

Chemistry 210 -- Fall Semester 1997

Chapter 12

Alkynes aka Acetylenes

Electronic Structure

Carbons are sp hybridized. σ bond and two orthogonal p orbitals generate π bonds.

Bond length and strength: 1.20 Å and 200 kcal/mol (strongest and shortest CC bond).

By comparison of the C σ bond to the C=C and C-C bond strengths, we may dissect the three bonds and assign individual bond strengths of 88, 64, and 48 kcal/mol.

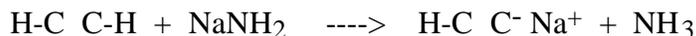
Acidity

The acetylenic C-H is quite acidic! Big difference compared to C-H bonds in alkanes and alkenes.

The pK_a values of ethanol, acetylenes, and ammonia are 16, 25, and 35.

The pK_a values of alkanes, olefines, and acetylenes are >60, 44, and 25.

Amides deprotonate acetylenes and alcohols (the base of a weaker acid is a stronger base).



The alkynyl anions can then be used in nucleophilic displacement reactions, see below.

Nomenclature

Ending -ine or -yne.

Double bonds receive lower number than do triple bonds.

Example 1: 1-hepten-6-yne

Example 2: HC \equiv C-CH₂-CHMe-CH₂-CH₂-CH=CH-CH₂

Unsaturated side chains.

CH₃-CH₂-CH₂-CH₂- butyl

CH₃-CH₂-CH=CH- 1-butenyl

CH₃-CH₂-C \equiv C- 1-butyne H-C \equiv C- ethynyl

Preparation

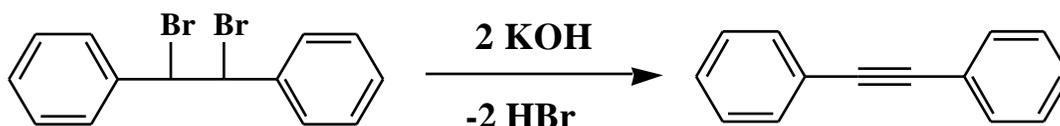
(a) Pyrolysis of Methane (Industrial only)



(b) Alkynes *via* Double Elimination

1,2-dihalides can form alkynes by elimination of two HX under the influence of strong base (KOH in alcohol). Sequence: 1,2-dihalide \rightarrow vinylhalide \rightarrow acetylene.

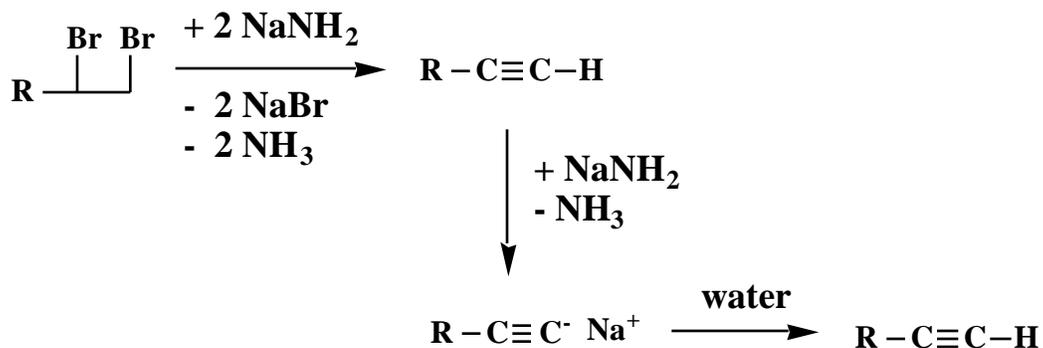
Example 1: Nonterminal acetylene formation from stilbene (NaNH₂ or KOH in CCl₄).



Example 2: 3-chloro-2-buten-1-ol with NaNH₂ in CCl₄ gives the *alcoholate* of 2-butyne-1-ol in 85% yield and protonation with dilute acid regenerates the alcohol.



Example 3: Terminal acetylene formation. The base makes the acetylide anion and the acetylene is reformed by hydrolysis.



