Chapter 13 (Solomons and Fryhle) discusses conjugation and various reactions of 1,3-dienes. The reactions include the very important Diels-Alder reaction, which features the reaction of a 1,3-diene with an alkene to give a cyclohexene ring.

\[
\text{\begin{tikzpicture}
\begin{scope}[scale=0.5
\node at (0,0) {\text{An example of a Diels - Alder reaction}};
\draw[thick,->] (-2,0) -- (2,0);
\draw[thick,->] (0,-2) -- (0,2);
\end{scope}
\end{tikzpicture}}
\]

In CHE 321 we discussed various ways to make alkenes, but we did not discuss methodology for making dienes. Fortunately we can apply some of our standard CHE 321 reactions to this important problem.

1. **Elimination Reactions to give 1,3 dienes.** Here are some simple examples

A) \[
\begin{align*}
\text{O} & \quad \text{Li} \\
1, & \quad \text{H}^+ \\
2, & \quad \text{H}^+ \\
\text{OH} & \quad \text{t-Bu}
\end{align*}
\]

In A a vinyl Li reagent is added to a ketone to give an alcohol. Acid catalyzed elimination will give the most substituted and thus most stable diene. In B free radical bromination at the allylic positions gives a tertiary bromide. Elimination with hydroxide gives the most stable diene. Elimination with a hindered base gives the most accessible isomer.

In special circumstances we can make a diene via a double elimination reaction.

C) \[
\begin{align*}
\text{C} & \quad \text{Br} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

D) \[
\begin{align*}
\text{Br} & \quad \text{Br}
\end{align*}
\]

This works in the case C of cyclohexene because the alternate alkyne product would be too strained. But it will not work in an acyclic case D because the preferred product will be the alkyne not the diene.
2. Di-enolates. Here is a special synthesis of a diene involving enolate chemistry.

\[
\begin{align*}
\text{O} & \quad \text{ClSi(CH}_3\text{)}_3 \\
\text{NEt}_3 & \rightarrow \quad \text{O} \quad \text{Si}
\end{align*}
\]

We know that a ketone is in equilibrium with its enol form.

\[
\text{O} \quad \text{H} \quad \text{OH}
\]

If we add a trimethylsilyl chloride (TMSCl) and a base like triethylamine, NEt₃ we can trap the enolate with the TMS group. This TMS protecting group can be removed at some later time in a reaction scheme.

\[
\begin{align*}
\text{N} & \quad \text{Si} \\
\text{O} & \quad \text{O} \quad \text{Si} \\
\text{H} & \quad \text{Cl}
\end{align*}
\]

Later in the course we will add additional methods of 1,3-diene synthesis. Don’t worry about them now.

3. Organometallic Coupling Reactions. These reactions are discussed in Special Topic H, pages 1016-1017.

4. Wittig Reaction. This reaction is a very useful method of making alkenes, it can also be used to make a diene. It is discussed in Chapter 16, pages 711-715,