Chapter 9: Alkynes

9.1: Sources of Alkynes (please read)

9.2: Nomenclature

Systematic Nomenclature: Prefix-Parent-Suffix
Naming Alkynes: Suffix: -yne

Many of the same rules for alkenes apply to alkynes

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

9.3: Physical Properties of Alkynes (please read)

9.4: Structure and Bonding in Alkynes: sp Hybridization

\[
\text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H}
\]

bond angles:
\[
\text{H} - \text{C} - \text{C} = 180^\circ \quad \text{(linear geometry)}
\]

bond distances:
\[
\text{C} - \text{H} = 106 \text{ pm} \\
\text{C} \equiv \text{C} = 120 \text{ pm}
\]

Each carbon is \(sp\) hybridized – linear geometry

C\equiv C bond consists of one \(\sigma\)-bond (\(sp\) hybridized orbitals) and two \(\pi\)-bond (unhybridized \(p\)-orbitals) (see ch. 2 notes)

Bond dissociation energies (\(\Delta H^{\circ}_{C-C}\))
\[
\Delta H^\circ \text{C} \equiv \text{C} = 611 \text{ KJ/mol} \\
\Delta H^\circ \text{C} \equiv \text{C} = 820 \text{ KJ/mol} \\
\Delta H^\circ \text{C} - \text{C} = 368 \text{ KJ/mol} \\
\Delta H^\circ \text{C} - \text{C} = 368 \text{ KJ/mol}
\]

\(\pi\)-bond = 243 KJ/mol \(\pi\)-bonds = 452 KJ/mol

\[
226 \text{ KJ/mol per } \pi \text{-bond}
\]

The \(\pi\)-bond of an alkene is \(~17 \text{ KJ/mol more stable}\) than the \(\pi\)-bond of an alkyne.
9.5: Acidity of Acetylene and Terminal Alkynes

In general, the C-H bond of hydrocarbons are very weak acids. The R-C≡C-H bond of a terminal acetylene is weakly acid, pK_a ~26.

A strong base can deprotonate terminal acetylenes to generate an acetylide anion.

\[
\begin{align*}
R-C≡C-H & \quad + \quad B^- \quad \text{Na}^+ & \quad \text{R-C≡C-H} & \quad + \quad B^+ \quad \text{Na}^+ \\
pK_a &= 26 & \text{pK}_a &= \text{?}
\end{align*}
\]
9.6: Preparation of Alkynes by Alkylation of Acetylene and Terminal Alkynes - Acetylide anions are strong nucleophiles and will undergo nucleophilic substitution reactions with primary alkyl halides, resulting in the formation of a C-C bond.

\[
\begin{align*}
R\equiv C\equiv C^\cdot + H^\equiv C\equiv C-Br & \xrightarrow{\text{THF}} R\equiv C\equiv C\equiv C\equiv C^\cdot + NaBr \\
\text{new C-C bond formed}
\end{align*}
\]

Alkylation of acetylide anions is a general method of making higher alkynes from simpler alkynes.

\[
\begin{align*}
H\equiv C\equiv C\equiv C\equiv H + H_2N^-Na^+ & \rightarrow H\equiv C\equiv C^- \\
H\equiv C\equiv C^- + H_2CH_2CH_2C-Br & \rightarrow H_2CH_2CH_2C\equiv C\equiv C\equiv H \quad \text{pentyne} \\
H_2CH_2CH_2C\equiv C\equiv C\equiv H + H_2N^-Na^+ & \rightarrow H_2CH_2CH_2C\equiv C\equiv C^- \\
H_2CH_2CH_2C\equiv C^- + H_2I & \rightarrow H_2CH_2CH_2C\equiv C\equiv CH_3 \quad 2\text{-hexyne}
\end{align*}
\]

Alkylation of acetylide anions is generally limited to primary alkyl halides. Acetylide anions act as a base with secondary and tertiary alkyl halides resulting in E2 elimination.

9.7: Preparation of Alkynes by Elimination Reactions

Double dehydrohalogenation reaction

\[
\begin{align*}
R\equiv C\equiv C\equiv C\equiv C\equiv C\equiv CH_3 + H_2N^-Na^+ & \rightarrow R\equiv C\equiv C\equiv C\equiv C\equiv CH_3 \\
\text{3 equivalents of NaNH}_2 \text{ are required for preparing terminal alkynes from from 1,2- or 1,1-dihaloalkane.}
\end{align*}
\]
9.8: Reactions of Alkynes - alkynes undergo addition reactions similar to alkenes.

