Restrictions on Grignard Reagents - what they can't do.
- Grignard is basic - can't be formed from cmpds. w/ functional grps. more acidic than an alkene (pka > 44)
- Can do rxns. w/ cmpds w/ acidic functional grps. either
  EX: \(-\text{OH}, \text{NH}_2, \text{NHR}, \text{CO}_2\text{H}, -\text{C} = \text{C} \text{-H}\)

- Cannot have a carbonyl or epoxide functional grp.
- Don't do SN2

Alkyl Lithium Reagents
\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{EqLi}} \text{CH}_3\text{CH}_2\text{CH}_2\text{-Li} + \text{LiBr}
\]
- Similar reactivity to Grignard reagent:

\[
\begin{align*}
\text{H} & \xrightarrow{1} \text{CH}_3\text{Li} \xrightarrow{2} \text{H}_2\text{O} \\
& \xrightarrow{\text{CH}_3\text{-OH}} \text{CH}_3
\end{align*}
\]

Don't do SN2
\[
\text{CH}_3\text{-C} = \text{C}^+\text{Na}^+ \xrightarrow{\text{SN}_2} \text{CH}_3\text{C} = \text{C}-\text{CH}_2\text{CH}_3 \\
\text{from Alkene Addition}
\]

\[
\text{CH}_3\text{-CH} = \text{CH}_3 + \text{CH}_3\text{-C} = \text{C}^+ \xrightarrow{\text{S_N}_2/\text{H}_2\text{O}} \text{CH}_3\text{-C} = \text{C} \bigg(\text{CH}_3\bigg) - \text{OH}
\]

- Best wt primary carbon substrate.

**Lithium Dialkyl Cuprates:**

\[
2\text{CH}_3\text{CH}_2\text{CH}_2\text{-Li} + \text{CuI} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CuLi}
\]

### Ex.

\[
\text{CH}_3\text{-Cu-Li} + \text{CH}_3\text{-CH}_2\text{-Br} \xrightarrow{\text{SN}_2} \text{CH}_3\text{-CH}_2\text{-CH}_3
\]

Any typical **SN**<sub>2</sub>-like **SN**<sub>2</sub> substrate should work!

- Works best wt primary alkyl halide, or, some secondary alkyl halides which are cyclic:

\[
\text{Cl} \xrightarrow{\text{CH}_3\text{-Cu-Li}} \text{CH}_3\text{-CH}_2\text{-CH}_3
\]

### Ch. 13: Conjugated, unsaturated System

**Examples of conjugated systems:**

\[
\text{H}_2\text{C} = \text{CH} - \text{H} \xrightarrow{\text{resonance}} \text{H}_2\text{C} = \text{C} - \text{CH}_3
\]

3 porbital overlap means we can get delocalization of \( \pi \) electrons.

**Allyl cation:**

\[
\text{CH}_2\text{=CH} - \text{CH}_2 \leftrightarrow \text{CH}_2 = \text{C} = \text{CH}_2
\]

Again, 3 porbitals in a row → delocalization.
Looking at π-electron molecular orbitals of a 3-C system

\[ \pi^* \]

\[ \pi_{no} \quad \text{non-bonding} \]

\[ \pi \text{ bonding} \]

\[ \text{allyl cation} \quad \text{H}_2\text{C} = \text{CH} - \text{CH}_2 \]

\[ \text{allyl radical} \quad \text{H}_2\text{C} = \text{CH} - \text{CH}_2 \]

\[ \text{allyl anion} \quad \text{H}_2\text{C} = \text{CH} - \text{CH}_2 \]

*Allyl* is stable because \( 2\pi_- \) in lowest E orbital (full)

\( \pi^* \) bond is spread over 3 C's - a more accurate depiction is:

\[ \text{H}_2\text{C} = \text{C}^- \text{H}^- = \text{CH}_2 \]

each bond has a bond order of 1/2

**Dienes:** 2 conjugated double bonds:

\[ \text{all } \text{sp}^2 \text{ C's, each dbl bond conjugated} \]

\[ \text{NOT conjugated - has } \text{sp}^3 \text{C in between, referred to as isolated} \]
simplest ex. of a conjugated diene = 1,3-butadiene:

\[ \text{CH}_2=\text{CH}-\text{CH}≡\text{CH}_2 \]

Bond lengths: 1.34 Å 1.47 Å

Shorter than a normal sp²-sp³ single bond

\( \text{CH}_3-\text{CH}_3 \)

1.54 Å

Shorter due to partial double bond character in resonance

butadiene wants to adopt a planar conformation

- 2 ways:
  - S-trans: \[ \rightarrow \]
  - more stable
  - lead stable

\[ \Delta H = -127 \text{ kJ/mol} \]

\[ \text{H}_2/\text{Pt} \]

\[ \rightarrow \]

\[ \Delta H = -239 \text{ kJ/mol} \]

(we expected -127x2=-254)

- Smaller \( \Delta H \) due to added stability from conjugation.

\[ \text{CH}_2=\text{CH}-\text{CH}≡\text{CH}_2 + \text{HCl} \xrightarrow{\text{(eq)}} \ 	ext{CH}_2=\text{CH}-\text{CH}−\text{CH}_3 \]

major product (expected)

\[ \text{H}_2-\text{Cl} \]

\[ \text{Cl}^\ominus \]

\[ \text{CH}_2-\text{CH}≡\text{CH}-\text{CH}_3 \]

minor prod.