Alkynes

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Nomenclature

• “-yne” is the suffix indicating an alkyne

• Numbering of chain with triple bond is set so that the smallest number possible is assigned to the first carbon of the triple bond

Begin numbering at the end nearer the triple bond.

6-Methyl-3-octyne
(New: 6-Methyl-oct-3-yne)

1-Hepten-6-yne
(New: Hept-1-en-6-yne)

4-Methyl-7-nonene-1-yne
(New: 4-Methyl-non-7-en-1-yne)

Butyl
(an alkyl group)

1-Butenyl
(a vinylic group)

1-Butynyl
(an alkynyl group)

(New: But-1-enyl)

(New: But-1-ynyl)
Physical Properties and Applications

Physical Properties

• Similar to alkenes and alkynes
• small molecular weight alkynes are gases and then become liquid as the weight increases (more van der Waal forces).
• They are insoluble in water.

Applications

• Acetylene (ethyne) torch – used in welding. Burns to give a very high temperature flame.
• Used primarily as starting materials for alkenes or alkanes.
• Functional group can be found in molecules – but not common.
Synthesis - Elimination

- Elimination is the best way to make alkynes
Synthesis – Chain Elongation

• This is by using an existing alkyne and extending the chain when the alkyne is terminal (ONLY)

\[ \text{CH}_3\text{C} ≡ \text{C} \text{H} \xrightarrow{(1) \text{NaNH}_2/\text{liq. NH}_3} \text{CH}_3\text{C} ≡ \text{C} \text{H}_3 \]

• Remember from acid – base strengths, alkynes are strongest acids amongst the hydrocarbons.

• One can use only a strong base (e.g. NH\textsubscript{2}\textsuperscript{−}) to abstract the alkyne proton to give the alkynide anion.

\[ \text{H} \text{C} ≡ \text{C} \text{H} + \text{NaNH}_2 \xrightarrow{\text{liq. NH}_3} \text{H} \text{C} ≡ \text{C} \text{Na}^+ + \text{NH}_3 \]
\[ \text{CH}_3\text{C} ≡ \text{C} \text{H} + \text{NaNH}_2 \xrightarrow{\text{liq. NH}_3} \text{CH}_3\text{C} ≡ \text{C} \text{Na}^+ + \text{NH}_3 \]
The alkynide ion can then be used as a nucleophile for any substrate (that has a leaving group)

Depending on the substrate substitution or elimination can occur. (next slide)

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}≡\text{CH} \xrightarrow{1. \text{NaNH}_2, \text{NH}_3} \xrightarrow{2. \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}≡\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{1-Hexyne} \quad \text{5-Decyne (76%)}
\]

\[
\text{H}―\text{C}≡\text{C}―\text{H} \xrightarrow{\text{NaNH}_2} \left[\text{H}―\text{C}≡\text{C}:\text{Na}^+\right] \xrightarrow{\text{RCH}_2\text{Br}} \text{H}―\text{C}≡\text{C}―\text{CH}_2\text{R} \\
\text{Acetylene} \quad \text{A terminal alkyne}
\]

\[
\text{R―C}≡\text{C}―\text{H} \xrightarrow{\text{NaNH}_2} \left[\text{R―C}≡\text{C}:\text{Na}^+\right] \xrightarrow{\text{R’CH}_2\text{Br}} \text{R―C}≡\text{C}―\text{CH}_2\text{R’} \\
\text{A terminal alkyne} \quad \text{An internal alkyne}
\]
Synthesis – Chain elongation

- Reactions with 2º and 3º alkyl halides gives dehydrohalogenation, converting alkyl halide to alkene.

[Diagram showing reaction with bromocyclohexane and butyne-1-sodium salt to form cyclohexene, where another reaction path is indicated as not forming a product.]
Reactions of Alkynes

• Most reactions are addition (just like alkenes)

• But alkynes have twice the hydrogen deficiency index of alkenes so all additions are twice (2 mols) than that of alkenes (1 mol)

• Alkynes are also more oxidized than alkenes (alkynes have less number of hydrogens), so some reactions will give the more oxidized product (alkenes give alcohols whereas alkynes will give aldehydes)

• Addition Reactions
  • Hydrohalogenation (HX)
  • Halogenation ($X_2$)
  • Hydration ($H_2O$)
  • Hydrogenation ($H_2$) (reduction)

• Oxidative cleavage
Reaction – Addition of HX

• The addition is Markovnikov’s addition (Note: the product is a germinal dibromine)

\[
\text{C}_4\text{H}_9\text{C}≡\text{CH} \xrightarrow{\text{HBr}} \text{C}_4\text{H}_9\text{C}=\text{CH}_2 \xrightarrow{\text{HBr}} \text{C}_4\text{H}_9\text{C}–\text{CH}_3
\]

2-Bromo-1-hexene 2,2-Dibromohexane

• The addition is anti Markovnikov when peroxide is used.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}≡\text{CH} \xrightarrow{\text{HBr \ (peroxides)}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}–\text{CH}\text{Br} \quad (74\%)
\]
Reactions – Addition of $X_2$

