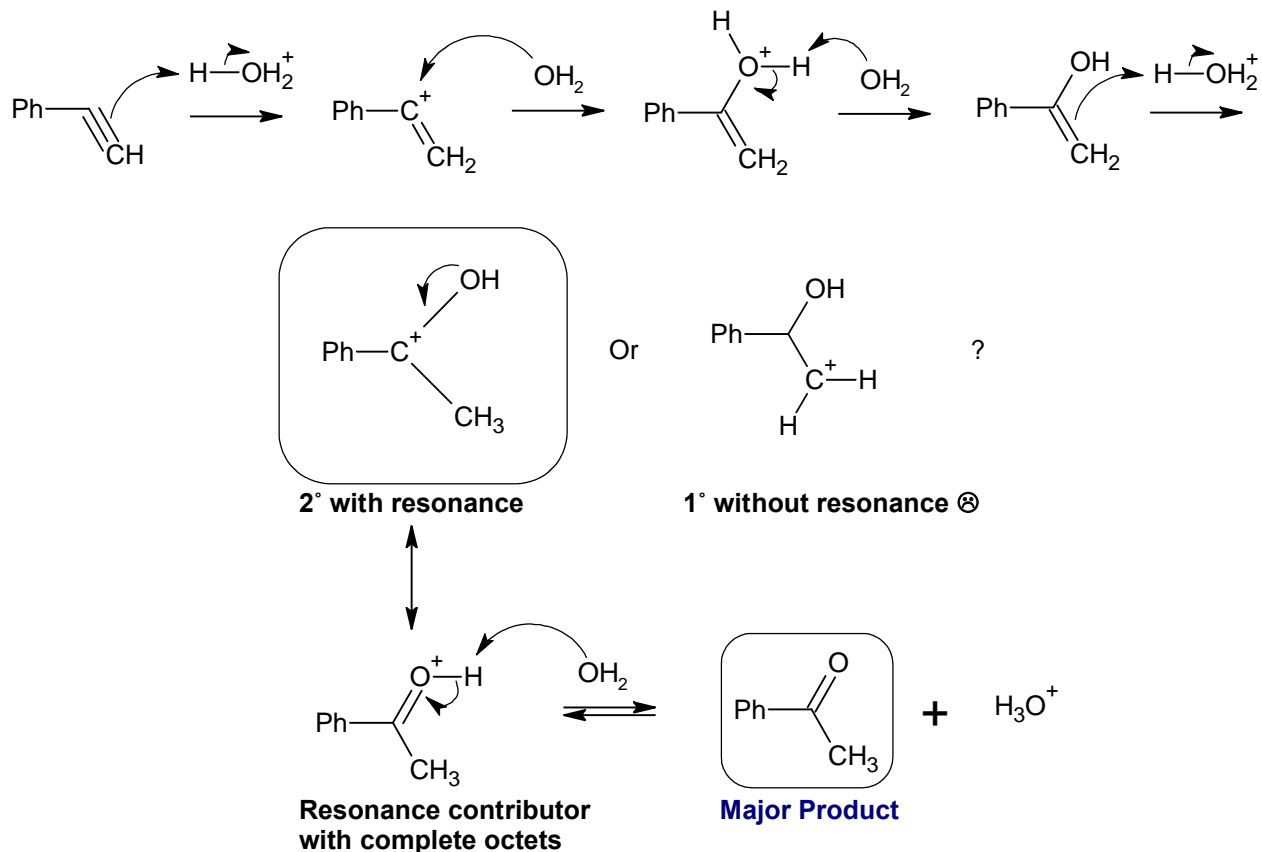
Carbocation intermediate:
Resonance, but no extra stability
 ☺ **Rearrange to 3° with resonance**



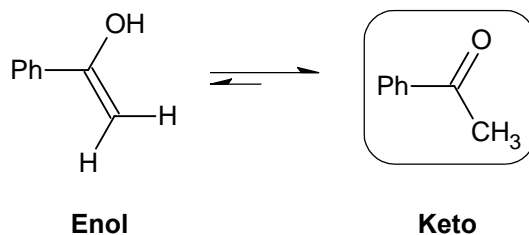
❖ **Alkynes and H₃O⁺**



Mechanism:

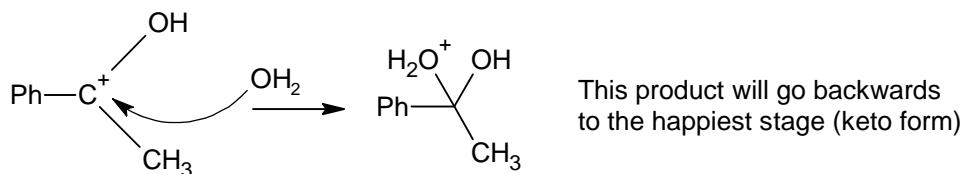


The intermediate labeled “1° without resonance ⊕” can proceed to deprotonation and formation of an enol. The keto product is favored greatly.



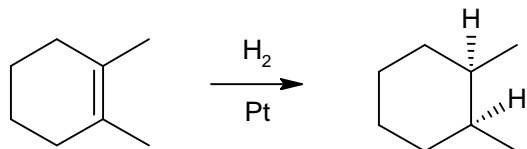
These products are **tautomers**, which are created through *tautomerization*, a process where a hydrogen atom migrates to another carbon and a double bond shifts to an adjacent bond.

Why not?



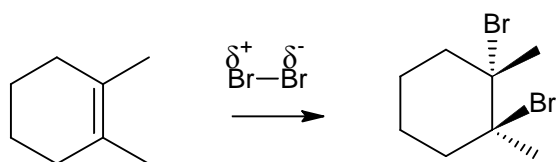
❖ Miscellaneous Additions

a) Catalytic Hydrogenation



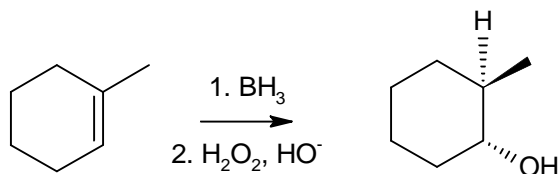
- **Syn-addition:** new things are added on the same face
 - Markovnikov's rule does not apply
 - No nucleophile or electrophile
 - Catalyst is a transition metal
 - Think of it as "removing" the pi bond
-

b) Addition of Br₂



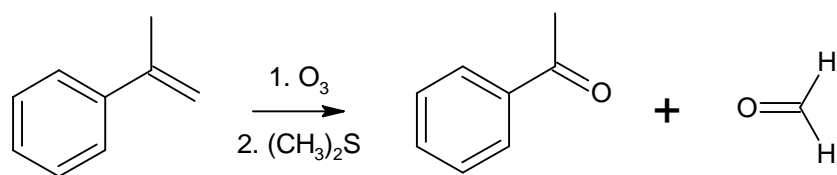
- **Anti-addition**
 - Markovnikov's rule does not apply
 - **Electrophile = Br₂** (induced δ^+ / δ^- when Br₂ approaches the pi bond)
 - **Nucleophile = alkene**
-

c) Hydroboration-Oxidation



- **Syn-addition**
 - **Anti-Markovnikov**
 - **Electrophile = BH₃** (Borane, because of the open octet)
 - **Nucleophile = alkene**
 - Addition of water on the alkene converts it into an alcohol
-

d) Ozonolysis



- **Syn-addition**
 - No nucleophile or electrophile
 - Ozone (O_3) reacts with an alkene and forms carbonyls
 - o Imagine the pi bond splitting in half and each end bonding to oxygen
-