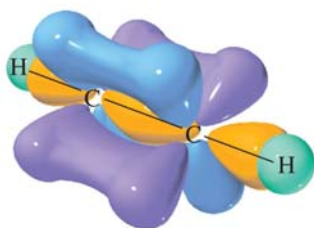
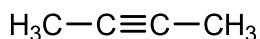


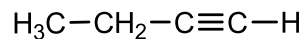
Alkynes: Structure and Acidity



Reminder: Alkynes have sp -hybridized carbons, linear (180°) geometry.

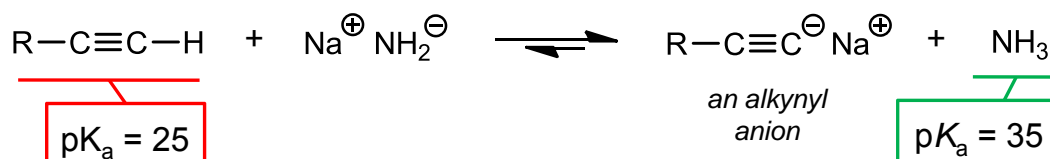


an *internal* alkyne



a *terminal* alkyne

The terminal proton of alkynes is slightly acidic.



So, strong bases deprotonate terminal alkynes.

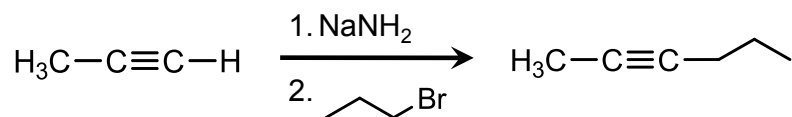
Alkynes: Structure and Acidity

Acid	Conjugate base	Hybridization	s character	pK_a	
$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}-\text{C}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}-\text{C}^- \\ & \\ \text{H} & \text{H} \end{array}$	sp^3	25%	50	weakest acid stronger acid
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C}^- \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	sp^2	33%	44	
$:\text{NH}_3$	$:\ddot{\text{N}}\text{H}_2^-$	(ammonia)		35	
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	$\text{H}-\text{C}\equiv\text{C}^-$	sp	50%	25	
$\text{R}-\text{OH}$	$\text{R}-\ddot{\text{O}}^-$	(alcohols)		16–18	

More s character = Electrons more closely held to nucleus
 = Anion better compensated by nuclear charge

Synthesis with Alkynyl Anions

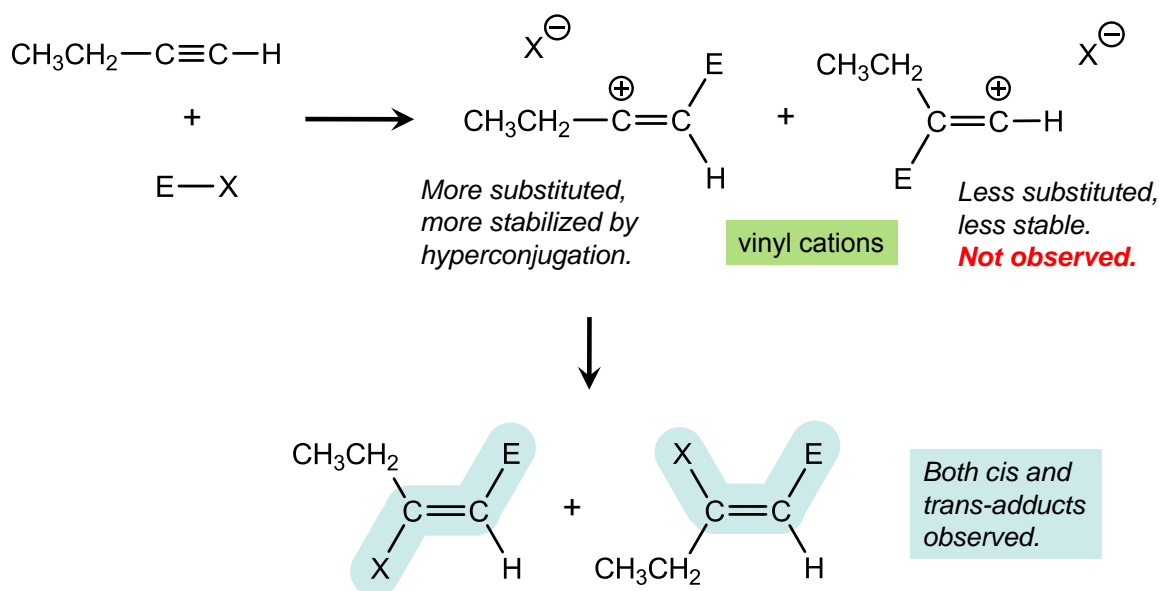
S_N2 on 1° halides:



Alkynyl anions are also strong bases, so S_N2 doesn't work well on 2° or 3° halides. (E2 interferes.)

