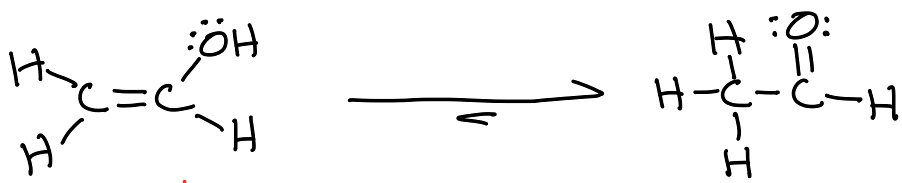

Energizer

New Concept → The following species are in equilibrium, and the more stable species is the "keto" form



enol form

keto form

This process is called "tautomerization" as in "keto-enol tautomerization"

Favored (a C=O pi bond is stronger than a C=C pi bond)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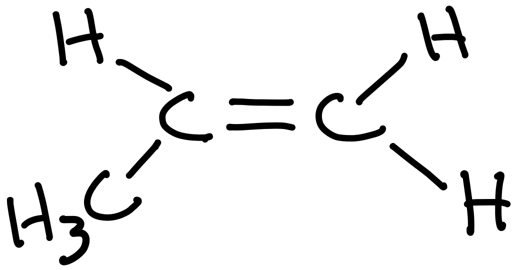

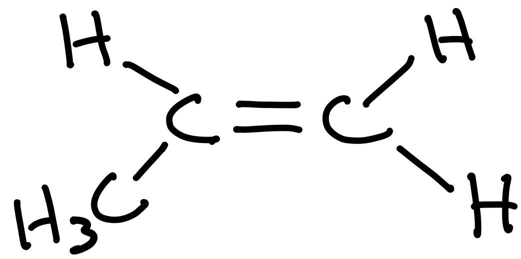

$H_3C-C\equiv C-H$ $H_3C-C\equiv C-H$

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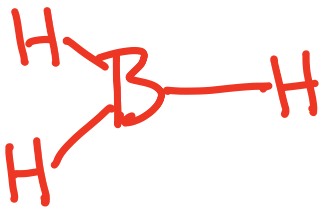
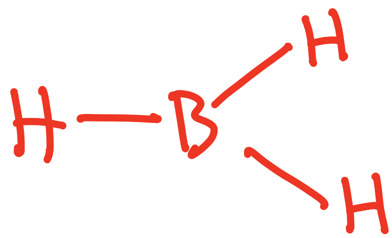
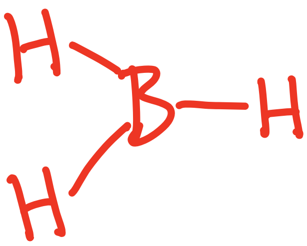
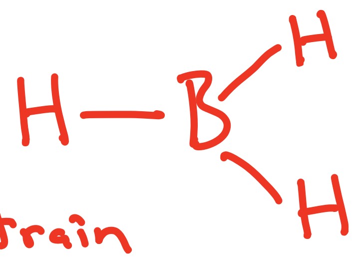