(c) Large Alkynes from Small Alkynes

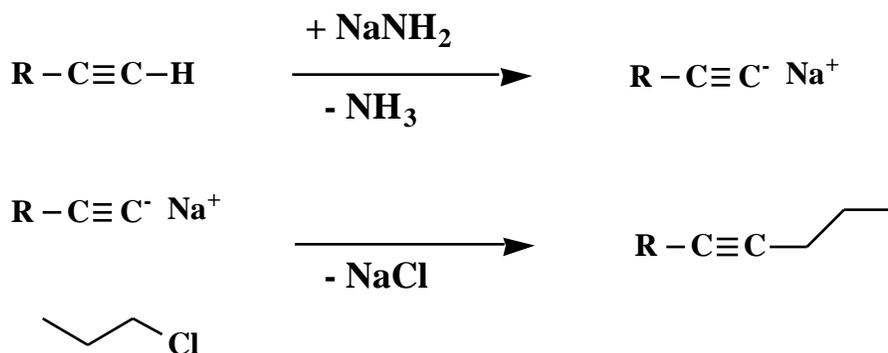
We use the property of alkynes to form acetylides. These acetylides are nucleophilic enough to undergo S_N2 reactions with alkyl halides.

There are two steps involved: (a) formation of the acetylide and (b) its reaction with an alkyl halide or (c) its reaction with a ketone (Grignard Reaction)

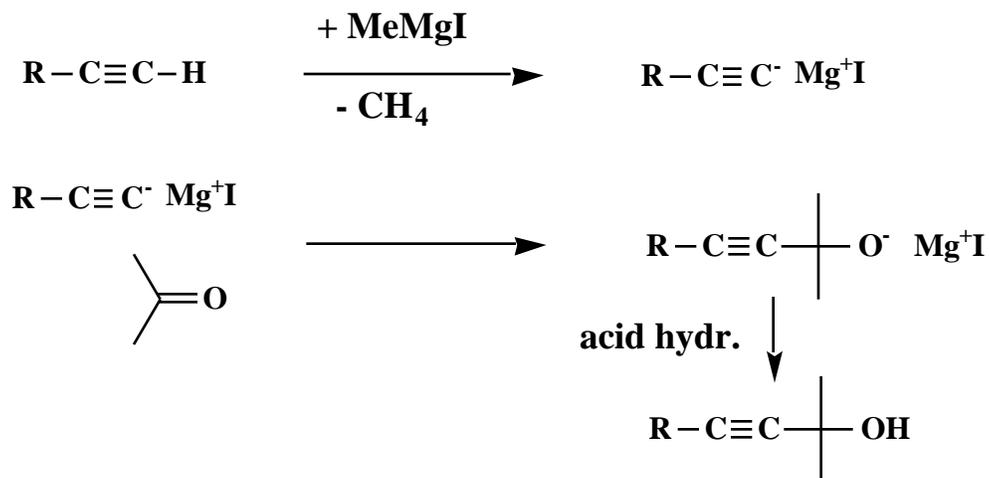
(a.1) Treat alkyne with strong base (NaNH₂) to form the sodium acetylide.

(a.2) Treat alkyne with GR to form the acetylide Grignard reagent.

Example 1: Reaction with Alkyl Halide.



Example 2: Grignard Reaction.



X₂ and HX Additions

Trans HX addition (mostly) occurs following the Markownikow rule. Sometimes two HX are added and the product of single addition (the alkene) cannot be isolated.

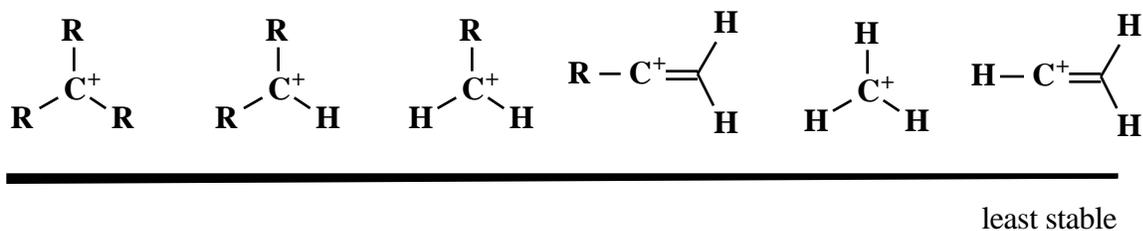
However, the triple bond is less nucleophilic than the double bond and strong “small cation” Lewis acid catalysts are required in some cases.