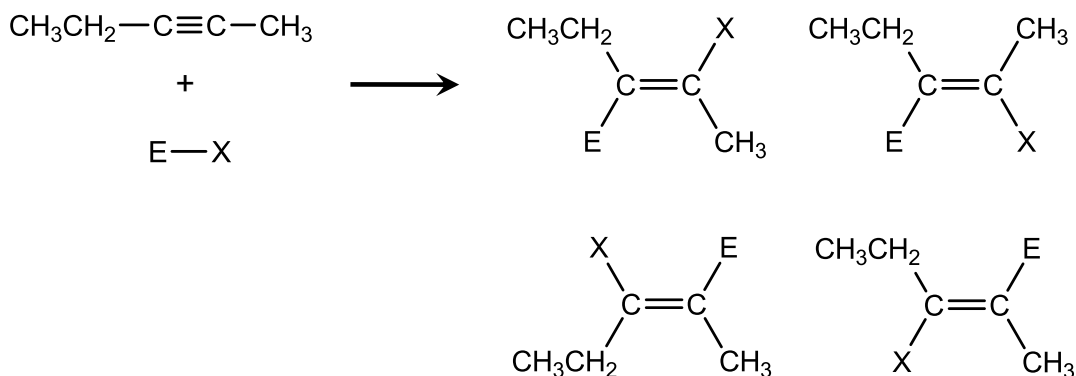
Electrophilic Addition to Terminal Alkynes

Follows Markovnikov's rule, passing through the most stable carbocation.



Electrophilic Addition to Internal Alkynes

No basis for regioselectivity. All possible products observed.

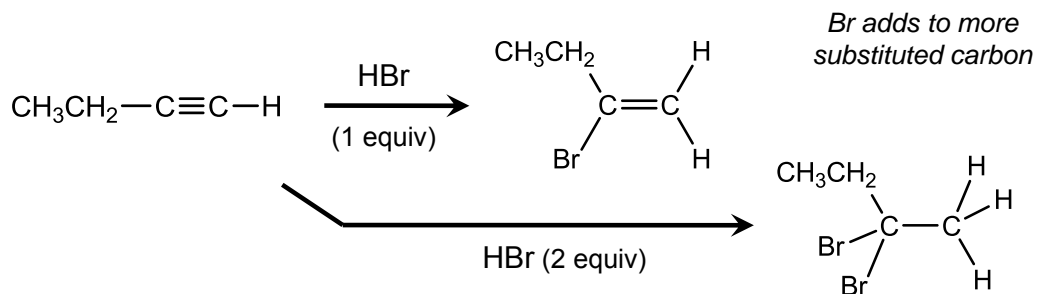


No selectivity means not very useful.

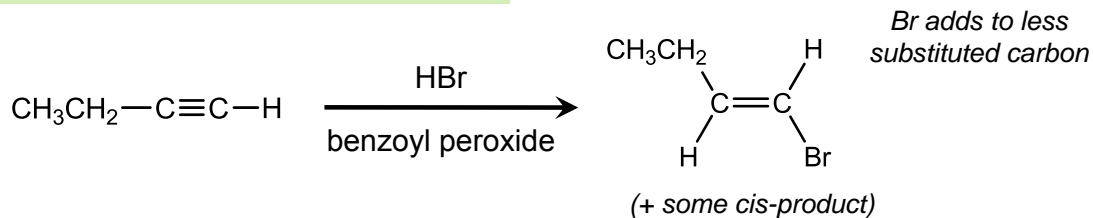
Hydrohalogenation of Terminal Alkynes

Identical conditions and selectivity to alkenes.

