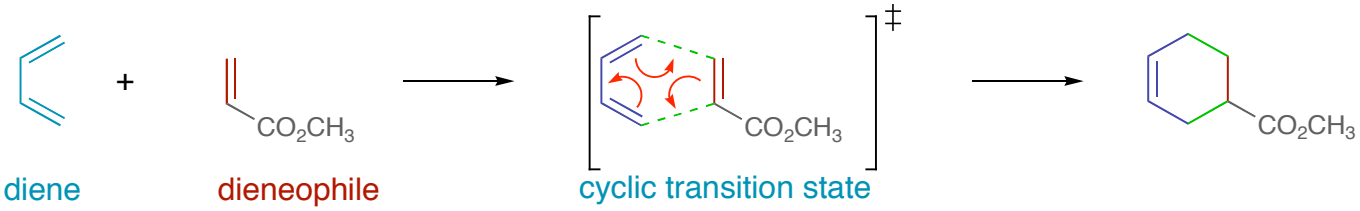
Chem 342 • Organic Chemistry II

Lecture Summary 06 - 28 Jan 2009

Chapter 14 - Conjugated Dienes and Ultraviolet Spectroscopy

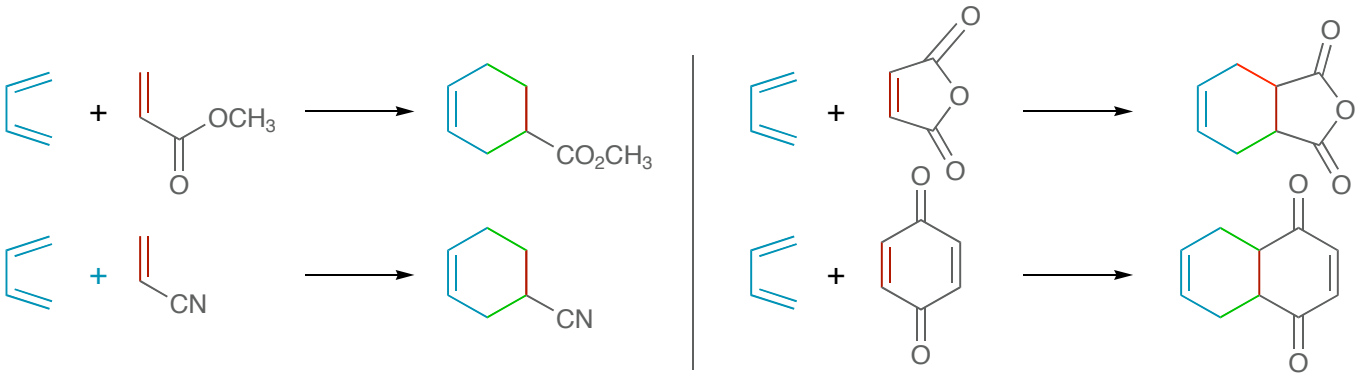
Diels-Alder Reaction

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.



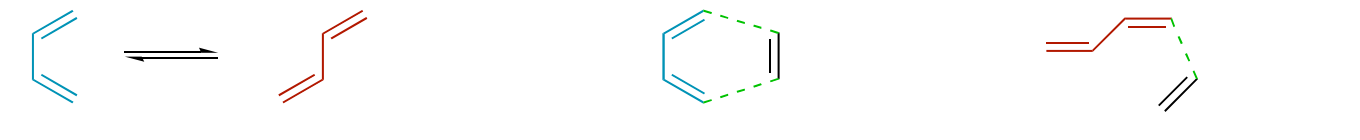
Dieneophile

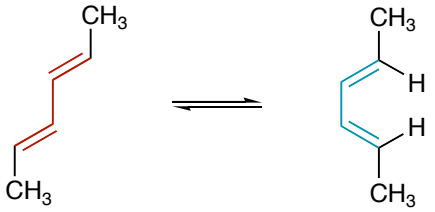
Many dienophiles participate in Diels-Alder reactions. Electron withdrawing groups that are usually utilized are carbonyls or other groups with pi-bonds to a heteroatom (eg. N of nitrile).



