



c) Conversion of a vicinal dihalide into an alkyne

H3C-C-C-CH3 NaNH2 H3C-C=C-CH3 Br H

Vicinal dihalide

Note this alkane is not terminal



Time capsule -> This is a double E2 reaction

When creating a terminal alkxne you must use 3 equivalents of NaNH2 as a first step -> AND -> you need a second step that is mild acid -> HCI/HQ

Internal alkyne example:

CH3-CHBr-CHBr-CH3 2eq. NaNH2> H3C-C=C-CH3

Big Deal - allows conversion of an alkane to an alkane

H₃C =
$$CH_3$$
 Br H
H₃C - $C-C-C-CH_3$ H Br Racemic
 $A = C = C - CH_3$ CH₃- $C = C - CH_3$ Br H₃CC + $C = C - CH_3$ H₃CC + $C = C - CH_3$ H₃CC + $C = C - CH_3$ H₃CC + $C = C - CH_3$ H₃CC + $C = C - CH_3$ H₃CC + $C = C - CH_3$ H₃CC + $C = C - CH_3$ H₃CC + $C = C - CH_3$ H₃CC + $C = C - CH_3$ H₃CC + $C = C - CH_3$ H₃CC + $C = C - CH_3$

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-enal tautomerization"

Favored

(a C=0 pi bond
is stronger than
a C=C pi bond)



$$C = C + H$$

$$H_3 = C + H$$

$$H_3 = C + H$$

Steric Strain H-B H Much less Steric Strain

No steric strain No real preference

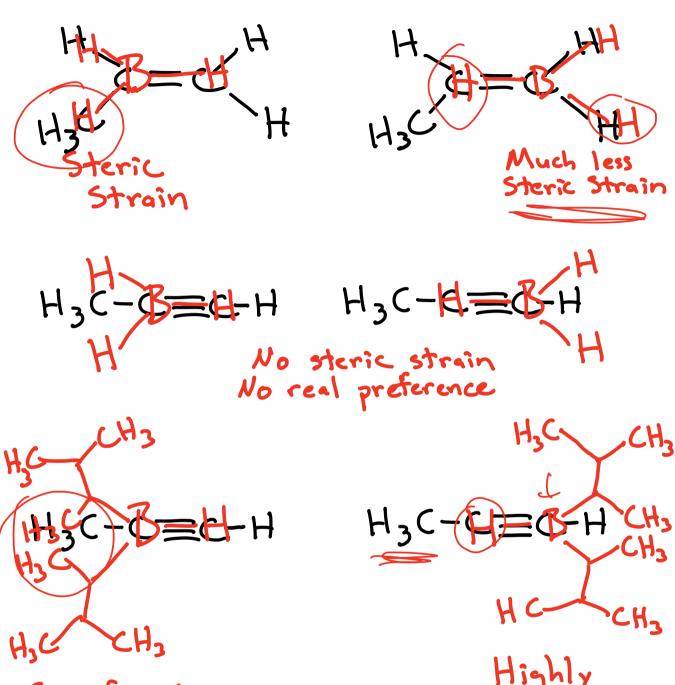
Significant Steric Strain H₃C CH₃

H - B CH₃

CH₃

H C CH₃

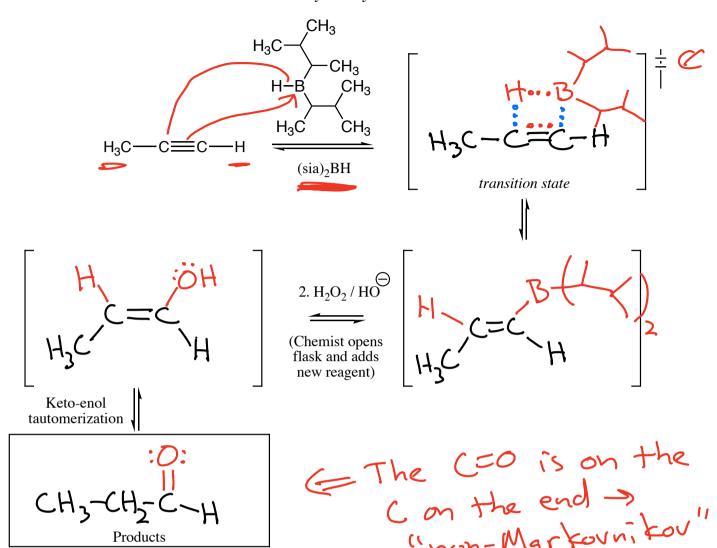
Highly Preferred



Significant Steric Strain

Highly Preferred

Terminal Alkyne Hydroboration



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.H2O2/HO-> enol-> keto

Regiochemistry: non-Markevnikou

$$\frac{1. BH_{3}}{2. H_{2}O_{2}/Ho^{2}}$$

$$\frac{1. (sie)_{2}BH}{2. H_{2}O_{2}/Ho^{2}}$$

$$\frac{1. (sie)_{2}BH}{2. H_{2}O_{2}/Ho^{2}}$$

Hydration of an alkyrne using
Hg Soy, H₂Soy, H₂O

(H₃-C=C-H HgSoy
H₂Soy
Source of H₂Soy
OH

Hg atom
departs

CH₃-C-CH₃

Keto

Markovnikov

Horizon

Hor

Reduction of Alkynes

1) Hydrogenation H2 Pt°, Pd°, Ni° Hydrogenation does not ordinarily stop at the alkene

$$CH_{3}-C=C-CH_{3} \xrightarrow{H_{2}} Pt^{\circ}$$

$$H_{3}C-CH_{3}$$

$$H_{2} Pt^{\circ}$$

$$CH_{3}-CH_{2}-CH_{2}-CH_{3}$$

$$Syn_{3}h_{ess_{2}} \longrightarrow Alkane$$

Lindlar Catalyst -> special catalyst that

If stops the hydrogenation

Found by experiment at the cis-alkene

not designe

syn addition

Pdo on CaCo3, Pb salts quinoline

CH3-C=C-CH3 H2 C=CH3 Catalyst Zalkene

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 alkyres
Na° in NH3

Sodium -> (Na°) is a very strong one electron reducing agent because Nath has a filled octet in its valence shell

> Formation of a filled outet for Nath gives a strong motive for Na to transfer its unpaired electron

NH3 — sused as solvent and the source of protons

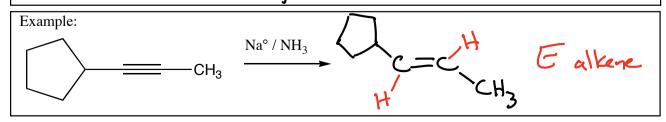
other solvents like H20
react violently with Na°

Reduction of Alkynes Using Sodium and Ammonia

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

Regiochemistry: N/A

Stereochemistry: Arti -> E products



Reductions of alkynes -> 3 choices