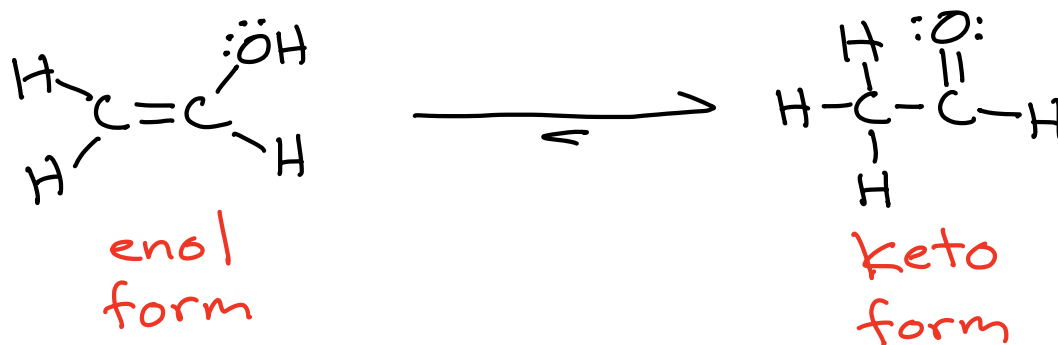




2nd Midterm Preview

Nomenclature/Concepts	103
Mechanisms	72
Reactions ("Box problems")	110
Apply what You Know	<u>20</u>
	305

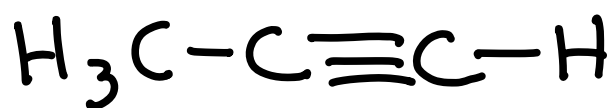
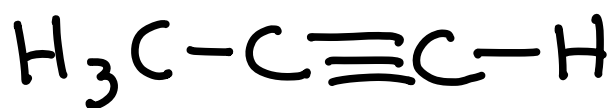
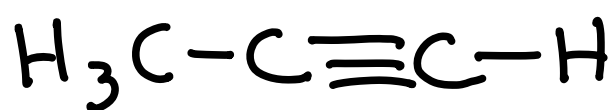
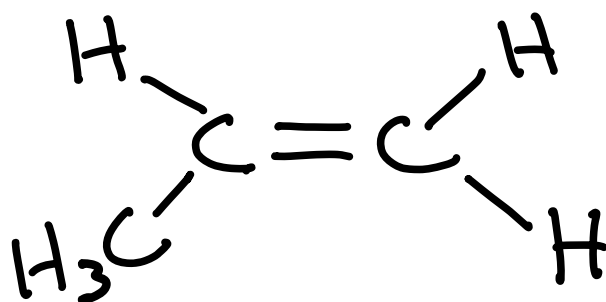
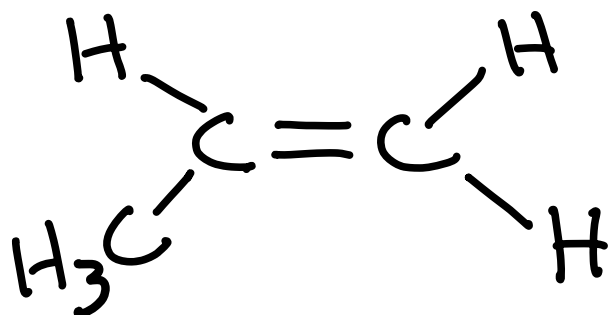
New Concept → The following species are in equilibrium, and the more stable species is the "keto" form

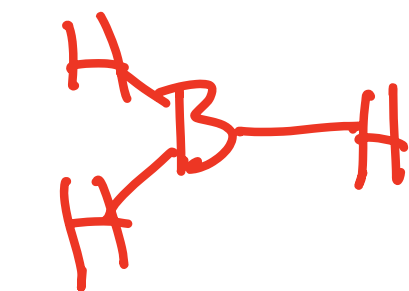


This process is called "tautomerization" as in "keto-enol tautomerization"

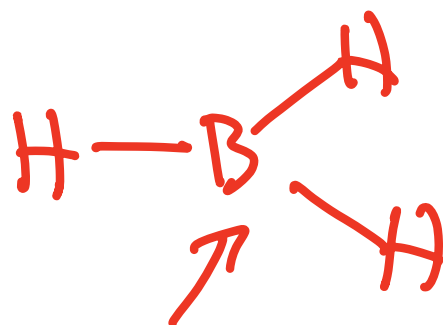
Favored
(a $\text{C}=\text{O}$ pi bond is stronger than a $\text{C}=\text{C}$ pi bond)



