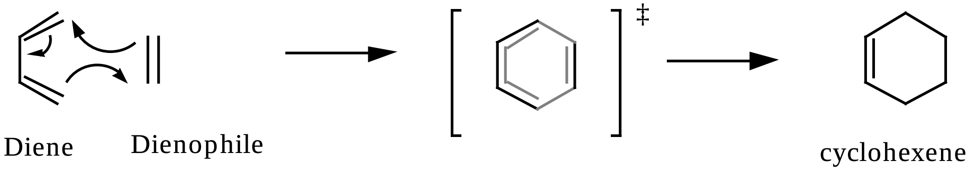
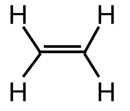
Diels-Alder Reaction **(a very important reaction)**

Reaction between a conjugated diene and an alkene (dienophile) to give a cyclohexene

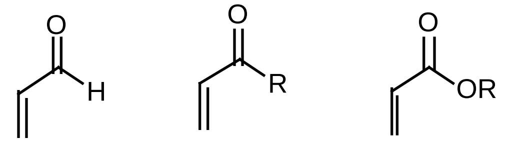


The Diels-Alder reaction is favored by electron withdrawing groups on the dienophile and electron donating groups on the diene.

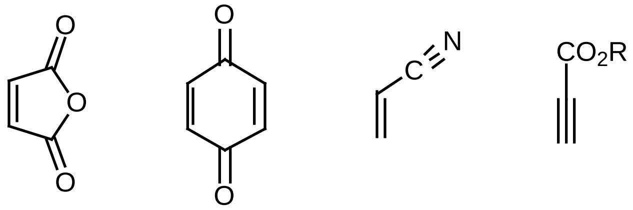
Good Dienophiles:



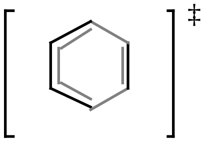
ethylene
(unreactive)



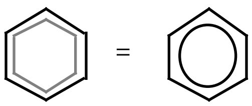
conjugated carbonyls (aldehydes, ketones and esters)



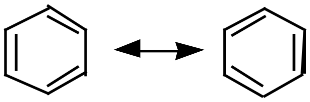
Mechanism: Pericyclic Reaction- proceeds in a single step via an "aromatic" transition state.



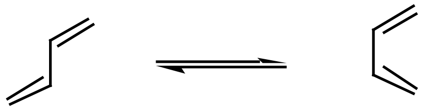
Diels-Alder
Transition State



Benzene



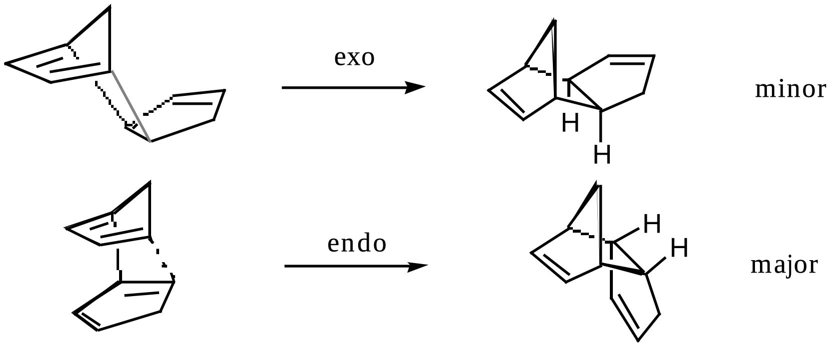
The diene must adopt an s-cis conformation to be reactive:



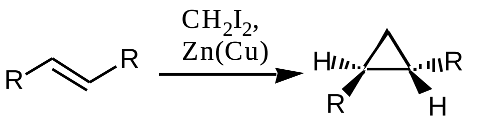
s-trans
(unreactive conformation)

s-cis
(reactive conformation)

Endo vs. Exo Transition State: Generally, the endo transition state is favored.

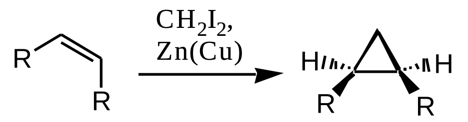


Stereochemistry: In pericyclic reactions, the stereochemistry of the reactants is preserved in the product. Recall the cylcopropanation of alkenes by carbenes which is also a pericyclic reaction.



