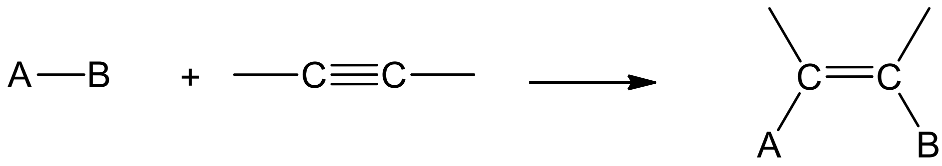
CHEM 261 Dec 04, 2015

Reactions of Alkynes

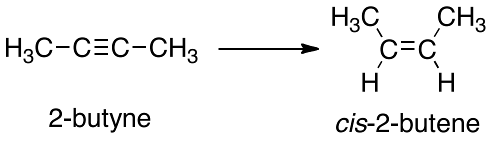
1. Addition (analogous to alkenes)



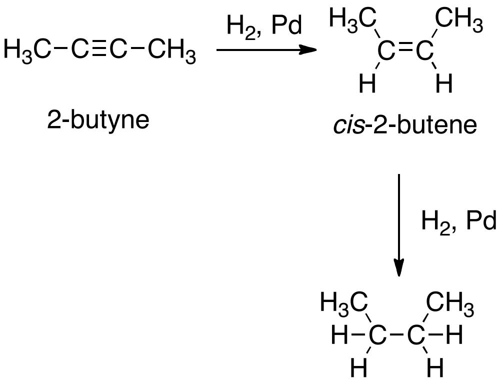
2. At terminal carbon bearing H

Addition reactions

1. Hydrogenation

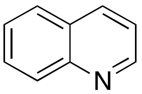


H_2 and catalyst. However, a less reactive catalyst is needed to stop reaction at the cis-2-butene product.



Lindlar's Catalyst:

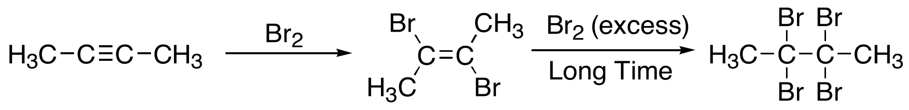
Pd, $BaSO_4$ (or $CaCO_3$ is often used in place of $BaSO_4$), and quinoline (see below):



- These conditions allows for selective hydrogenation of alkynes to alkenes.

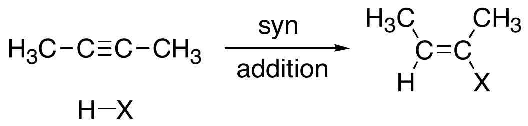
2. Halogenation

- The halogenation reaction gives a trans addition (anti)



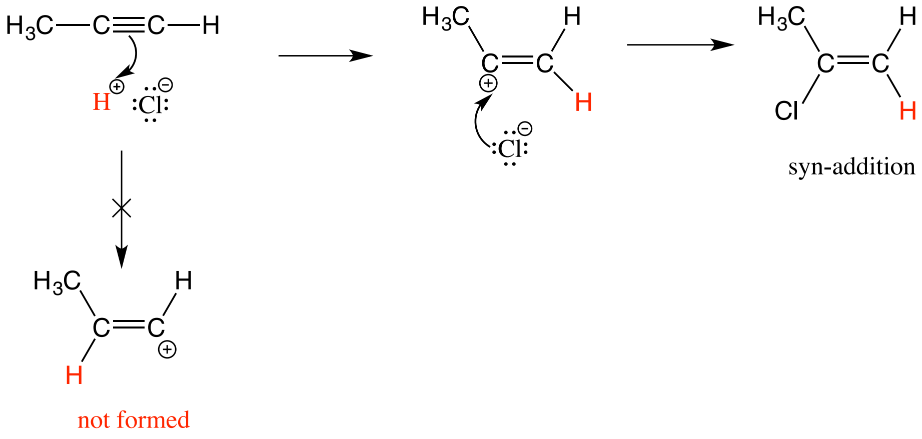
3. HX Addition (syn)