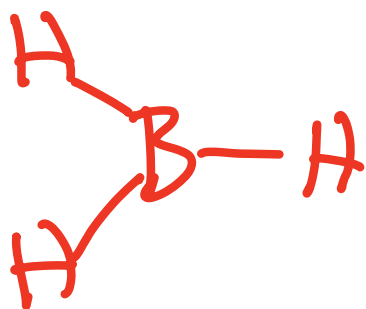




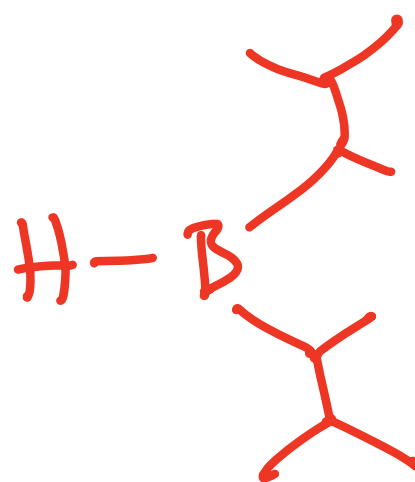
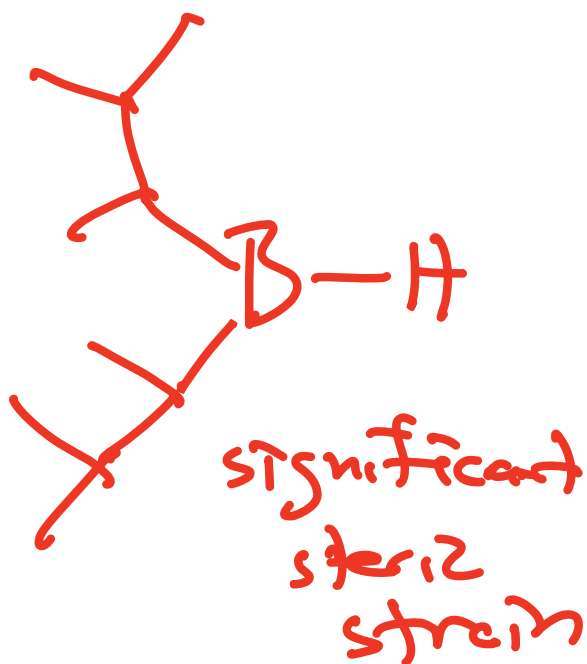
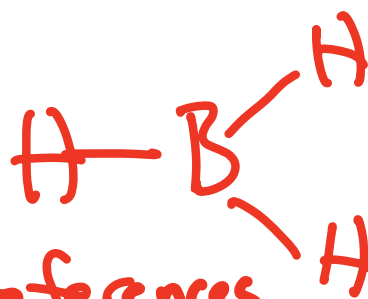
steric strain



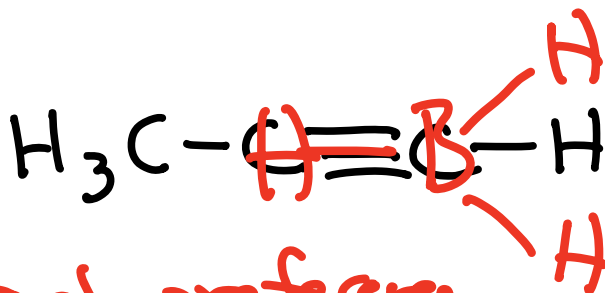
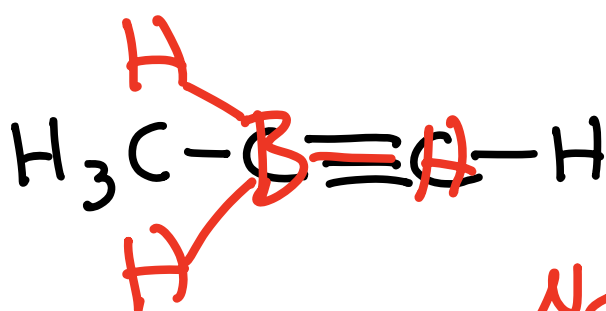
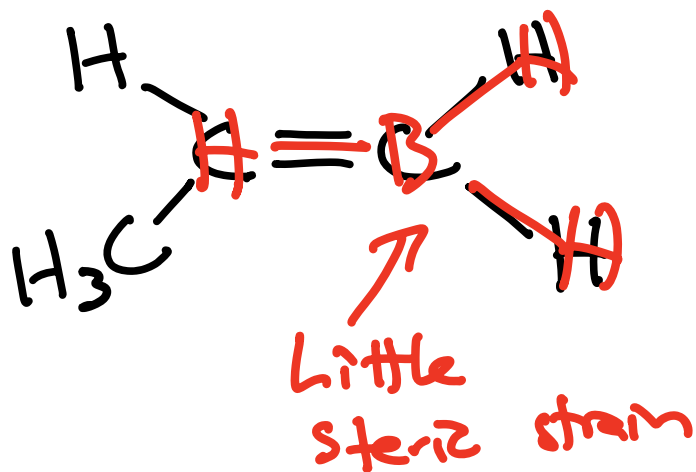
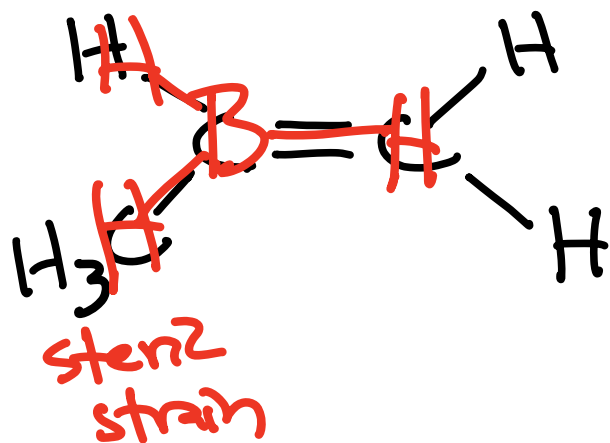
little steric strain