Famous example: Vinyl chloride formation. (Not modern)

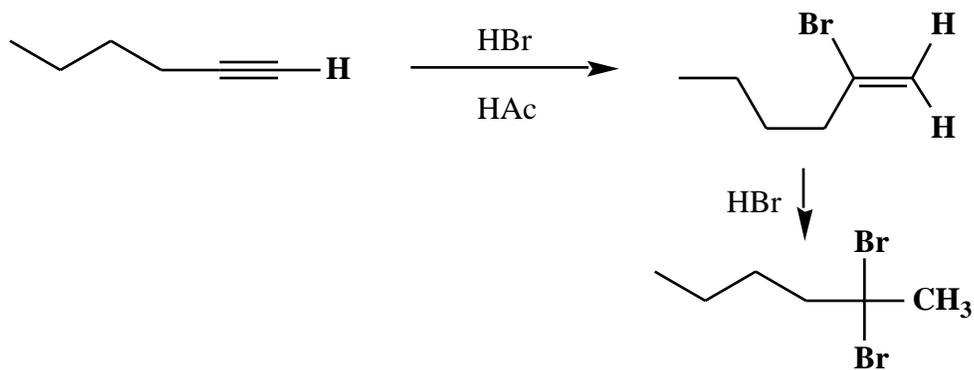


Mechanism

Protonation or in general the electrophile addition leads to a “vinyl cation” which then adds the nucleophile in the second step. These unsaturated *vinyl cations* are not so stable; comparable stability with methyl cation.



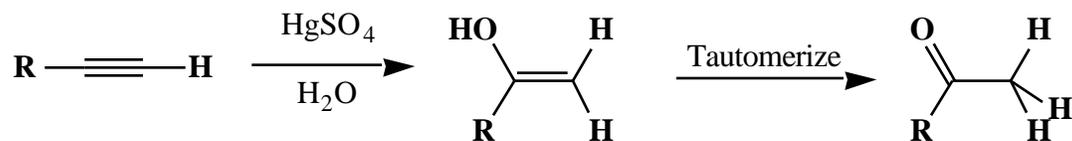
Example: HBr addition to 1-Hexyne



Example: Br₂ addition (twice) to 1-butyne in “tetra”.

Hydration of Alkynes

Requires a “small metal cation” catalyst. Very important reaction to make methylketones from terminal alkynes. (Non-terminal alkynes give a mixture of two products.) The initial product is the Markownikow enol which then undergoes tautomerization (H shift) to the more stable ketone.



Mechanism

- (1) Add HgSO_4 to the triple bond and form a (bridged) vinyl cation.
- (2) Add water and lose a proton from it; effectively you added OH.
- (3) Eject the HgSO_4 with dilute acid. H replaces the HgSO_4 .
- (4) Tautomerize the enol to the keto form.

Hydroboration of Alkynes

Like the hydration, hydroboration gives carbonyls but the mechanism does not involve carbenium ions. The mechanism is just like in the hydroboration of the alkenes. We get alcohols -- here they are enols -- and then ketones because of tautomerization.

Works well for symmetric ketones, e.g. 3-hexyne which will give exclusively 3-hexanone.

Mechanism

- (1) Add BH_3 in THF to make vinylic borane
- (2) Oxidize with hydrogenperoxide in alkaline water (NaOH) to get the enol.
- (3) Tautomerize the enol to get the ketone.

<p>Major Difference Concerns Regiochemistry</p>

<p>Metal cation catalysed Hydration -- M Product -- Term. Alkyne \Rightarrow Ketone</p>
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<p>Hydroboration-Oxidation -- Anti-M Product -- Term. Alkyne \Rightarrow Aldehyde</p>
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Reduction of Alkynes

(a) Catalytic hydrogenation reduces alkynes more easily than alkenes; the heats of hydrogenation are 42 and 33 kcal/mol for the sequence acetylene - ethylene - ethane.

Lindlar catalysts allow to stop hydrogenation at the alkene stage. Pd on CaCO₃ and treated with PbAc₂ and quinoline.

(b) Lithium or sodium in ammonia reduction. Li dissolves below -33°C in liquid ammonia giving a blue solution that contains free electrons and Li⁺ cation. *Trans* alkenes result.



Mechanism

- (1) Single electron addition gives a radical anion.
- (2) Protonation with ammonia gives a neutral vinylic radical.
- (3) Add another electron to give the vinyl lithium -- stereochemistry decided here.
- (4) Protonation with ammonia to give the alkene.

Oxidative Cleavage of Alkynes

Powerful oxidizing reagents (KMnO₄, O₃) give the products with highest possible oxidation state. That is, each R-C will become an acid carbon R-COOH and each H-C will become HCOOH (CO and H₂O) which is then further oxidized to CO₂ and water.