- Addition reactions of alkynes are similar to those of alkenes
- Intermediate alkene reacts further with excess reagent
- Regioselectivity is according to Markovnikov

\[ \text{CH}_3\text{CH}_2\text{C}≡\text{CH} \xrightarrow{\text{Br}_2/\text{CH}_2\text{Cl}_2} \text{Br}
\]

1-Butyne \hspace{2cm} (E)-1,2-Dibromo-1-butene \hspace{2cm} 1,1,2,2-Tetrabromobutane
Reactions – Addition of H\textsubscript{2}O

- Hydration of alkynes give aldehydes and ketones
- Reagents used are
  - HgSO\textsubscript{4} in H\textsubscript{2}SO\textsubscript{4} to give ketones (Markovnikov’s product)
  - BH\textsubscript{3}:THF and H\textsubscript{2}O\textsubscript{2} to give aldehydes (Anti Markovnikov’s product)

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}≡\text{CH} & \xrightarrow{\text{H}_2\text{O}, \text{H}_2\text{SO}_4, \text{HgSO}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}=\text{CH}_2 \\
\end{align*}
\]

1-Hexyne

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}≡\text{CH} & \xrightarrow{\text{BH}_3, \text{THF}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}=\text{CH}_2 \\
\end{align*}
\]

1-Hexyne

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}≡\text{CH} & \xrightarrow{\text{H}_2\text{O}_2, \text{pH} 8} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\end{align*}
\]

Hexanal (70%)

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Reaction – Reduction

- Addition of \( \text{H}_2 \) over a metal catalyst (such as palladium on carbon, \( \text{Pd/C} \)) converts alkynes to alkanes (complete reduction).
- The addition of the first equivalent of \( \text{H}_2 \) produces an alkene, which is more reactive than the alkyne so the alkene is not observed.
- Hydrogenation of alkyne with \( \text{H}_2 \) and \( \text{Pd} \) or \( \text{Pt} \) will reduce the alkyne to the alkane.

\[
\text{CH}_3\text{C}≡\text{CCH}_3 \xrightarrow{\text{Pt}} [\text{CH}_3\text{CH}≡\text{CHCH}_3] \xrightarrow{\text{Pt}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]

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Reaction – Reduction (cis/trans)

- Addition of H₂ using chemically deactivated palladium on calcium carbonate as a catalyst (the *Lindlar catalyst* – Pd-CaCO₃) produces a *cis alkene*
- The two hydrogens add *syn* (from the same side of the triple bond)

\[
\begin{align*}
\text{CH₃CH₂CH₂C≡CCH₂CH₂CH₃} & \xrightarrow{\text{H}_2, \text{Lindlar catalyst}} \text{CH₃CH₂CH₂CH₂CH₃} \\
\text{4-Octyne} & \rightarrow \text{cis-4-Octene} \xrightarrow{\text{H}_2, \text{Pd/C catalyst}} \text{Octane}
\end{align*}
\]

- Alkali metals dissolve in liquid ammonia (below –33 °C) function as reducing agents
- Alkynes are reduced to *trans* alkenes with sodium or lithium in liquid ammonia

\[
\begin{align*}
\text{CH₃CH₂CH₂CH₂C≡CCH₂CH₂CH₂CH₃} & \xrightarrow{\text{Li, NH}_3} \text{CH₃CH₂CH₂CH₂CH₂CH₃} \\
\text{5-Decyne} & \rightarrow \text{trans-5-Decene (78%)} \xrightarrow{\text{Pd/C catalyst}} \text{Octane}
\end{align*}
\]
Reaction – Oxidative Cleavage

• Strong oxidizing reagents (O₃ or KMnO₄) cleave internal alkynes, producing two carboxylic acids
• Terminal alkynes are oxidized to a carboxylic acid and carbon dioxide

An internal alkyne

\[ R\text{C}≡\text{CR'} \xrightarrow{\text{KMnO}_4 \text{ or } O_3} R\text{C}≡\text{C}OH + \text{HO}C\text{R'} \]

A terminal alkyne

\[ R\text{C}≡\text{C}H \xrightarrow{\text{KMnO}_4 \text{ or } O_3} R\text{C}≡\text{C}OH + \text{O}≡\text{C}≡\text{O} \]
Qualitative Analysis

• Alkynes are very similar to alkenes in reactions so the qual tests are the same (i.e. decolorization of bromine and brown ppt of MnO₂).

• However since alkynes have twice the hydrogen deficiency of alkenes, one can do a quantitative test along with qualitative test; an alkyne will react with twice the amount of bromine as an alkene would. So simply counting the number of bromine drops until the color stays will give an idea of whether there is an alkyne or alkene.

• But – that is also not a determinant if you have no idea what groups you are starting with because a dialkene will react with the same amount of bromine as one alkyne!
Key Words/Concepts

- Addition reactions
  - Halogenation
  - Hydrohalogenation
  - Hydration
  - Hydrogenation (cis and trans)
- Oxidative cleavage