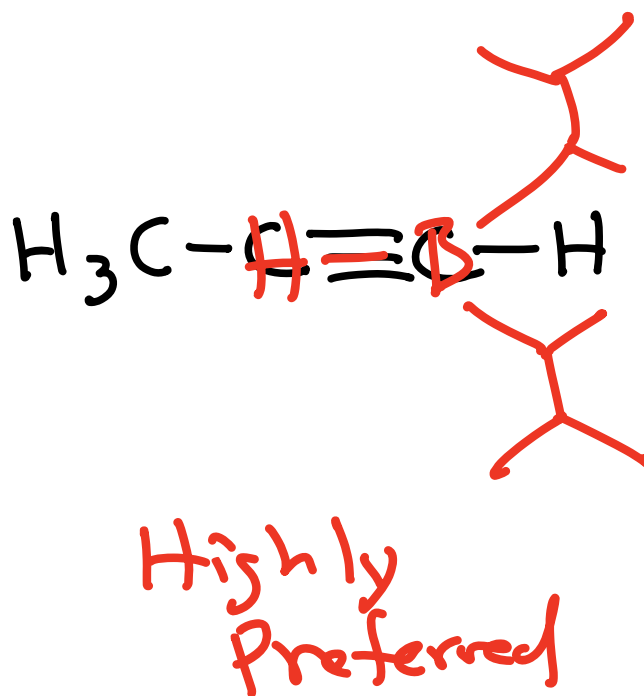
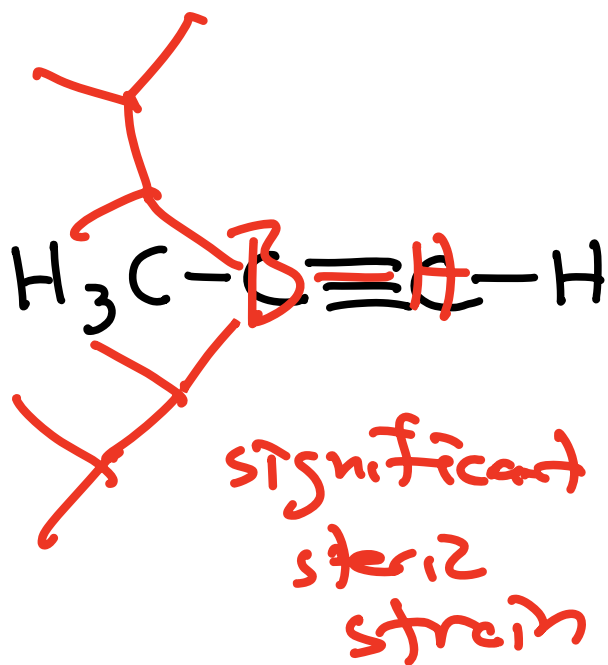
No real preferences



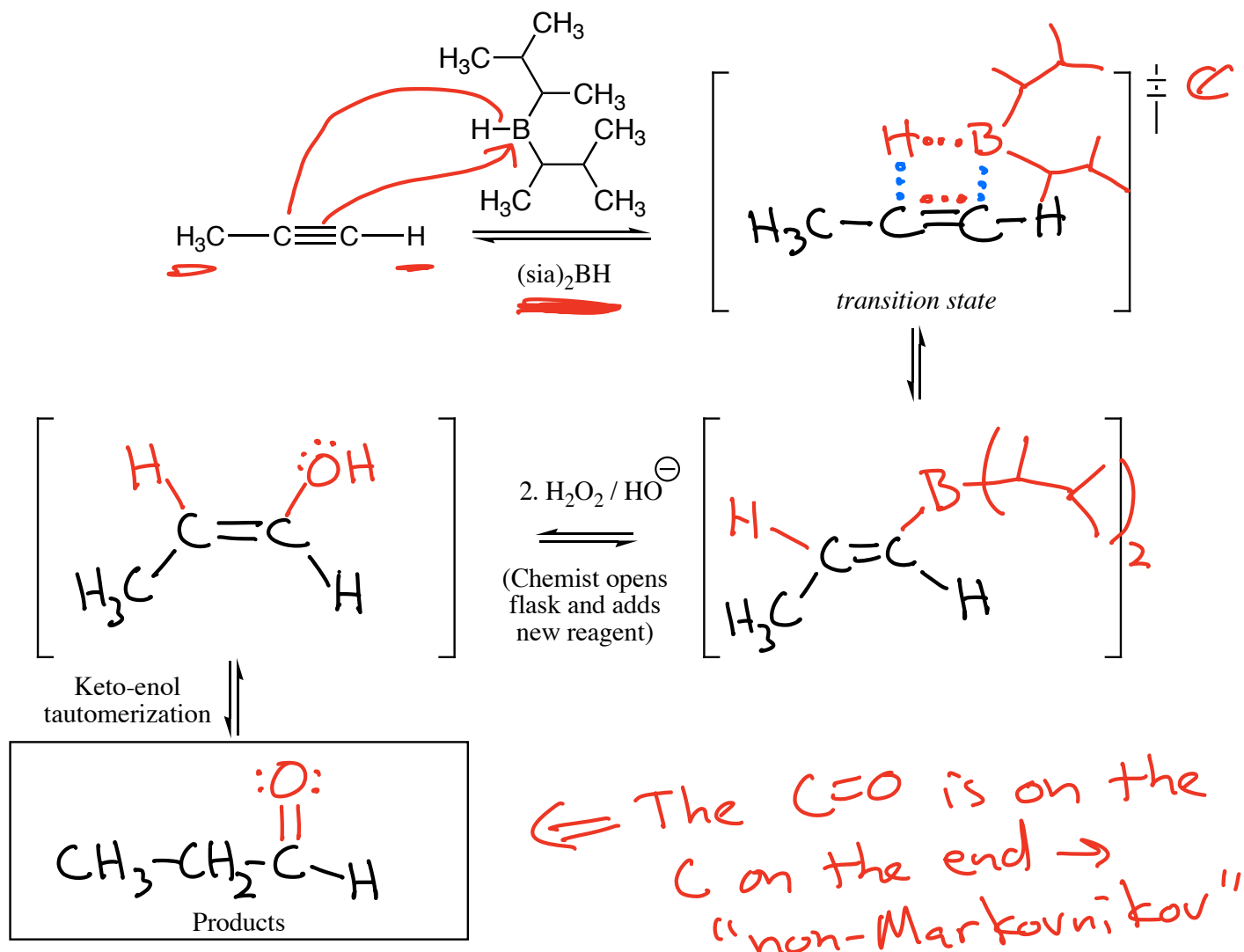
Highly Preferred



No real preference



Terminal Alkyne Hydroboration

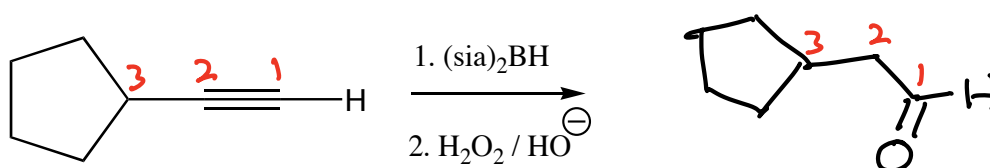


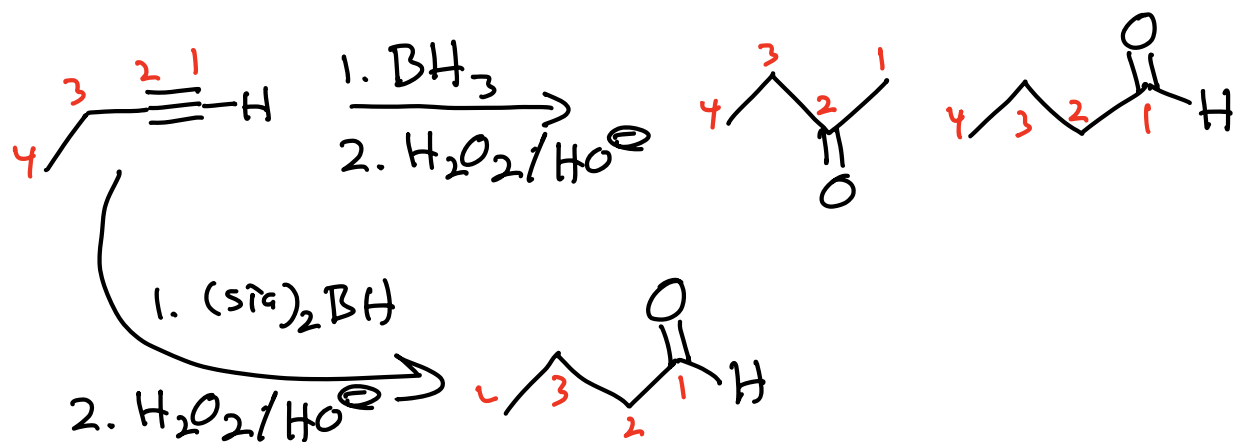
Summary: The $(\text{sia})_2\text{BH}$ reacts so the B atom attaches to the C atom on the end. The four-membered ring transition states makes both bonds simultaneously. $2. \text{H}_2\text{O}_2 / \text{HO}^\ominus \rightarrow \text{enol} \rightarrow \text{keto}$

