Alkynes

Alkynes are compounds that contain a carbon-carbon triple bond

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

Acetylene
(common name for Ethyne)

overall many reactions are similar to alkene reactions
- therefore observe many reactions that are electrophilic additions to multiple bonds and oxidation reactions
Nomenclature

Follow same rules as seen for alkenes
- find longest continuous chain containing the triple bond
- number the chain so that the lowest number is obtained for the triple bond
- use a –yne suffix with the correct root name

\[
\begin{align*}
\text{\begin{tikzpicture}
\draw (0,0) -- (2,0) -- (3,0);
\end{tikzpicture}} & \quad \text{2-heptyne} \\
\text{\begin{tikzpicture}
\draw (0,0) -- (2,0) -- (3,0);
\fill (2,0) circle (2pt) node[below] {Br};
\end{tikzpicture}} & \quad \text{6-bromo-3-heptyne}
\end{align*}
\]
Electronic Structure

Remember where electrons are held for an alkyne

The triple bond refers to one $\sigma$ and two $\pi$ bonds
-the two $\pi$ bonds are orthogonal to each other

As the number of bonds increases between two carbons, the bond length decreases
- C-C triple bond: bond length 1.20 Å
- C-C double bond: bond length 1.33 Å
- C-C single bond: bond length 1.54 Å
Acidity

One effect of the increase in number of bonds (and bond length changes) is the acidity of an sp hybridized carbon-hydrogen bond.

As the resultant lone pair of electrons (the pair formed after the proton is abstracted in an acid-base reaction) becomes closer to the positively charged nucleus the lone pair is MORE STABLE.

As the stability of the deprotonated form increases the conjugate is more acidic.

Therefore while abstracting an sp$^3$ or sp$^2$ hybridized C-H is difficult, an sp hybridized C-H bond can easily be abstracted with common bases.
Learn the acidity of terminal Alkynes versus other alkyl groups and bases

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \rightarrow \quad \text{CH}_3\text{CH}_2^\ominus \quad \text{pKa} \quad 50 \\
\text{H} & = \quad \rightarrow \quad \text{H}^\ominus \quad \text{pKa} \quad 44 \\
\text{NH}_3 & \quad \rightarrow \quad \text{NH}_2^\ominus \quad \text{pKa} \quad 35 \\
\text{R} & = \quad \rightarrow \quad \text{R}^\ominus \quad \text{pKa} \quad 25 \\
\text{ROH} & \quad \rightarrow \quad \text{RO}^\ominus \quad \text{pKa} \quad 16
\end{align*}
\]

Therefore while alkoxides cannot deprotonate an alkyne, amides can easily deprotonate
Acidity of sp hybridized C-H allows creation of useful nucleophile

\[
\begin{align*}
R\equiv H & \quad \rightarrow \quad R\equiv^- \\
R\equiv^- & \quad \rightarrow \quad R\equiv^\ominus \\
R\equiv^\ominus & \quad \rightarrow \quad R\equiv^- \\
R\equiv^- & \quad \rightarrow \quad R\equiv R'
\end{align*}
\]

Hence an internal alkyne can be synthesized from a terminal alkyne
Can react nucleophilic acetylide with other electrophiles

\[ \text{R} \equiv \text{O} \rightarrow \text{R} \equiv \text{H} \]

ketone

aldehyde

formaldehyde
Can also synthesize alkynes by elimination route

\[
\begin{array}{c}
\text{R} \quad \text{H} \quad \text{H} \\
\text{X} \quad \text{X} \\
\end{array}
\quad \xrightarrow{\text{KOH, } \Delta} 
\begin{array}{c}
\text{R} \\
\equiv \\
\text{R} \\
\end{array}
\]

Need very strong conditions for this reaction to occur

Harder to eliminate the second hydrogen halide group than the first

With this route often obtain a mixture of rearranged products where the alkyne has shifted to another position
Reactions of Alkynes

Many reactions are similar to reactions of alkenes studied earlier

Reduction of alkynes
With two $\pi$ bonds important to realize a variety of structures can be obtained depending upon the reducing conditions used

If use hydrogen gas with a variety of metal catalysts (Pt, Pd, Ni are common choices) it is hard to stop at the alkene, the alkyne will be fully reduced to the alkane
Alkyne to Alkene

To stop at the alkene stage the alkyne needs to be reduced with a weaker catalyst

One approach is to use a “poisoned” catalyst (Lindlar’s catalyst) the catalyst has impurities added which lower the effectiveness of the metal surface

\[
\begin{align*}
R-\equiv-R & \xrightarrow{H_2 \text{ and Lindlar's catalyst}} R=\equiv=\equiv R \\
\end{align*}
\]

