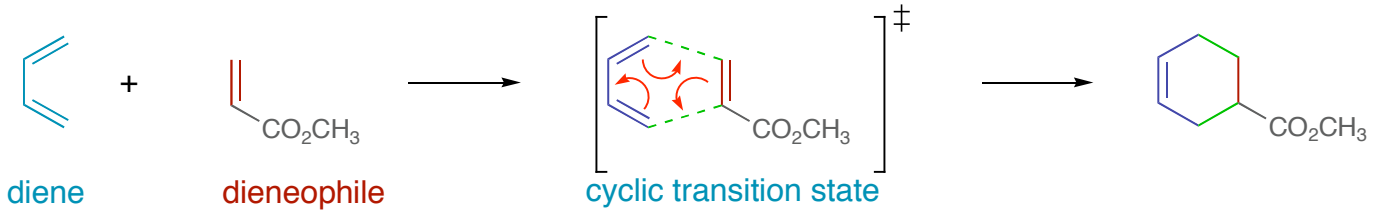
Chapter 14 - Conjugated Dienes and Ultraviolet Spectroscopy

Diels-Alder Reaction

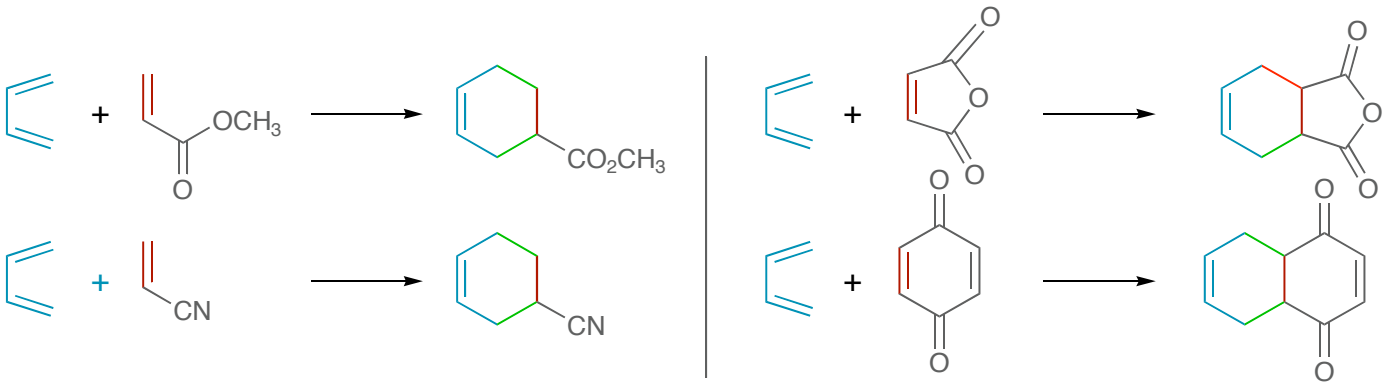
The Diels-Alder cycloaddition involves the reaction of a conjugated diene and an alkene to form a new 6-membered ring. The reaction works best if the diene is electron rich and the dienophile is electron poor (contains an electron withdrawing group (EWG)). The reaction occurs in one step through a cyclic transition state.



diene dieneophile cyclic transition state

Dieneophile

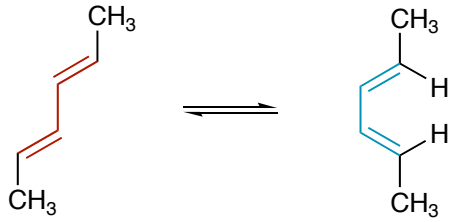
Many dienophiles participate in Diels-Alder reactions. Electron withdrawing groups that are usually utilized are carbonyls or other groups with pi-bonds to a heteroatom (eg. N of nitrile).



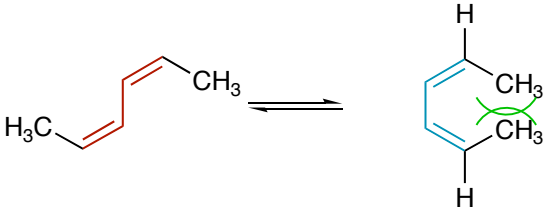
Diene

The conformation of the diene is very important for the Diels-Alder reaction. It must be in the s-cis conformation to react. Dienes in rings where the conformation is forced to be s-cis are the best. Sterics can influence the conformation of the dienes. Also, if the conjugated diene is in a ring, it could be forced to be in a conformation that cannot do a Diels-Alder reaction.