Regiochemistry: non-Markovnikov

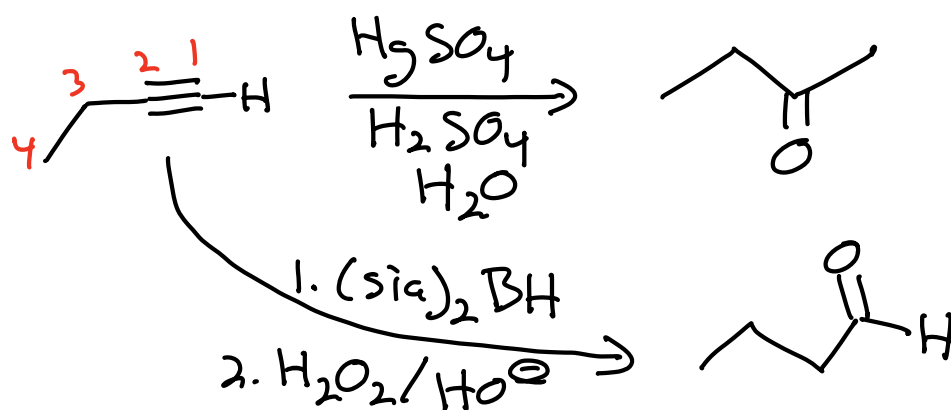
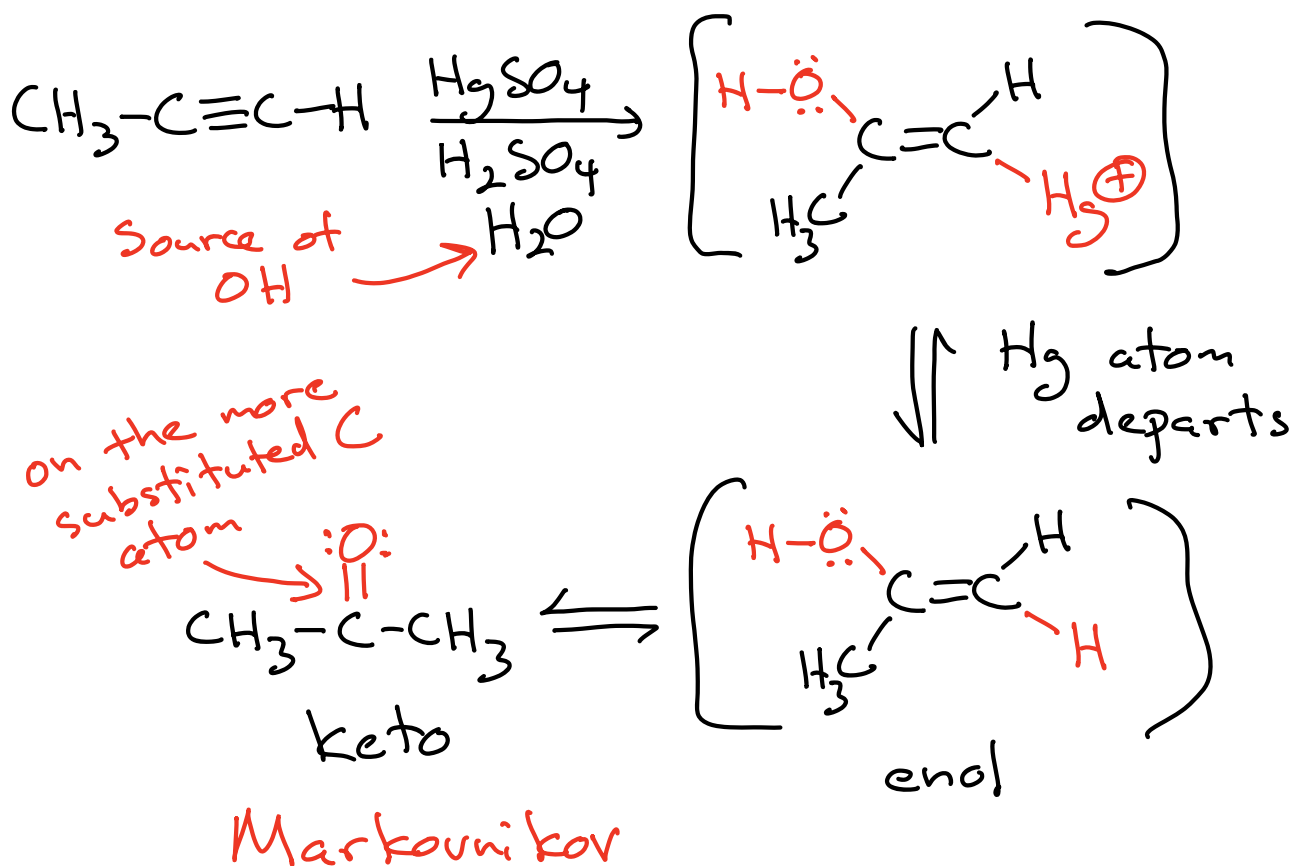
Stereochemistry: N/A

Example:





Hydration of an alkyne using $\text{HgSO}_4, \text{H}_2\text{SO}_4, \text{H}_2\text{O}$



Stinking Molecules! → We have evolved to avoid spoiled food that would make us sick } We are VERY sensitive to these molecules!

products of bacterial breakdown



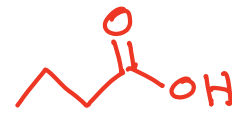
Rotten Fish



Rotten Mammal

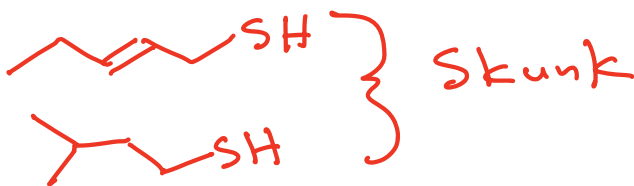


Rotten Eggs



Barf!

Neutralize with a base → ammoniac or baking soda to remove the smell!



Skunk

Natural Gas

90% - 95% methane

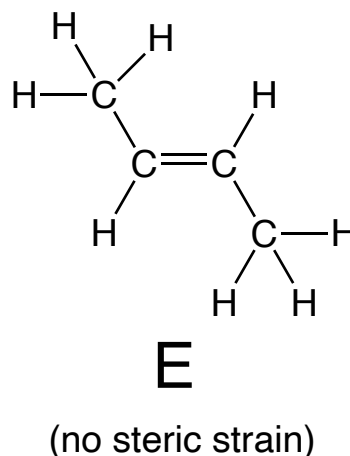
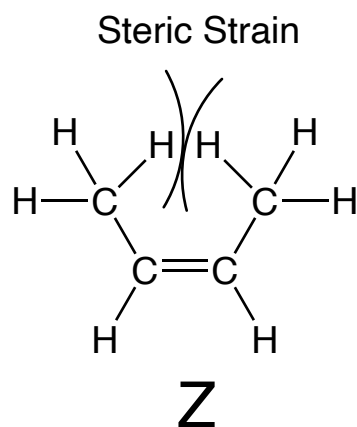
5% - 10% ethane

+SH and CC(C)SC added as an odorant so it can be detected → Texas tragedy inspired this innovation



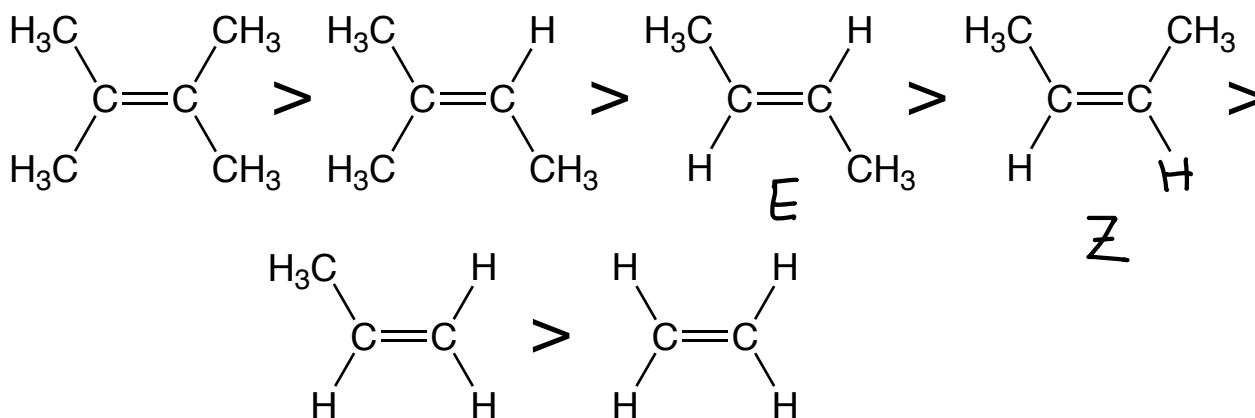
Special Alkene Bonus: Important material you will need to know!

Alkene stability part 1: Z (cis) groups larger than H atoms will crunch into each other causing steric strain.