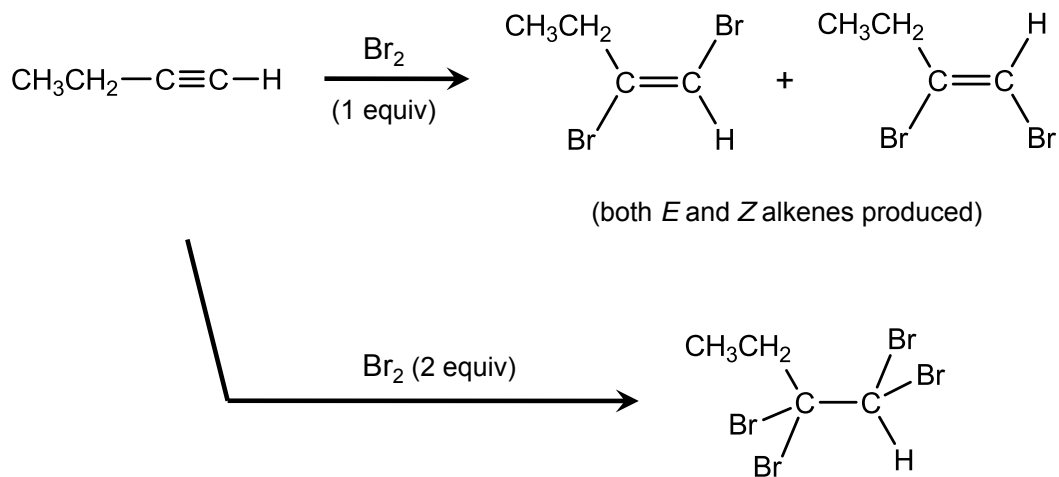
Markovnikov addition of H-Br:



Anti-Markovnikov addition of H-Br:

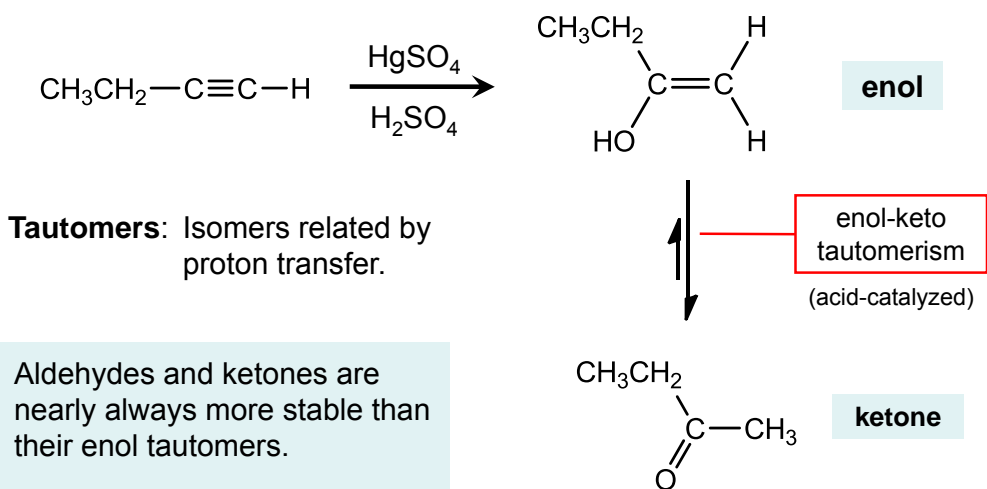


Halogenation of Alkynes



Markovnikov Hydration of Alkynes

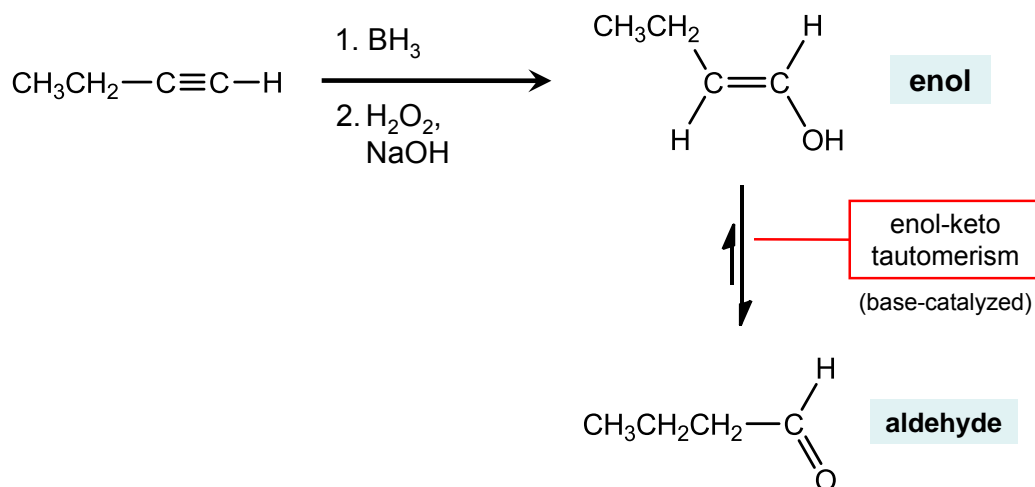
Forms an alkenyl alcohol—an enol—as a reactive intermediate.
But the eventual product is a ketone.