Increasing oxidation state

9.9: Hydrogenation of Alkynes - The hydrogenation of an alkyne cannot be stopped at the alkene stage under normal hydrogenation conditions (H₂, metal catalyst)

\[ R_1-C≡C-R_2 + H_2, Pd/C \rightarrow [H_2, Pd/C] \rightarrow H_2, Pd/C \rightarrow H \]

cis alkene intermediate

The π-bonds of alkenes are slightly more reactive toward hydrogenation than the π-bond of an alkene.

Lindlar’s catalyst: “poisoned” palladium catalyst
\[ Pd \text{ on } CaCO_3 + Pb(OAc)_4 + \text{quinoline (amine)} \]

“poisons” reduce the catalysts activity so only the most reactive functional groups are hydrogenated

Hydrogenation can be stopped at the cis-alkene stage with Lindlar’s catalyst

9.10: Metal-Ammonia Reduction of Alkynes - Dissolving Metal Reduction: Li(0) metal in liquid ammonia (NH₃)

\[ \text{Li(0) in NH}_3 \rightarrow e^+ \text{ (solvated electron)} \]

\[ R_1-C≡C-R_2 + \text{Li, NH}_3, (CH_2)_3\text{COH} \rightarrow H \]

trans-alkene
9.11: Addition of Hydrogen Halides to Alkynes
Addition of HX to acetylenes: Markovnikov addition

only useful for terminal or symmetrical acetylenes ($R_1 = R_2$)

Mechanism?

rate = $k [\text{alkyne}][HX]^2$

Carbocation Stability

$gem$-dihaloalkanes are obtained with excess HX - addition follows Markovnikov's rule

Anti-Markovnikov addition of HBr to terminal alkynes in the Presence of peroxides (radical mechanism)
9.13: Addition of Halogens to Alkynes

\[ R_1\text{C}≡\text{C}R_2 + X_2 \rightarrow R_1\text{C}≡\text{CR}_2X + X_2 \]

**anti addition of** \( X_2 \)

9.12: Hydration of Alkynes

Alkenes → Alcohols

Alkynes → Ketones or Aldehydes

Hg (II) catalyzed hydration of alkynes: similar to oxymercuration - Markovnikov Addition

\[ R-C≡C-H + \text{HgSO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow R-\text{H} + \text{R}_1CH=\text{C}=\text{O} + \text{H}_2\text{SO}_4 \]

Tautomerization - equilibrium between two isomers (tautomer), which differ by the migration of a proton and a \( \pi \)-bond.

Keto-enol tautomerization - normally favors the keto form (C=O)

\[ \Delta H^\circ = 611 \text{ KJ/mol} \]
\[ \Delta H^\circ = 735 \text{ KJ/mol} \]

Keto-enol tautomerization is acid-catalyzed
Hydroboration of Alkynes - anti-Markovnikov hydration of an alkyne (complementary to the Hg(II) catalyzed method)

\[
\text{R} = \text{C} \equiv \text{C} - \text{H} 
\xrightarrow{1) BH_3, THF}
\text{Aldehyde product}
\xrightarrow{2) H_2O_2, NaOH}
\text{Aldehyde}
\]

Hg(II)-catalyzed hydration and hydroboration are equivalent for internal alkynes

\[
\text{R}_1 - \text{C} \equiv \text{C} - \text{R}_2 
\xrightarrow{1) BH_3, THF}
\text{Ketone products}
\xrightarrow{2) H_2O_2, NaOH}
\text{Ketone products}
\]

Hydration of an internal alkyne is only useful for symmetrical acetylenes (\(R_1 = R_2\))

9.14: Ozonolysis of Alkynes

Ozonolysis of alkenes (sect. XX):

\[
\text{R}_1 - \text{C} = \text{C} - \text{R}_2 
\xrightarrow{1) \text{O}_3}
\text{ketones and aldehydes}
\xrightarrow{2) \text{Zn}}
\text{R}_1 - \text{C} = \text{C} - \text{R}_2
\]

Ozonolysis of Alkynes

\[
\text{R} = \text{C} \equiv \text{C} - \text{H} 
\xrightarrow{1) \text{O}_3}
\text{Carboxylic acid}
\xrightarrow{2) \text{Zn}}
\text{Carboxylic acids}
\]

Alkynes are less reactive toward ozonolysis than alkenes. An alkenes can be oxidatively cleaved by ozone in the presence of an alkyne.
Prepare octane from 1-pentyne

\[
\text{H}_3\text{C}-\text{CH}_2-\text{C}≡\text{CH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

Prepare \((Z)-2\)-hexene from 1-pentyne

\[
\text{H}_3\text{C}-\text{CH}_2\text{CH}_2-\text{C}≡\text{CH} \rightarrow \text{Z-2-hexene}
\]

Prepare 4-octanone from acetylene

\[
\text{HC}≡\text{CH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{O}
\]