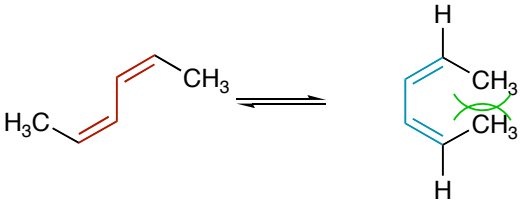
Diene

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.

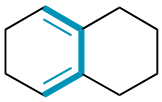




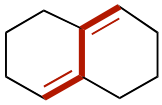
2-trans-4-trans-hexadiene
can do Diels-Alder



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



can do Diels-Alder

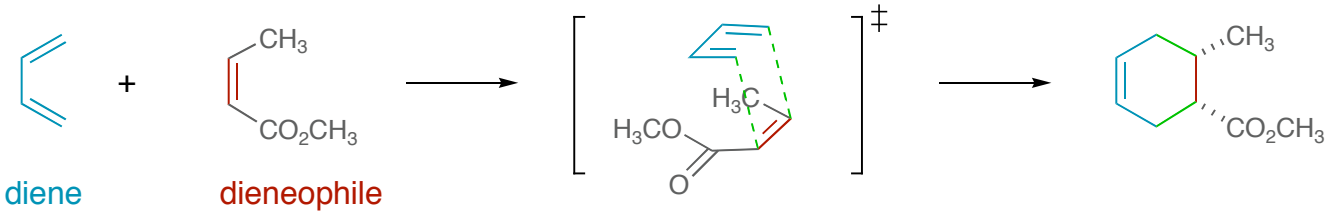


cannot do Diels-Alder

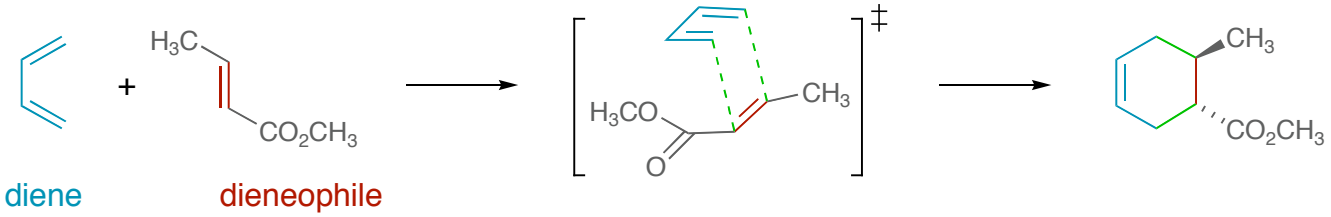
one of the best
dienes for Diels-Alder

Diels Alder Stereochemistry

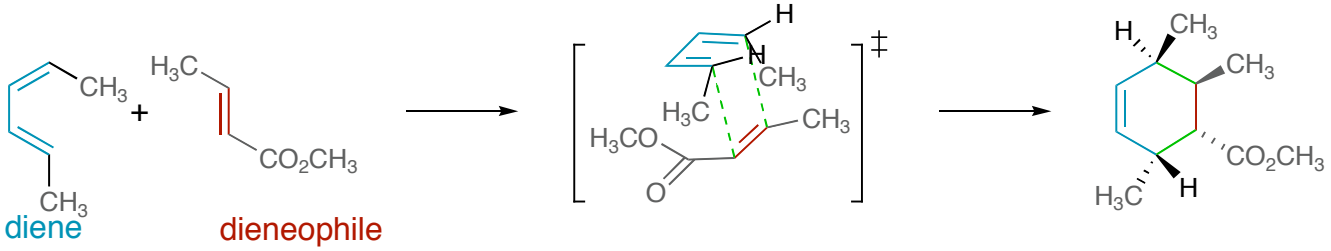
The reaction is stereospecific with regards to the dienophile stereochemistry. A cis-alkene will afford a cis-product and a trans-alkene will afford a trans-product. On the diene, what points into the diene will be up (if looking from the top in the drawing below) and what points away from the diene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