X= Cl, Br, I



Mechanism

Example: Addition of HCl to propyne (follows Markovnikov’s rule)



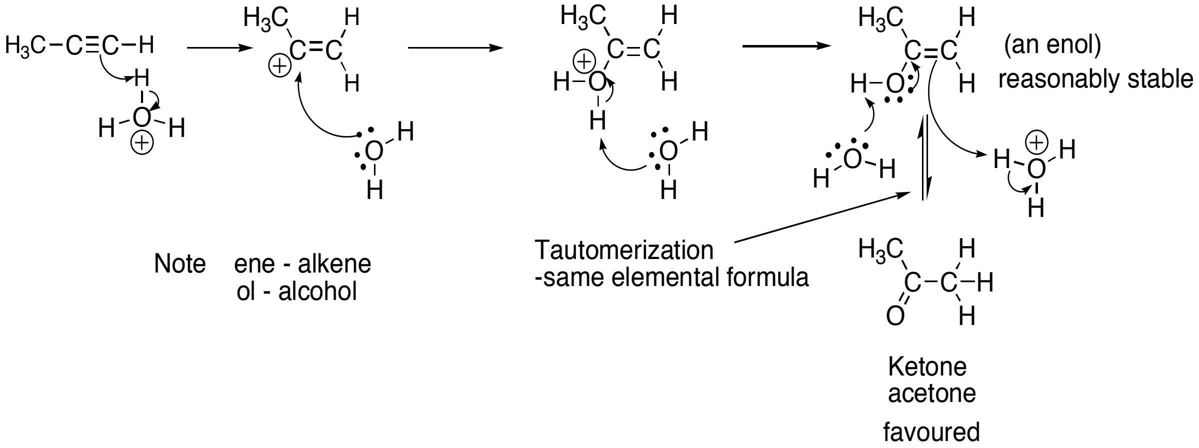
4. Addition of Water (requires acid)

Tautomers (e.g. keto/enol) are rapidly equilibrating structural isomers. The process is called **tautomerization**. Tautomerization is **NOT** the same as resonance. Resonance is the movement of electrons only.

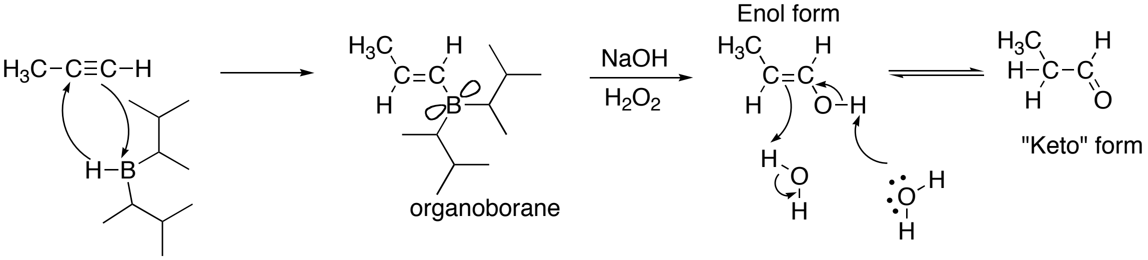
Remember

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^{\oplus} + HSO_4^{\ominus}$$

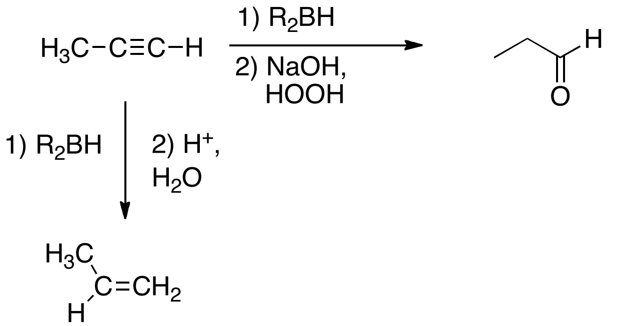
Mechanism:



5. Anti-Markovnikov Water Addition – Hydroboration-Oxidation

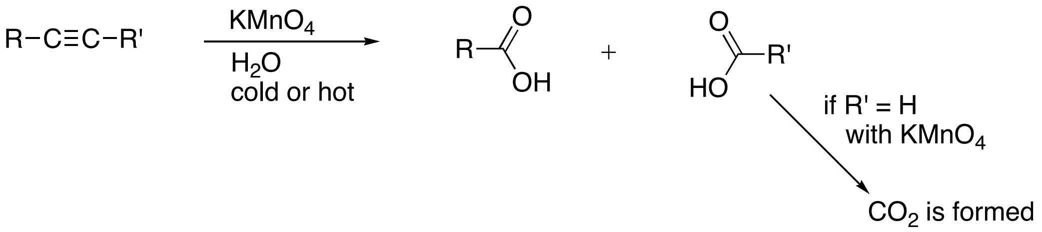


- Two possibilities for the reaction of organoboranes:
  1. Water and acid to add H and give the alkene
  2. NaOH and H_2O_2 to give the enol tautomer that converts (equilibrium) primarily to the keto tautomer (aldehyde shown below)

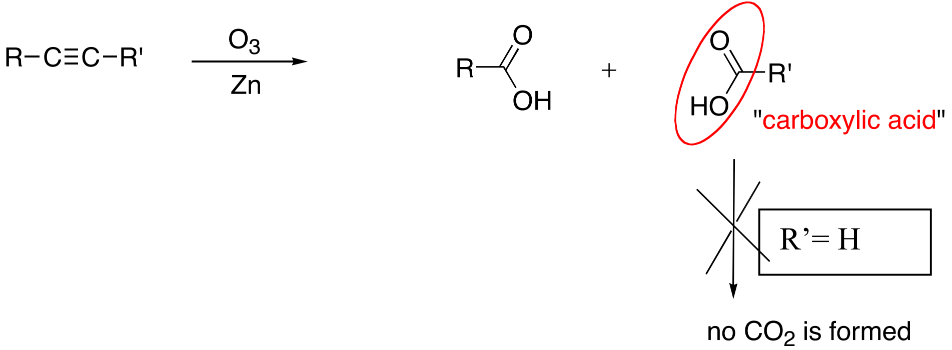


Oxidation of Alkynes

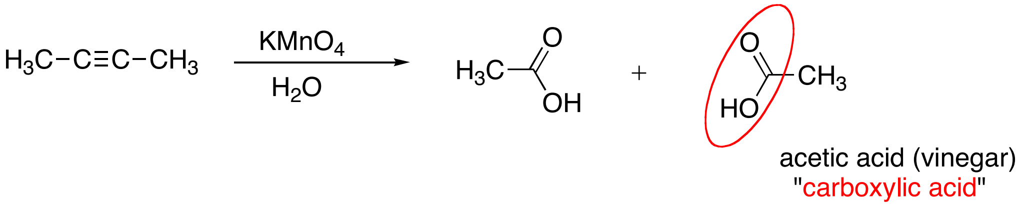
With potassium permanganate:



Ozonolysis:

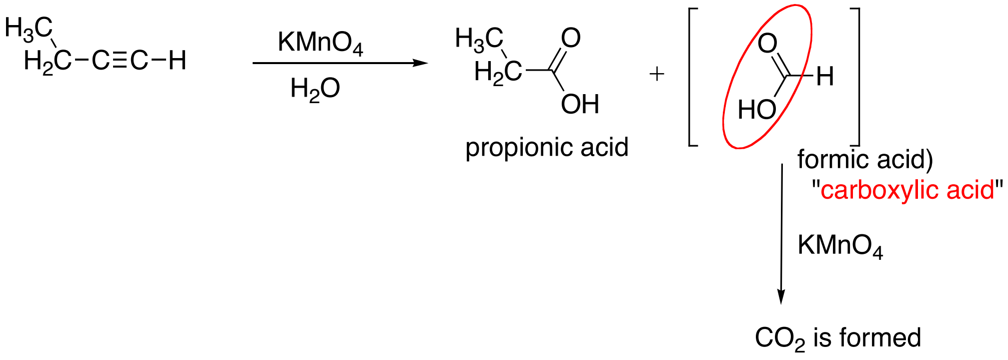


Oxidation of 2-butyne

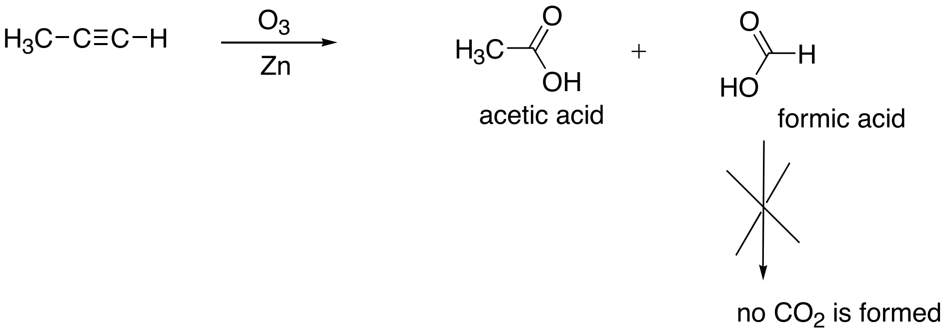


The same products are obtained by: 1) O_3 then 2) Zn

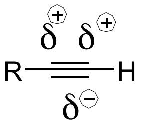
Oxidation of 1-butyne



Ozonolysis of propyne



Acidity of Alkanes / Alkenes / Alkynes:



$Pk_a = 26$

$$:NH_3 \rightleftharpoons :\ddot{N}H_2^{\ominus} + H^{\oplus}$$

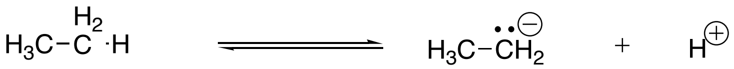
ammonia pKa = 36

$$H-\ddot{\underset{\cdot\cdot}{O}}-H \rightleftharpoons H-\ddot{\underset{\cdot\cdot}{O}}:^{\ominus} + H^{+}$$

Pka=16

Ethane / Ethene / Ethyne

Ethane

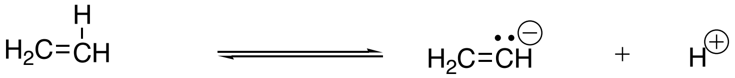


$$H_3C-\overset{H_2}{C}-H \rightleftharpoons H_3C-\ddot{C}H_2^{\ominus} + H^{\oplus}$$

$$Ka = \frac{[CH_3CH_2^{-}][H^{+}]}{[CH_3CH_3]} = 10^{-46}$$

pKa = 46

Ethene (ethylene)

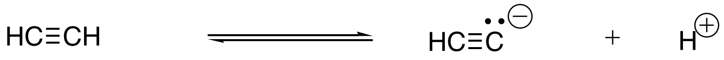


$$H_2C{=}CH_2 \rightleftharpoons H_2C{=}\ddot{C}H^{\ominus} + H^{\oplus}$$

$$Ka = \frac{[CH_2CH^-][H^+]}{[CH_2CH_2]} = 10^{-36}$$

pKa = 36

Ethyne (acetylene)



$$HC{\equiv}CH \rightleftharpoons HC{\equiv}\ddot{C}^{\ominus} + H^{\oplus}$$

$$Ka = \frac{[HC{\equiv}C^-][H^+]}{[HC{\equiv}CH]} = 10^{-26}$$

pKa = 26

How strong of a base is needed to deprotonate?

	acid		conjugate base
$HC{\equiv}C{-}H$ pKa = 26	$H_2N{-}H$	pKa ~ 36	H_2N^-
	$H_3C{-}H$	pKa ~ 45	H_3C^-
	$HO{-}H$	pKa ~ 15.7	HO^-

- H_2N^- and H_3C^- are strong enough bases to deprotonate a terminal alkyne, but water is not a strong enough.