Synthesis of Alkynes

- Double dehydrohalogenation

\[
\begin{align*}
\text{Br}_2 \xrightarrow{\text{ccl}_2} & \quad \text{Br} \xrightarrow{\text{vinyl dibromide}} \\
\text{CH}_3 \xrightarrow{\text{nanh}_2} & \quad \text{CH}_2 \xrightarrow{\text{gem dichloride}} \quad \Delta \\
\end{align*}
\]

- [Chemical equations and reactions]

\[
\begin{align*}
\text{H-} & \equiv -\text{H} \\
\text{H-} & \equiv -\text{NaO} \\
\text{1° RX - SN2} \\
\text{CH}_3 \equiv \quad 1) \text{nanh}_2 \quad \text{H-} \equiv \quad \text{NaO} \\
\end{align*}
\]
on to the first addition rexn!

**Hydrogenation** - the addition of H₂ to a π bond. No catalyst.

\[
\text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3 \\
\Delta H^\circ \sim -\text{50 Kcal/mol}
\]

Each too much - 88, toss in a catalyst.
Pt, Pd, Ni, Rh...

H₂ gets adsorbed onto surface of catalyst.
So does the alkene.

Can study heats of hydrogenation + compare alkene stabilities (even nonisomeric ones)

ethene < monosub. < disub. < trisub. < tetrasub.
Stereochemistry of Hydrogenation
- Syn addition: adding on same side
- Anti addition: adding from opposite sides
- Totally random (both ways happening)

\[ \sigma + \pi \]

\[ \sigma + \sigma \]
Hydrogenation of Alkynes -

1. \[ \equiv \equiv \xrightarrow{\text{H}_2/\text{Pt}} \equiv \] (Pd, Ni)

Alkyne reacts twice (2 eq. of H\(_2\))

2. Use a different catalyst.

\[ \text{Ni}_2\text{B} \quad (\text{P-2}) \quad \text{H}_2 \]

\[ \equiv \equiv \xrightarrow{\text{Ni}_2\text{B}(\text{P-2})} \equiv \]

Lindlar's catalyst:

\(\text{H}_2 \quad \text{Pd/CaCO}_3 \) quinoline

or

or both?

3. What if we want the (E) alkene?

\[ \equiv \equiv \xrightarrow{\text{Na}^0 \quad (\text{or Li}^0)} \equiv \equiv \xrightarrow{\text{NaH}} \equiv \]

\(\text{NH}_3 \) (with \(\text{EtOH}\) sometimes)

"dissolving metal reduction"
Wurks via e' transfer

\[
\text{N} + \overset{\cdot}{\text{Na}} \rightarrow \text{NH}_3
\]

a radical anion

\[
\text{NH}_3
\]

\[
\text{Na}^+ \quad \text{and} \quad \text{NH}_3^-
\]

Eliminations + Additions are "minor images"

make σ bonds

use up π bonds

\[
A-B + \overset{\cdot}{C} = \overset{\cdot}{C} \rightarrow A \overset{\cdot}{C} - \overset{\cdot}{C} - B
\]

generally energetically favorable

\[
\sigma + \pi \rightarrow 2\sigma
\]