Aldehydes and ketones are nearly always more stable than their enol tautomers.

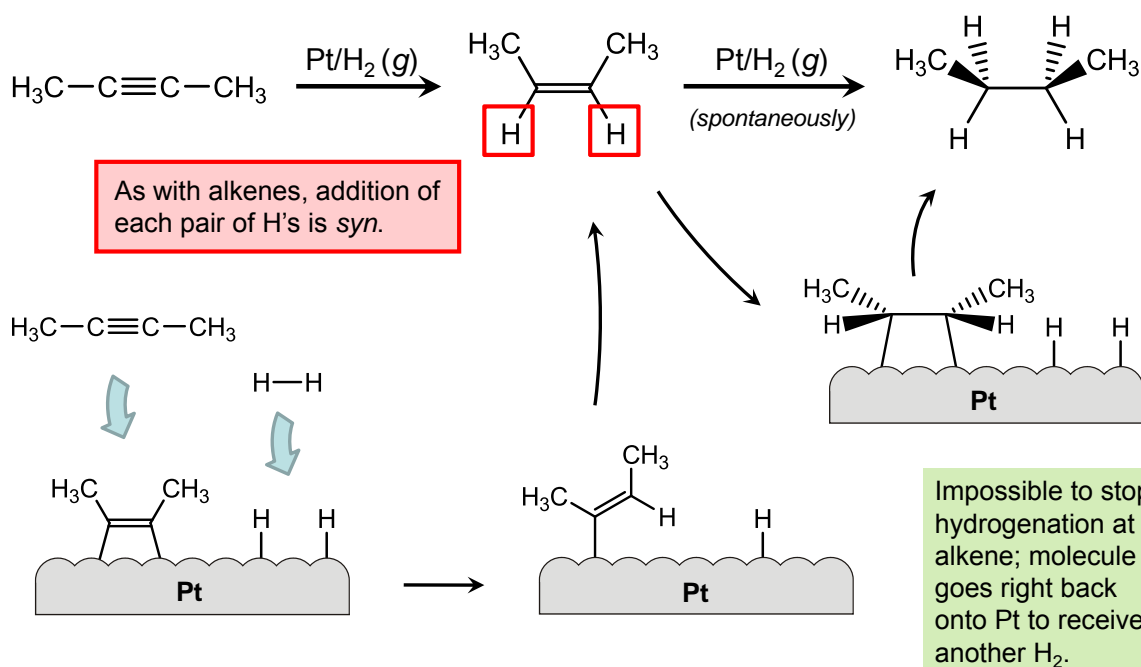
(Energy of C=O bond greater than that of C=C bond.)

Anti-Markovnikov Hydration of Alkynes



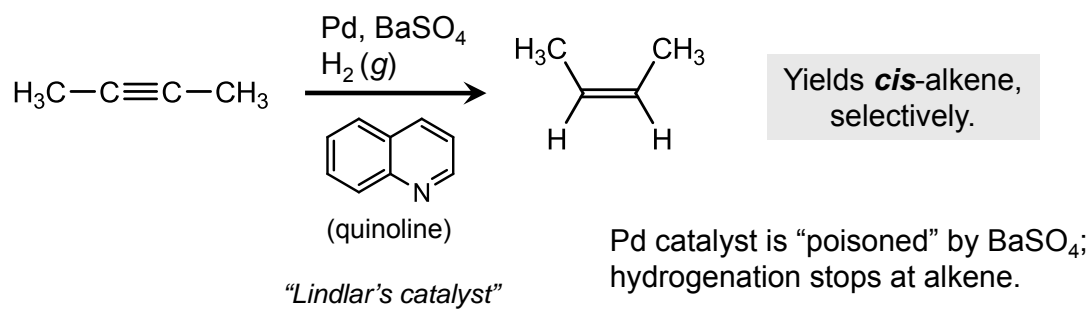
Catalytic Hydrogenation of Alkynes

Under standard conditions (Pt/H₂), alkynes are doubly hydrogenated to alkanes.



Selective Monohydrogenation of Alkynes

Alkynes → *cis*-alkenes:



Alkynes → *trans*-alkenes:

