The Diels-Alder Reaction: The endo rule

Diels-Alder stereochemistry can be predicted by the “endo” rule. Take the following reaction, where the diene is in black, the dienophile is in blue, and the newly formed bonds are in red:

\[
\text{Diene} + \text{Dienophile} \rightarrow \Delta \rightarrow \text{Product}
\]

We can predict the stereochemical outcome by looking at the transition states. The endo transition state will be the preferred one:

ENDO transition state

ENDO product (favored)

EXO transition state

EXO product (disfavored)

Two products are possible, and both contain a new bicyclic structure. “Endo” and “exo” describes the orientation of the substituents on the dienophile (in this case, the carboxylic acids) with the diene. In the endo orientation, the substituents point “down” towards the diene and the bridge is sticking “up.” In the exo orientation, the substituents point “up,” away from the diene.

Note that each of the products is drawn in three different ways. Make sure that you understand each one.
It is more difficult to predict the stereochemistry of a product with a diene that is not bridged. Take the following reaction:

\[
\begin{align*}
\text{Diene} & \quad + \quad \text{Dienophile} \\
\text{Diene} & \quad \Delta \quad \text{Product}
\end{align*}
\]

Here, there are hydrogens where the bridge was in the previous reaction, so they will go "up" like the bridge did in the endo transition state:

\[
\begin{align*}
\text{ENDO transition state} & \quad \rightarrow \quad \text{ENDO product} \\
\text{EXO transition state} & \quad \rightarrow \quad \text{EXO product}
\end{align*}
\]

In the endo orientation, the substituents point "down" towards the diene and the hydrogens are sticking "up." In the exo orientation, the substituents point "up," away from the diene.