Steric
Strain

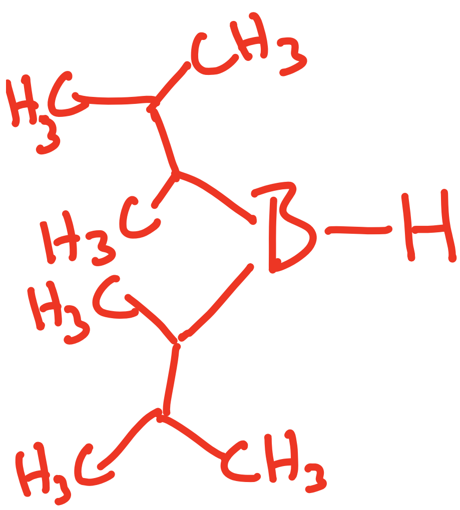


Much less
Steric Strain

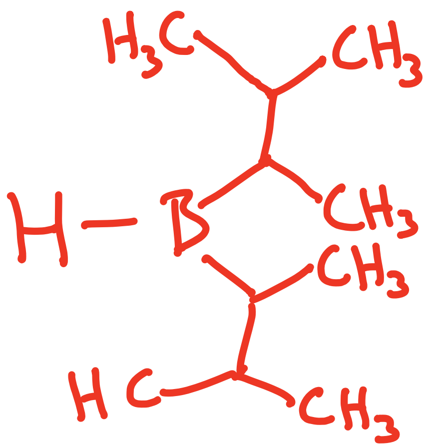




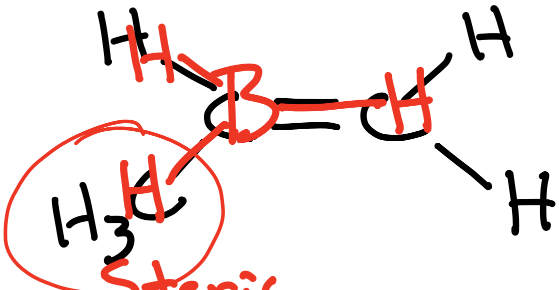
No steric strain
No real preference



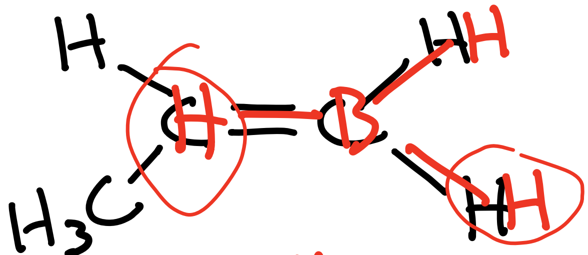
Significant
Steric
Strain