Alkene stability part 2: For reasons we are not able to tell you, more substituted alkenes have more stable (stronger) pi bonds than alkenes with more H atoms on their sp^2 -hybridized C atoms (despite there being steric strain present in the most substituted alkenes).

Strongest Pi Bond



Weakest Pi Bond

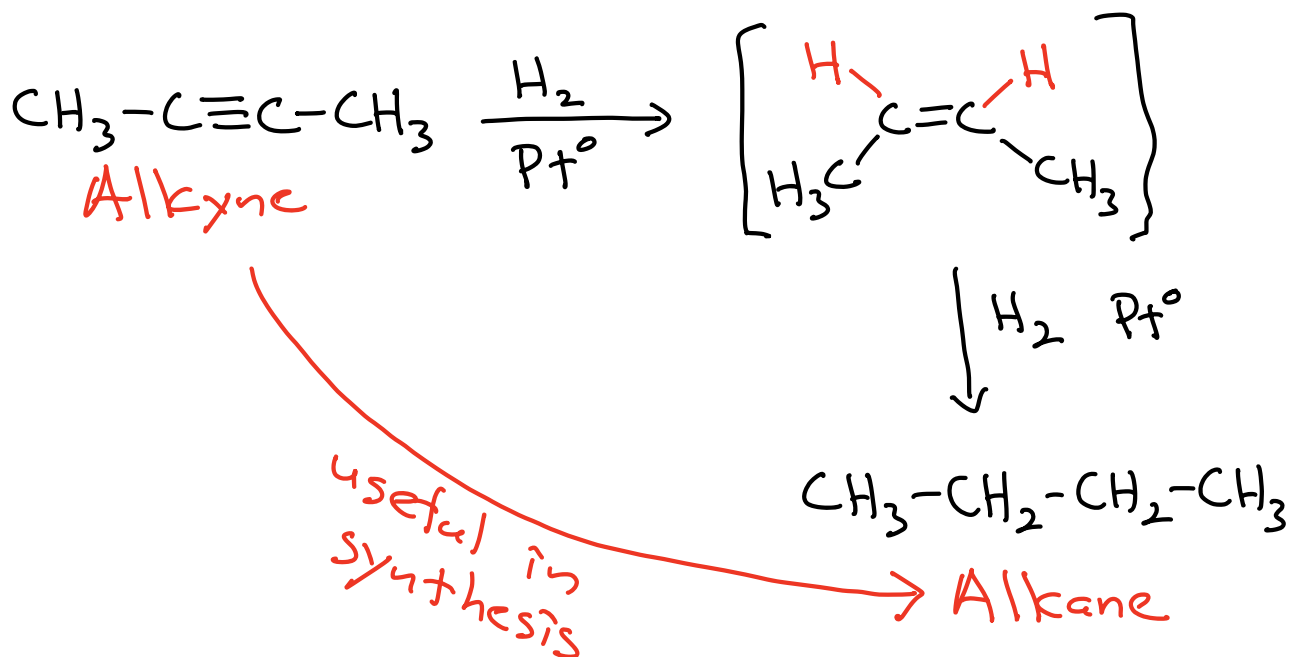


***Time Capsule:
Zaitsev's rule follows
this trend!!***

Reduction of Alkynes

1) Hydrogenation H_2 Pt^0, Pd^0, Ni^0

Hydrogenation does not ordinarily stop at the alkene



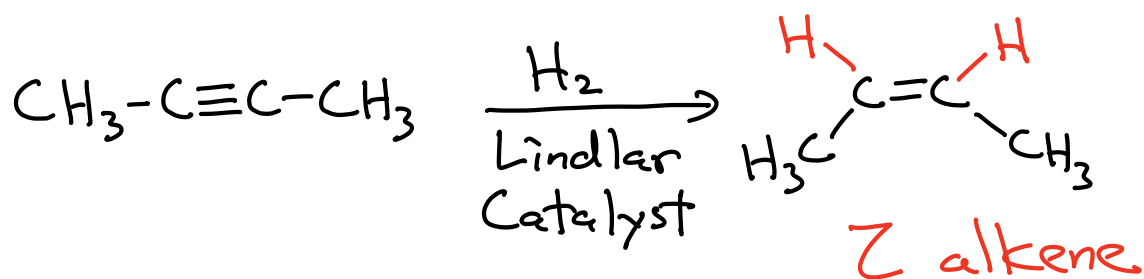
Lindlar Catalyst $\rightarrow$ special catalyst that stops the hydrogenation at the cis-alkene