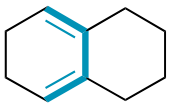
s-cis s-trans Can form both bonds at the same time Cannot form both bonds at the same time



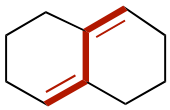
2-trans-4-trans-hexadiene
can do Diels-Alder



2-cis-4-trans-hexadiene
won't do Diels-Alder



can do Diels-Alder

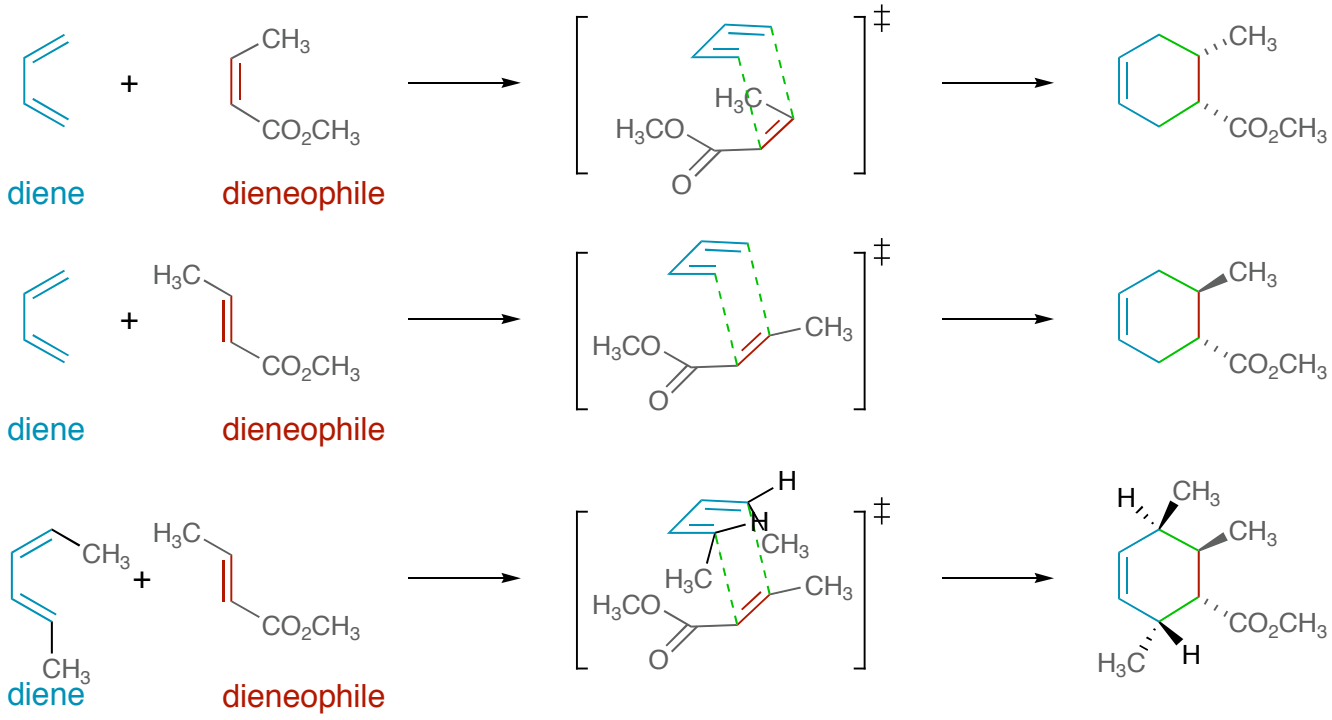


cannot do Diels-Alder

one of the best
dienes for Diels-Alder

Diels Alder Stereochemistry

The reaction is stereospecific with regards to the dienophile stereochemistry. A cis-alkene will afford a cis-product and a trans-alkene will afford a trans-product. On the diene, what points into the diene will be up (if looking from the top in the drawing below) and what points away from the diene will end up going down.



diene dieneophile

diene dieneophile

diene dieneophile