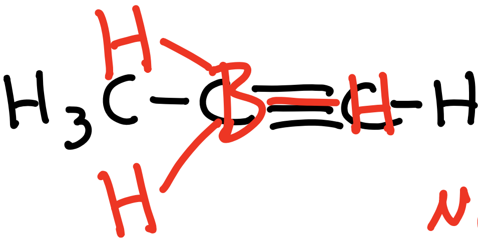
Highly
Preferred

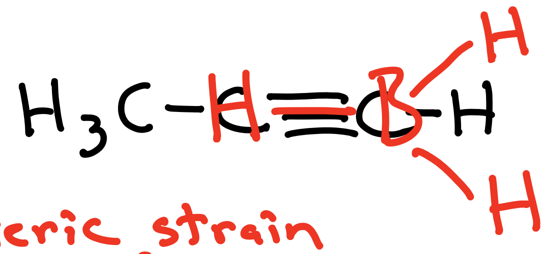


Steric Strain

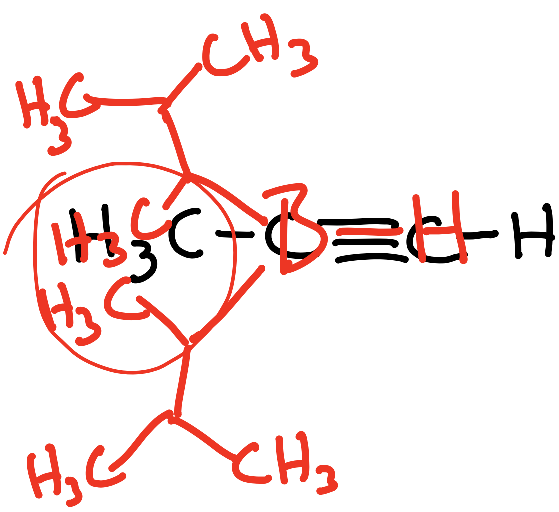


Much less Steric Strain

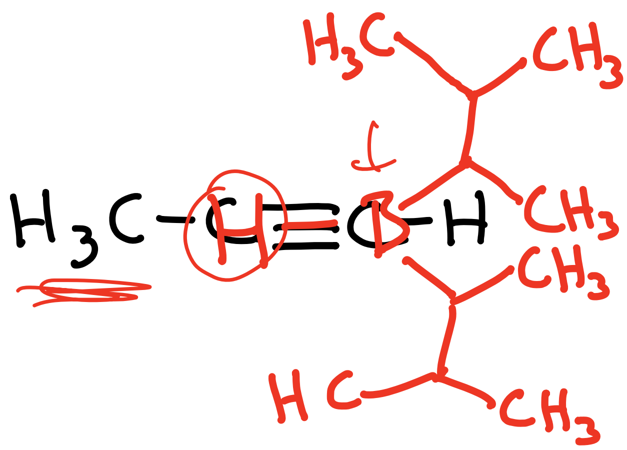




No steric strain
No real preference

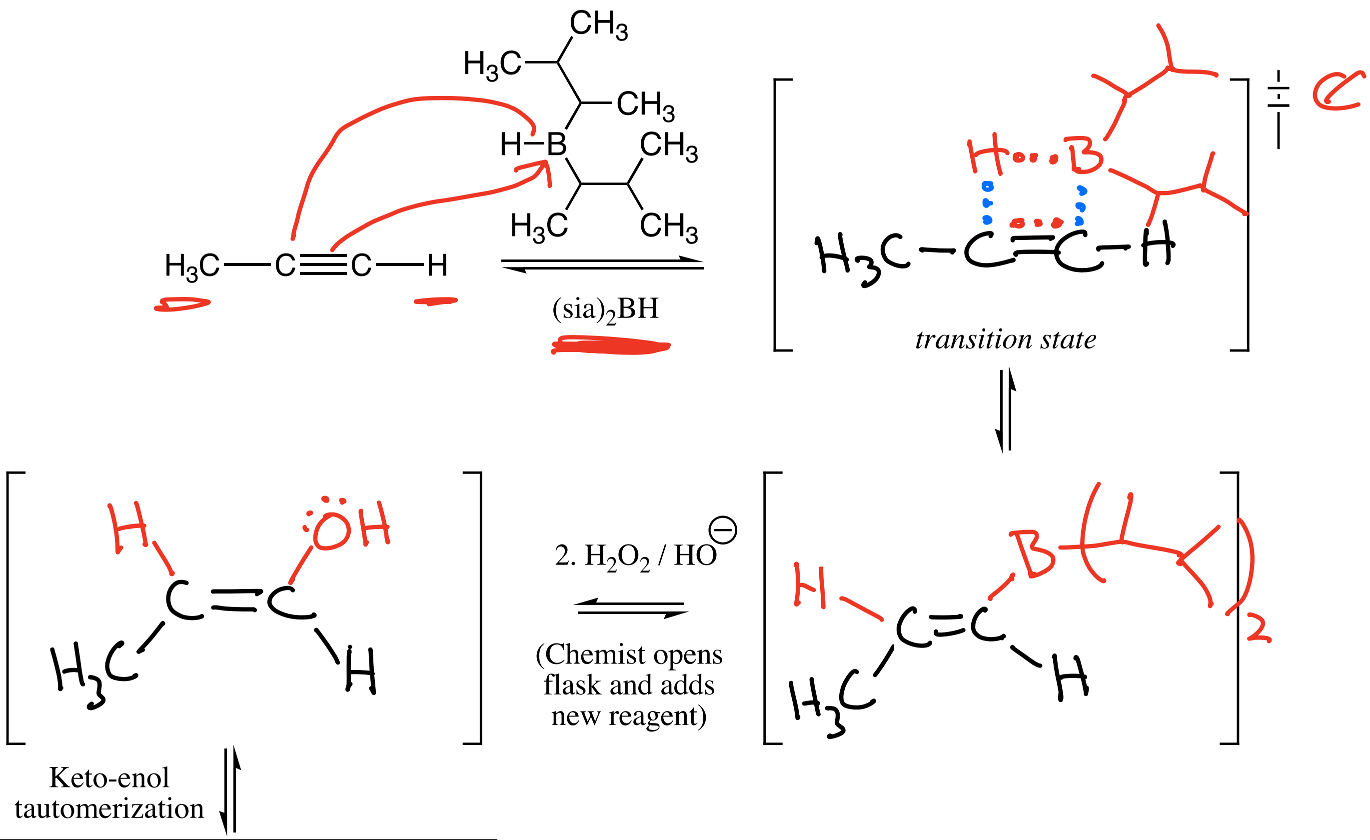