diene dieneophile

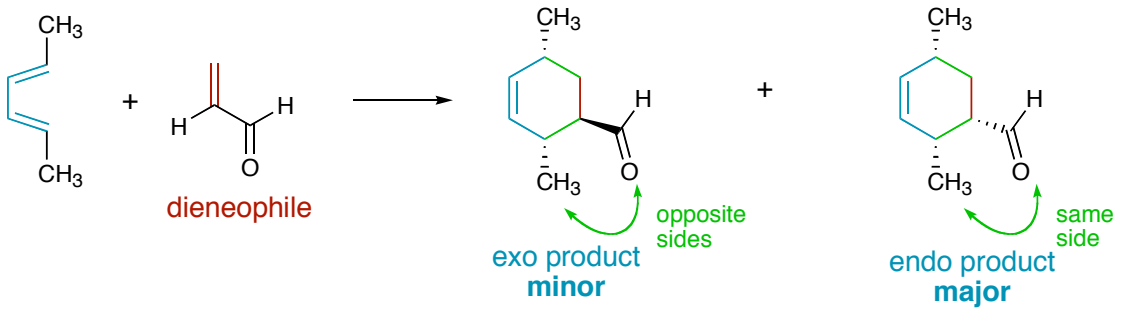


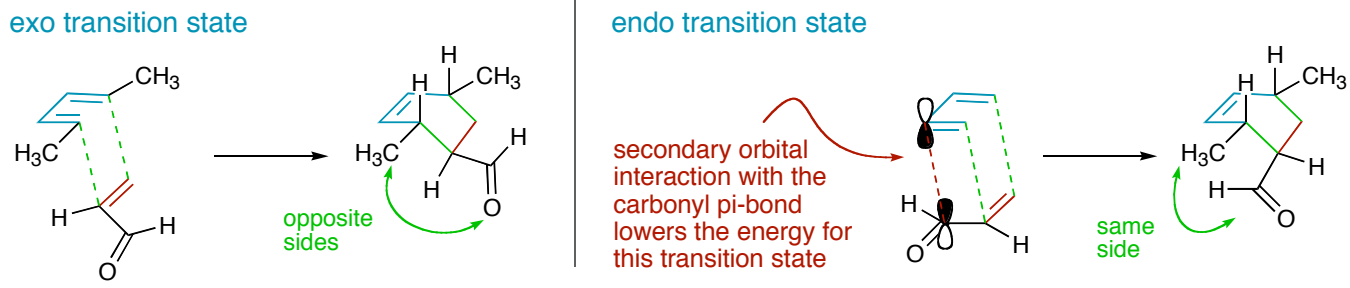
diene dieneophile



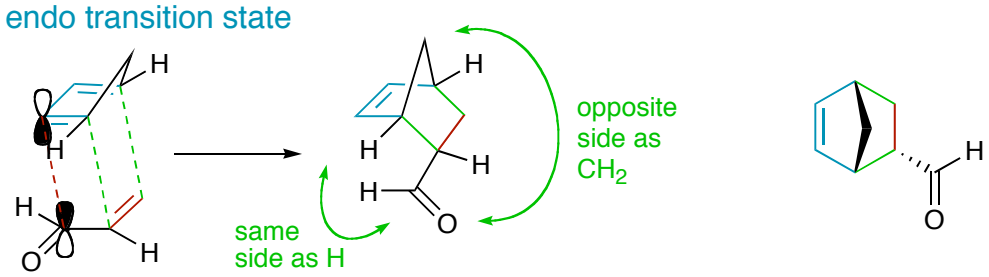
diene dieneophile

The Diels-Alder cycloaddition prefers to place the electron withdrawing group underneath the diene because the carbonyl pi-bond can interact with the diene pi-system. This gives rise to the endo product as the major product in the reaction.





Note that if the groups on the diene are pointing in, they will end up on opposite siteds in the ENDO transition state. For example, look at cyclopentadiene shown below.



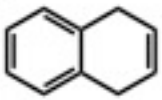
If you always draw the reaction with dienophile approaching from the bottom and looking at the product from the top - you can use these simple rules for the stereochemistry for ENDO:

The EWG will always be down in the product

Groups on the end of the diene pointing out will be down in the product

Groups on the end of the diene pointing in will be up in the product

Daily Quiz

Q: Which of the following has the most conjugated pi bonds?	☐ 1: 
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