$\Downarrow$

Found by experiment not designed

syn addition

Pd^0 on $CaCO_3$, Pb salts
quinoline



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° in NH_3

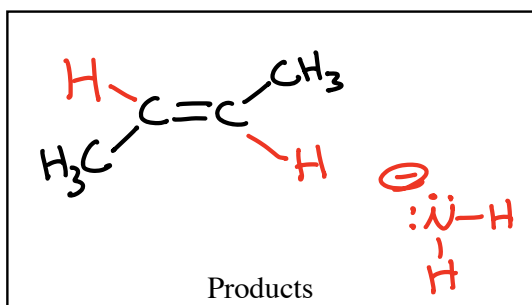
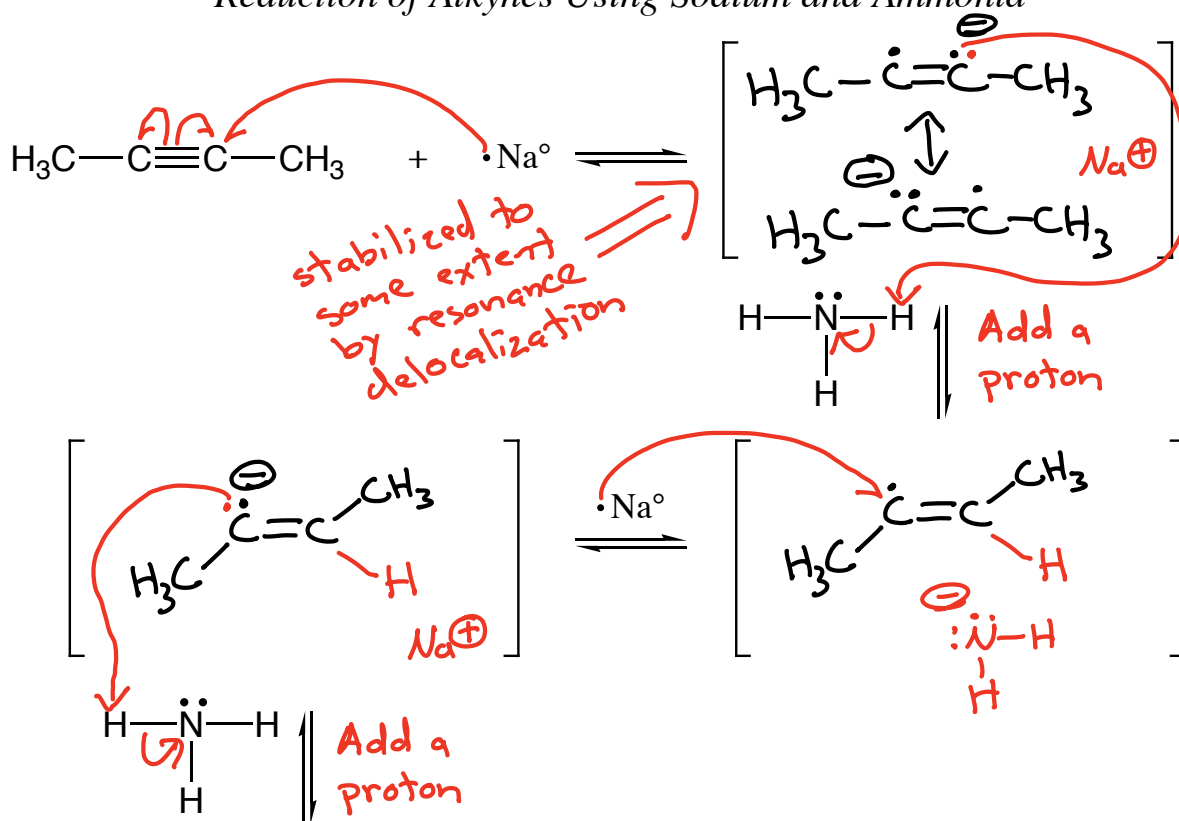
Sodium $\rightarrow (\text{Na}^\circ)$ is a very strong one electron reducing agent because $\text{Na}^\oplus$ has a filled octet in its valence shell

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

$\text{NH}_3 \rightarrow$ used as solvent and the source of protons

$\rightarrow$ other solvents like H_2O react violently with Na°

Reduction of Alkynes Using Sodium and Ammonia



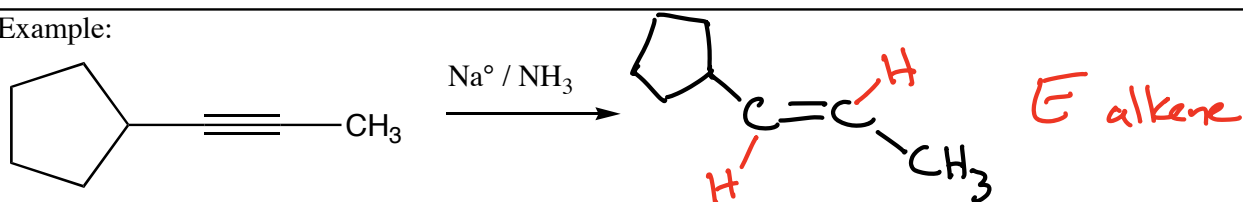
This reaction makes the more stable E alkene

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 $\rightarrow$ E products

Example:



Reductions of alkynes $\rightarrow$ 3 choices