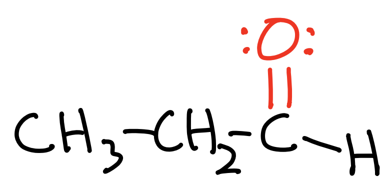
Significant Steric Strain



Highly Preferred

Terminal Alkyne Hydroboration



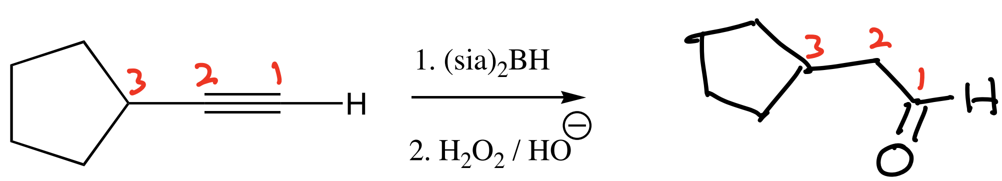


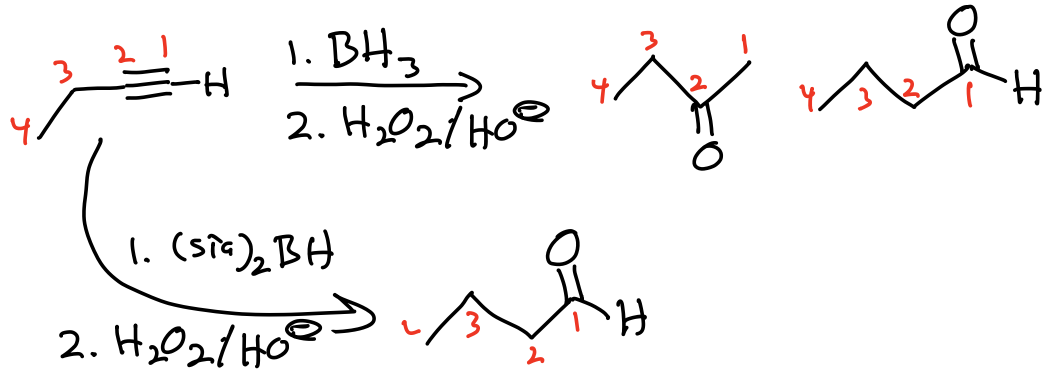
Products

⇐ The C=O is on the C on the end → "non-Markovnikov"

