Chapter 8: Alkynes

sp Hybridized Orbitals

hybridize one s-orbital and one p-orbitals

leave two p-orbital unhybridized

C≡C triple bonds - acetylene (C₂H₂)

106 pm 180°
H — C≡C — H
120 pm
Alkyne Nomenclature

**Systematic Nomenclature (IUPAC System)**
Prefix-Parent-Suffix

**Naming Alkynes**
Suffix: -yne

Many of the same rules for alkanes apply to alkenes

1. Number the carbon chain from the end of the carbon nearest the triple bond
2. The alkyne position is indicated by the number of the alkyne carbon in the chain
3. Compounds with two triple bonds are referred to as diynes, three triple bonds as triynes, etc

Preparation of Alkynes

a. Elimination reactions of 1,2-dihalides

*Recall:*

\[
\text{R}_1\text{R}_2\text{H} \xrightarrow{\text{KOH}} \text{R}_1\text{R}_2\text{R}_3 + \text{HOH + KX}
\]

\[
\text{R}_1\text{R}_2\text{H} \xrightarrow{\text{Br}_2} \text{R}_1\text{R}_2\text{Br} \xrightarrow{\text{NaNH}_2} \text{R}_1\text{R}_2 \text{H} + \text{HNNH}_2 + \text{NaBr}
\]

* cis or trans 1,2-dibromide

* vinyl bromide

\[
\text{R}_1\text{R}_2\text{H} \xrightarrow{\text{NaNH}_2} \text{R}_1\text{R}_2 \text{H} + \text{HNNH}_2 + \text{NaBr}
\]

* alkynes

b. From other alkynes. **Section 8.8 - 8.10**

**Terminal Alkyne:** triple bond is at the end of the carbon chain

**Internal Alkyne:** triple bond is not at the end of the carbon chain
Reactions of Alkynes:
Addition of HX- Markovnikov addition

![Addition of HX diagram]

Addition of $X_2$

![Addition of $X_2$ diagram]

Vinyl carbocations are generally less stable than the corresponding alkyl carbocation

**Carbocation Stability**

- $3^\circ$ alkyl
- $2^\circ$ alkyl
- $1^\circ$ alkyl
- $2^\circ$ vinyl
- methyl carbocation
- $1^\circ$ vinyl
Hydration of Alkenes

\[
\text{Alkenes} \xrightarrow{\text{hydration}} \text{Alcohols} \\
\text{Alkynes} \xrightarrow{\text{hydration}} \text{Ketones or Aldehydes}
\]

Mercury (II) Catalyzed Hydration: similar to oxymercuration - Markovnikov Addition

\[
\begin{align*}
R-C≡C-H & \xrightarrow{\text{HgSO}_4, \text{H}_3\text{O}^+} RCH_3 \\
R_1-C≡C-R_2 & \xrightarrow{\text{HgSO}_4, \text{H}_3\text{O}^+} R_1-CO-R_2 + R_1-C≡C-R_2
\end{align*}
\]

Keto-enol tautomeration
tautomer: constitutional isomers that interconvert

\[
\begin{align*}
\text{enol} & \xleftrightarrow{} \text{keto} \\
C=\text{C} & \quad \Delta H^\circ = 611 \text{ KJ/mol} \\
C-O & \quad \Delta H^\circ = 380 \\
O-H & \quad \Delta H^\circ = 436
\end{align*}
\]

\[
\begin{align*}
C=\text{O} & \quad \Delta H^\circ = 735 \text{ KJ/mol} \\
C-\text{C} & \quad \Delta H^\circ = 376 \\
\text{C-H} & \quad \Delta H^\circ = 420
\end{align*}
\]

\[\Delta H^\circ = -104 \text{ KJ/mol}\]
Keto-Enol Tautomerization and the Structure of DNA

Proposed structure:

Proposal inconsistent with Chargaff’s Rule

Watson-Crick (-Donohue) Base Pairing
Hydroboration of Alkynes

\[
\text{R-C≡C-H} \rightarrow 1) \text{BH}_3, \text{THF} \\
2) \text{H}_2\text{O}_2, \text{NaOH} \\
\text{aldehyde}
\]

\[
\text{R}_1\text{C≡C-R}_2 \rightarrow 1) \text{BH}_3, \text{THF} \\
2) \text{H}_2\text{O}_2, \text{NaOH} \\
\text{ketones}
\]