R groups are trans in the reactant

R groups are trans in the product

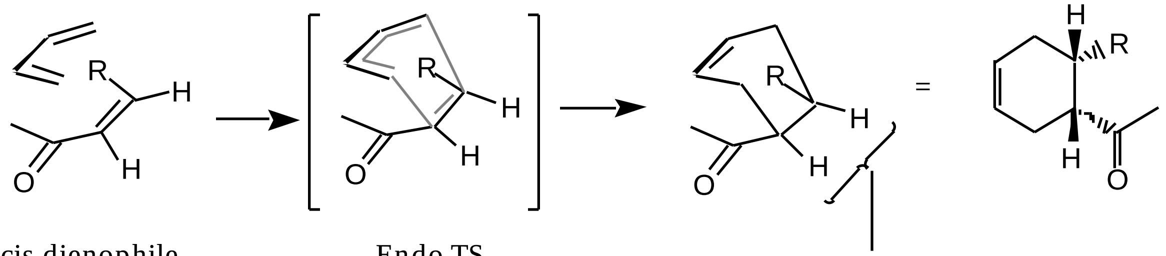


R groups are cis in the reactant

R groups are cis in the product

Dienophile: Groups that are cis on the dienophile will be cis in the product; groups that are trans on the dienophile will be trans in the product.

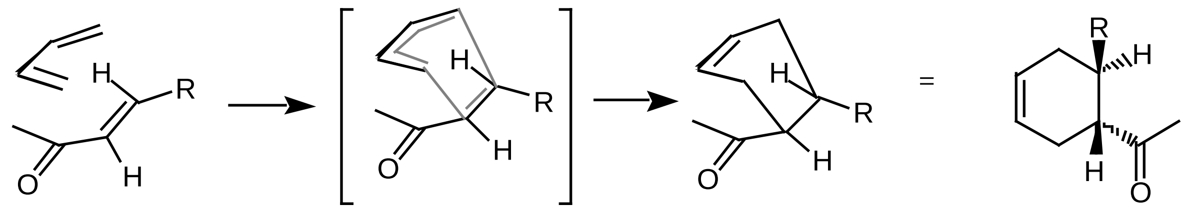
Endo TS:



cis dienophile

Endo TS

H's are cis

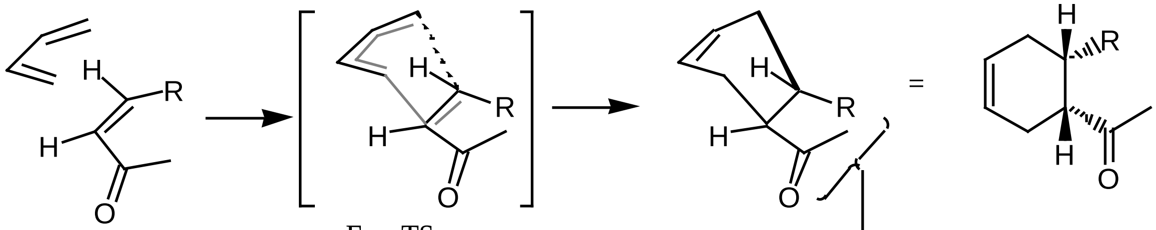


trans dienophile

Endo TS

H's are trans

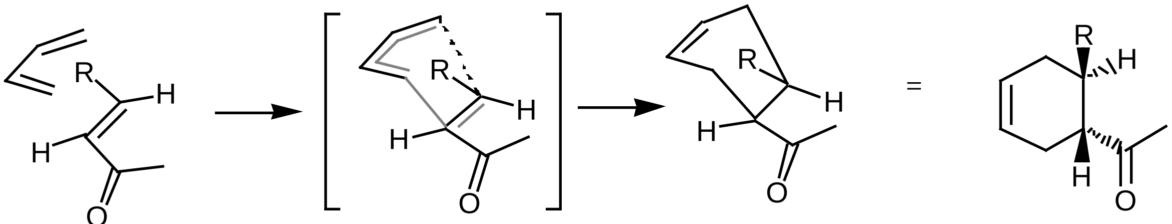
Exo TS:



cis dienophile

Exo TS

groups are cis

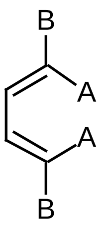


trans dienophile

Exo TS

groups are trans

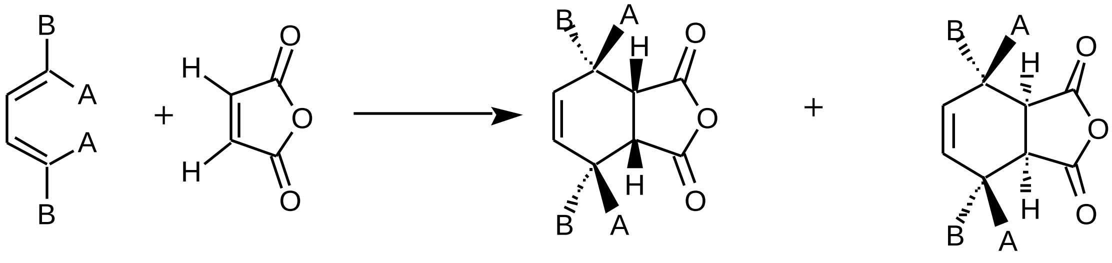
Diene:



In the s-cis conformation:

A= inner rim of diene
B= outer rim of diene

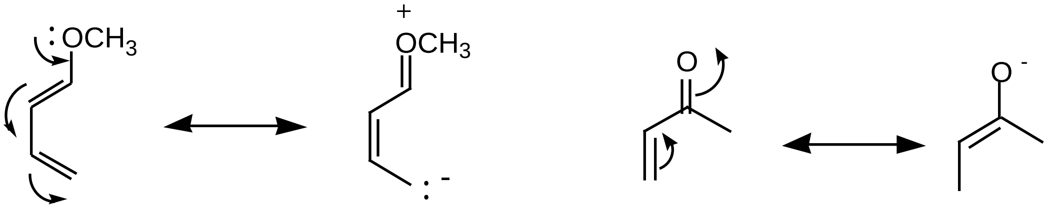
Groups on the inner rim of the diene will be cis in the product and groups on the outer rim of the diene will be cis in the product:



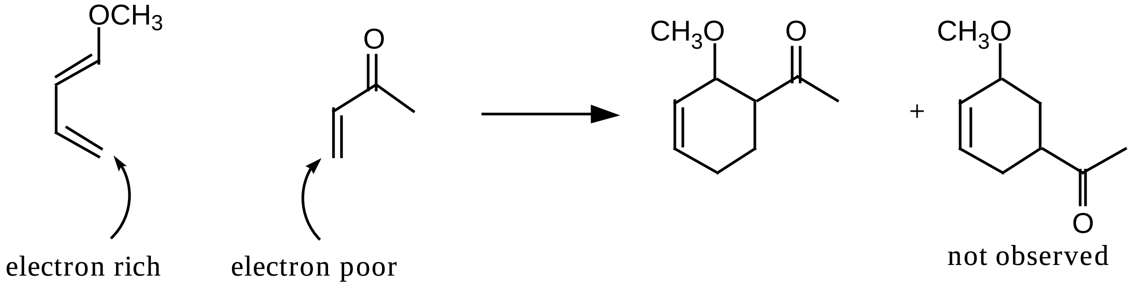
Endo TS   Exo TS

In the product, the groups of the dienophile that are endo in the transition state will be cis to the groups on the outer rim of the diene (in the s-cis conformation) .

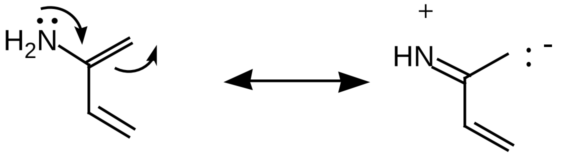
Regiochemistry: The regiochemistry of the Diels-Alder reaction is determined by the position of the electron donating groups of the diene, and is fully understood by molecular orbital theory. It may be easier to explain by simply looking at the resonance structures of the diene and dienophile. Typical electron donating groups on the diene are ethers, amines and sulfide; all have a non-bonding pair of electrons to donate.

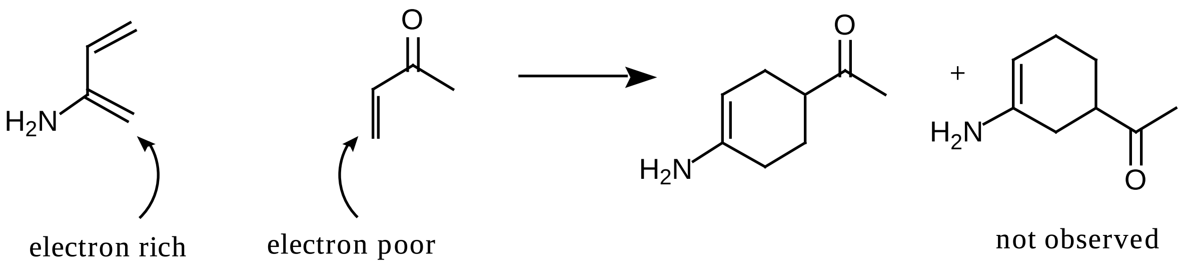


The regiochemistry of this Diels-Alder reaction is explained by looking at the dipolar resonance structures. The electron-rich carbon of the diene forms a bond with the electron-poor carbon of the dienophile.



When the electron donating groups is at the 2-position of the diene:





N.K. Dunlap and C.J. Rizzo (revised 12/97)