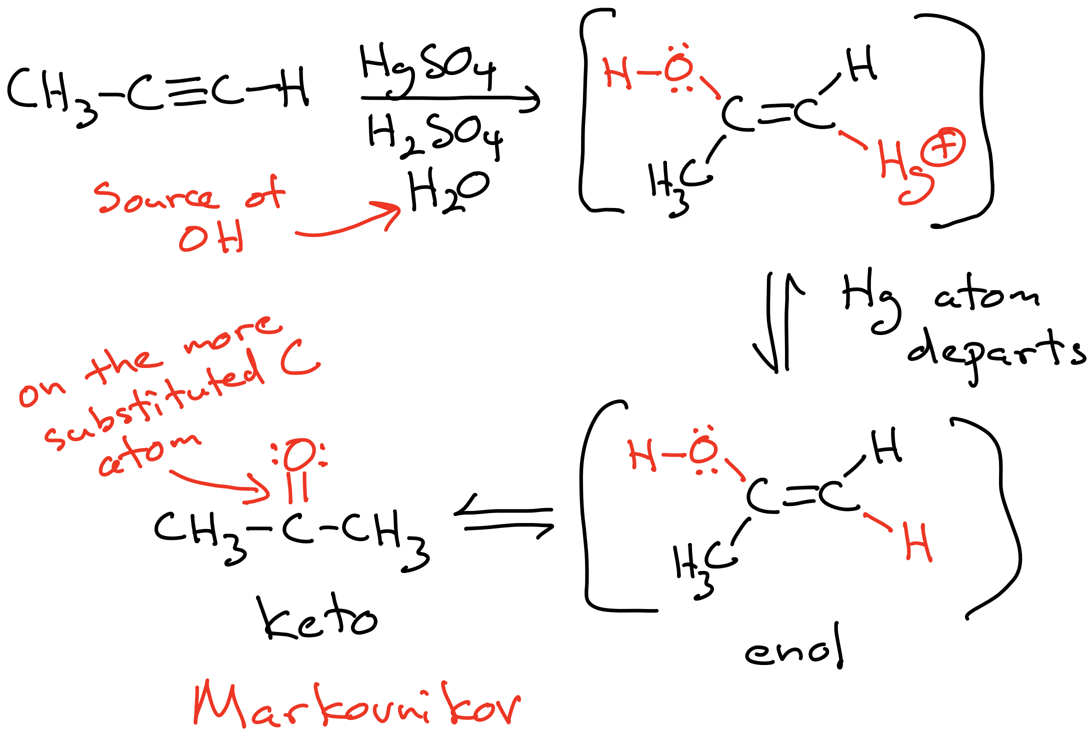
Summary: The $(sia)_2BH$ reacts so the B atom attaches to the C atom on the end. The four-membered ring transition states makes both bonds simultaneously. 2. H_2O_2/$HO^{\ominus}$ → enol → keto	
Regiochemistry:	non-Markovnikov
Stereochemistry:	N/A

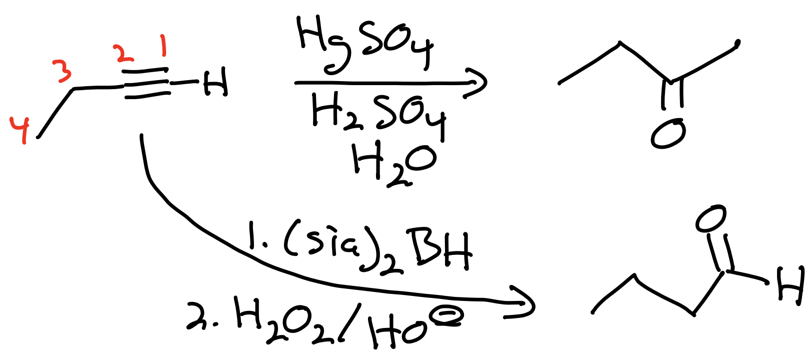
Example:




H
1. BH_3
2. H_2O_2/HO⊖
O
H
1. $(Sia)_2BH$
2. H_2O_2/HO⊖
O
H

Hydration of an alkyne using $HgSO_4$, H_2SO_4, H_2O

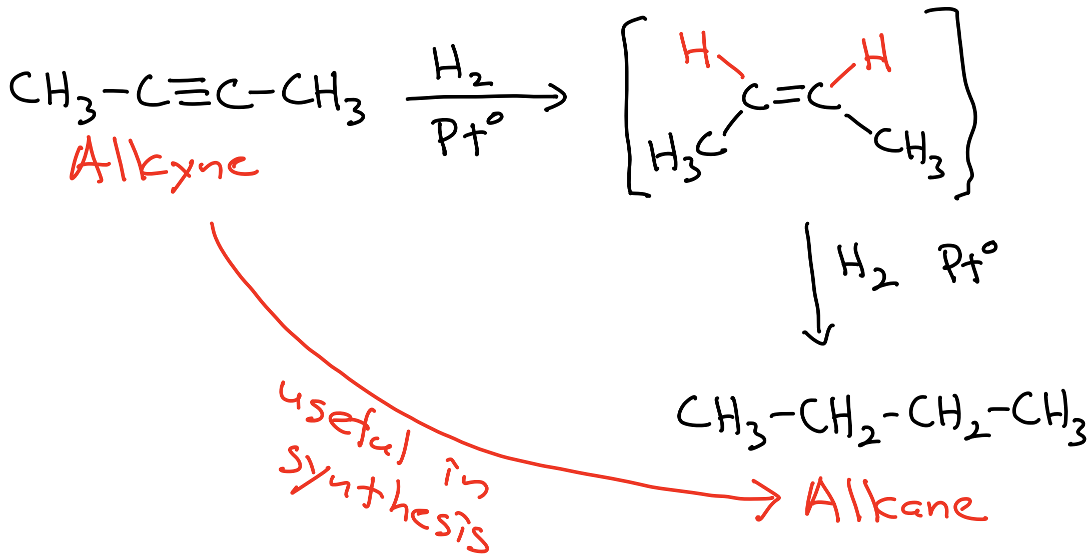




Reduction of Alkynes

1) Hydrogenation H_2 Pt°, Pd°, Ni°

Hydrogenation does not ordinarily stop at the alkene



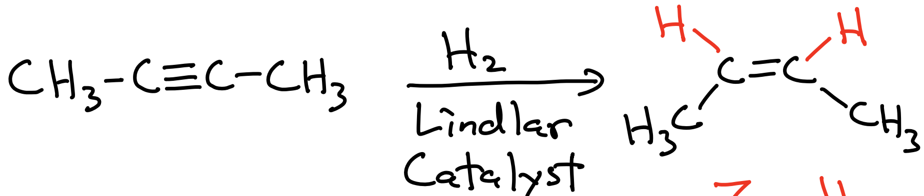
Lindlar Catalyst → special catalyst that stops the hydrogenation at the cis-alkene

syn addition

⇓

Found by experiment not designe

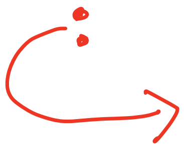
Pd° on $CaCO_3$, Pb salts quinoline



Z alkene

Time Out:

Regular Arrows



used to show movement of a pair of electrons

"Fish hook" Arrows

"fish hook" arrows are used to show movement of single electrons

Radical → a species with an unpaired electron → unstable so we encounter radicals as reaction intermediates

Time In:

2) Dissolving metal reductions of alkynes
Na^0 in NH_3

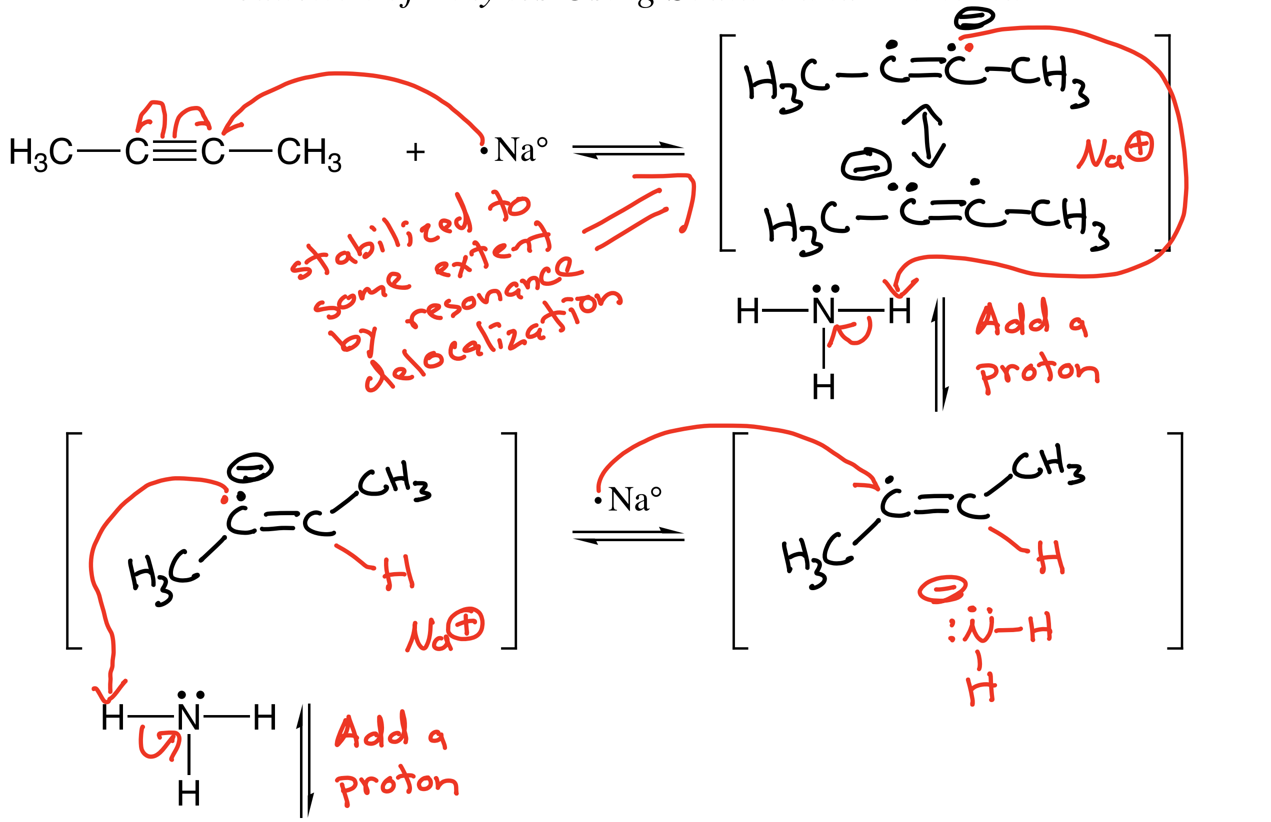
Sodium → (Na^0) is a very strong one electron reducing agent because $Na^{\oplus}$ has a filled octet in its valence shell

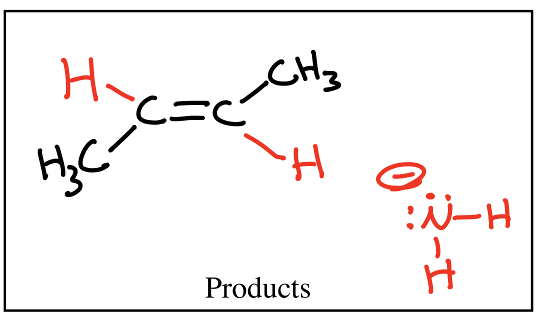
Formation of a filled octet for $Na^{\oplus}$ gives a strong motive for $\cdot Na^0$ to transfer its unpaired electron

NH_3 → used as solvent and the source of protons

→ other solvents like H_2O react violently with Na^0

Reduction of Alkynes Using Sodium and Ammonia





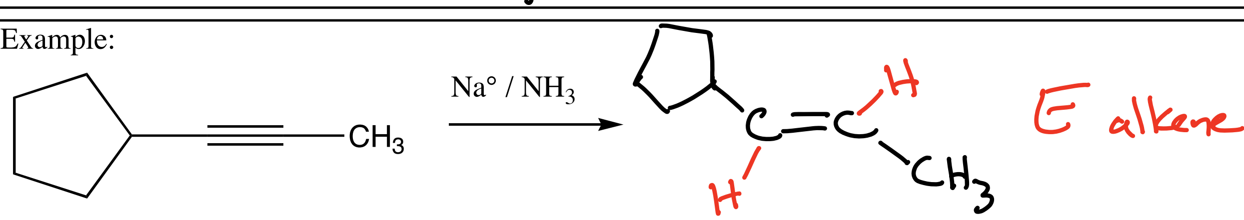
This reaction makes the more stable E alkene

Summary: Alkynes are reduced to E alkenes by Na° in NH_3 via two one-electron reductions by Na°, each of which is followed by adding a proton from the NH_3 solvent

Regiochemistry: N/A

Stereochemistry: Anti → E products

Example:



Reductions of alkynes → 3 choices