*Obtain cis reduction, because the alkyne must approach the metal surface from one direction, hence both hydrogens are added from the same side
Alkyne to trans-Alkene

To obtain a trans alkene from reduction of alkyne a different mechanism is required

Dissolving metal reduction yields the trans product

\[
R\equiv R \quad \xrightarrow{\text{Na/NH}_3} \quad R=H \quad H=H \quad H=R
\]

Reaction is run at low temperature so that the ammonia is a liquid (acts as solvent)

Mechanism involves dissolved electrons reducing the alkyne
Mechanism of Dissolved Metal Reduction

Na $\text{NH}_3$ $\rightarrow$ Na$^+$ $\text{NH}_3$ e$^-$

sterically place R groups apart

1) e$^-$ 2) $\text{NH}_3$

$\text{H}^\cdot$ $\text{R}$ $\rightarrow$  $\text{R}$ $\text{H}$

1) e$^-$ 2) $\text{NH}_3$

$\text{H}^\cdot$ $\text{R}$ $\rightarrow$  $\text{R}$ $\text{H}$
Hydrogen Halide Addition

Reaction occurs analogous to alkene additions
Obtain mixture of trans and cis products with internal alkynes

\[
\begin{align*}
R\equiv H & \xrightarrow{HX} R=H \xrightarrow{X}\oplus \text{H} \quad \xrightarrow{X}\oplus \text{H} \\
& \quad \quad \text{obtain more stable} \\
& \quad \quad \text{carbocation intermediate}
\end{align*}
\]

With second equivalent of HX can get second addition to alkene

Obtain geminal (on the same carbon) dihalogen due to more stable carbocation formed

Can stop at either stage (one addition or two additions) depending upon equivalents
In contrast to hydrogen halide addition, it is very difficult to stop at only one addition of halogen to an alkyne, mainly obtain two molar additions.
Hydration of Alkynes

To hydrate an alkyne a mercury catalyst is added (in contrast to alkene reactions when acidic water alone is sufficient)

\[ R\equiv H \xrightarrow{Hg^+} R\equiv Hg \xrightarrow{H^+} R\equiv HgO \]

The last step is a keto-enol equilibrium (equilibrium NOT resonance)
Keto-Enol Equilibrium

Generally the ketone form is more stable than the enol form (carbon-oxygen double bonds are relatively more stable)
Hydroboration

Hydroboration of alkynes can also occur
*need bulky reagent to prevent side reactions due to second $\pi$ bond
(Sia is an acronym for sec-isoamyl)

Notice hydroboration still occurs with syn addition and the regiochemistry is dictated by the stability of the initial carbocation intermediate
Oxidation of Borane Product

The borane can be oxidatively removed
(analogous to alkene reactions)

\[
\begin{align*}
\text{R} & \quad \text{H} \\
\text{H} & \quad \text{BR}_2 \\
\end{align*}
\xrightarrow{\text{H}_2\text{O}_2, \text{NaOH}}
\begin{align*}
\text{R} & \quad \text{H} \\
\text{H} & \quad \text{OH} \\
\end{align*}
\xrightarrow[\text{H}_2\text{O}_2, \text{NaOH}]{}
\begin{align*}
\text{R} & \quad \text{H} \\
\text{H} & \quad \text{O} \\
\end{align*}
\]

*if a terminal alkyne is used the product of this reaction sequence is an aldehyde after keto-enol equilibrium
Oxidation Reactions

The alkyne can also be oxidized similar to alkene reactions with transition metals
*cannot stop at oxidizing only one \( \pi \) bond

\[
\begin{align*}
\text{R} & \equiv \text{R} & \xrightarrow{\text{KMnO}_4} & \text{OHOOH} \\
\text{neutral} & & & \text{HOOR} \\
\rightarrow & & & \text{ROOR}
\end{align*}
\]

a geminol diol is equivalent to a carbonyl

The diketone can be overoxidized to two carboxylic acids when basic conditions are used

\[
\begin{align*}
\text{ROOR} & \xrightarrow{\text{KMnO}_4} \text{ROO}^- \\
\text{KOH, } \Delta & \rightarrow \text{ROO}^- \\
\xrightarrow{\text{H}^+} & \rightarrow \text{ROOH}
\end{align*}
\]
Ozonolysis

An ozonolysis will oxidize to only type of product
(exactly similar to alkene reactions)

\[
\begin{align*}
R & \equiv R \\
& \xrightarrow{1) \text{O}_3} \\
& \xrightarrow{2) \text{H}_2\text{O}} \\
& \rightarrow R\text{CO}_2\text{H}
\end{align*}
\]

With ozonolysis both ends of the alkyne become oxidized to the carboxylic acid stage