Hydrogenation of Alkynes

\[
\text{H-C≡C-H} \xrightarrow{\text{H}_2, \text{catalyst}} \text{H}_2\text{C}=\text{C}=\text{H} \quad \Delta H_{\text{hydrogenation}} = -176 \text{ KJ/mol}
\]

\[
\text{H}_2\text{C}=\text{C}=\text{H} \xrightarrow{\text{H}_2, \text{catalyst}} \text{H}_2\text{C}=\text{C}=\text{H} \quad \Delta H_{\text{hydrogenation}} = -137 \text{ KJ/mol}
\]

The second σ-bond of an alkyne is slightly more reactive toward hydrogenation.

Under normal hydrogenation conditions, hydrogenation of an alkyne can not be stopped at the alkene stage.

\[
\text{R}_1\text{C≡C-R}_2 \xrightarrow{\text{H}_2, \text{Pd}} \begin{bmatrix} \text{H} \\ \text{R}_1 \\ \text{R}_2 \end{bmatrix} \xrightarrow{\text{H}_2, \text{Pd}} \begin{bmatrix} \text{H} \\ \text{R}_1 \\ \text{R}_2 \end{bmatrix}
\]
Lindlar’s catalyst: “poisoned” palladium catalyst
Pd on CaCO₃ + Pb(OAc)₄ + quinoline (amine)

“poisons” reduce the catalyst’s activity so only the most reactive functional groups are hydrogenated

\[
\begin{align*}
\text{cis-addition of } H_2 \quad \text{Reaction can be stopped at the cis-alkene stage}
\end{align*}
\]

Dissolving Metal Reduction:
Li(0) metal in liquid ammonia (NH₃)
Li(0) in NH₃ → e⁻ (solvated electron)

\[
\begin{align*}
\text{trans-alkene}
\end{align*}
\]
Oxidative cleavage of alkenes (sect. 7.8):

Alkynes are less reactive toward oxidative cleavage than alkenes. Alkenes can be oxidatively cleaved in the presence of alkynes.

Oxidative Cleavage of Alkynes (sect. 8.7)

Alkynes are less reactive toward oxidative cleavage than alkenes. Alkenes can be oxidatively cleaved in the presence of alkynes.

Acidity of Terminal Alkynes

\[
\text{R-CC-C-H} \quad \text{R-CC-C-}^{-} + \text{H}^+ \quad \text{pKa} = 25
\]

Acetylide anion

\[
\text{R-CC-C-H} + \text{NaNH}_2 \quad \text{R-CC-C-}^{-} + \text{NH}_3 \quad \text{Na}^+ \quad \text{pKa} = 35
\]

\[
\text{H-C-C-H} \quad \text{H-C-C-}^{-} + \text{H}^+ \quad \text{pKa} = 45
\]

\[
\text{H-C-C-H} \quad \text{H-C-C-}^{-} + \text{H}^+ \quad \text{pKa} = 60
\]
Alkylation of the acetylide anion: formation of C-C bonds
a substitution reaction between a nucleophile and alkyl halide

Acetylide anions are strong nucleophiles and will undergo substitution reactions with alkyl halides

\[
\begin{align*}
R\text{C≡C}^- & + \text{R}^1\text{C}-\text{Br} & \xrightarrow{\text{THF}} & \text{R}^1\text{C≡C}^- + \text{R}^1\text{Br} \\
\text{new C-C bond formed}
\end{align*}
\]

The acetylide anion displaces bromide from the alkyl bromide forming a new C-C bond.

Alkylation is a general method of making alkynes from simpler alkynes.

Alkylation of acetylide anions is generally limited to primary alkyl bromides and iodide

Organic Synthesis

Synthesis: making larger, more complex molecules out of smaller ones using known and reliable reactions

Prepare octane from 1-pentyne

\[
\begin{align*}
\text{H}_3\text{CCH}_2\text{C≡CCH} & \xrightarrow{\text{a) NaNH}_2, \text{b) CH}_3\text{CH}_2\text{CH}_2\text{I}} \text{H}_3\text{CCH}_2\text{C≡CCH}_2\text{CH}_2\text{CH}_3 & \xrightarrow{\text{H}_2, \text{Pd}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]

Prepare Z-2-butene from 1-pentyne

\[
\begin{align*}
\text{H}_2, \text{Lindlar Catalyst}
\end{align*}
\]

work the problem backwards