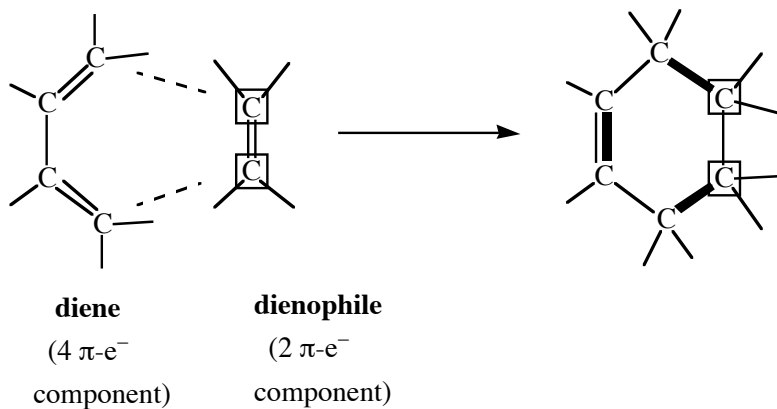


Lecture outline

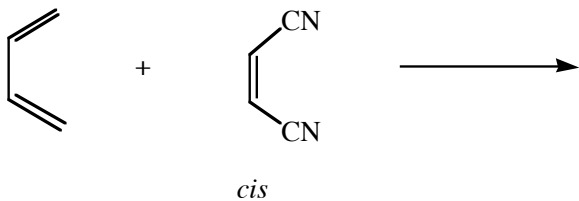
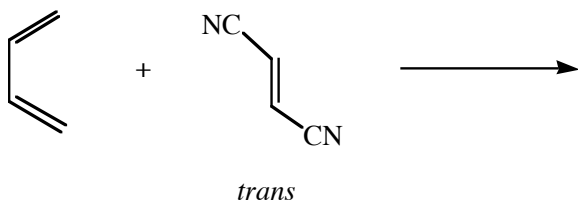
Diels-Alder Reaction



the dienophile is shown above as an alkene,
but it can also be a diene, alkyne, -N=N-, etc.

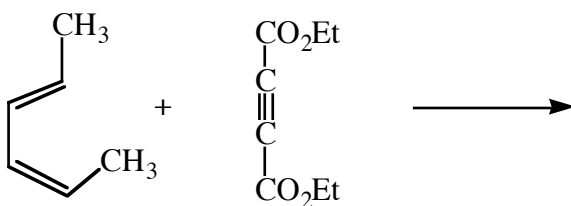
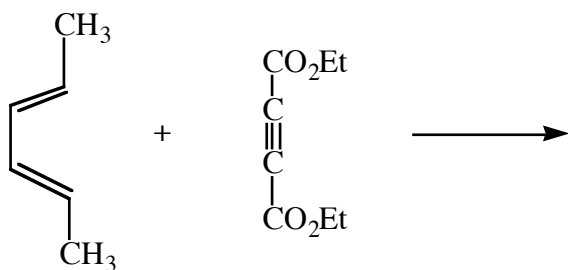
1. The reaction is stereospecifically *syn* with respect to each reactant

That the dienophile stereochemistry is preserved is illustrated by reaction of 1,3-butadiene with fumaronitrile (*trans*-1,2-dicyanoethylene) and maleonitrile (*cis*-1,2-dicyanoethylene).



What do these results imply about the mechanism of this reaction? What stereochemical outcome would you expect if the reaction were concerted? What if it were stepwise?

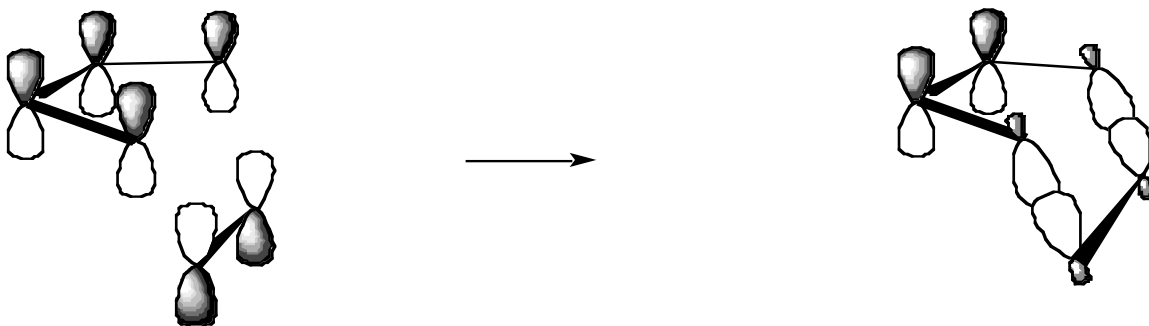
That the diene stereochemistry is preserved is illustrated by rxn of **diethyl acetylenedicarboxylate** ("DEAD" ... seriously) with *E,E*- and *E,Z*-2,4-hexadiene



What product would you expect from the *Z,Z*-diene?

2. The stereochemistry is clearly most consistent with a *concerted* mechanism — for all the bond making and breaking processes to occur simultaneously, the orbitals must all be aligned properly...

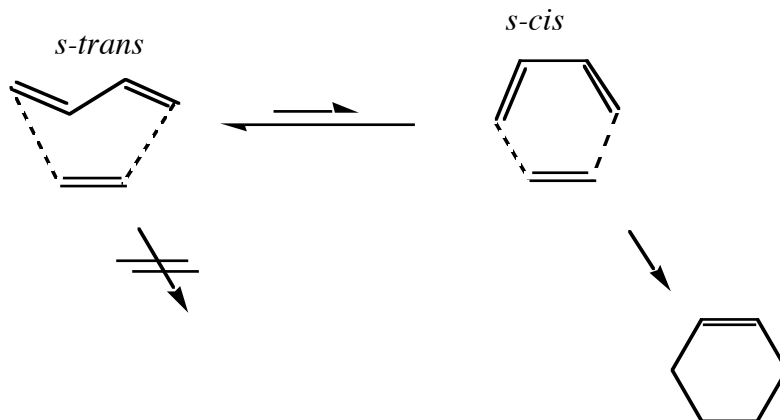
The diene and dienophile can't very well come together in the same plane, now can they? The new σ -bonds have to be formed by initial overlap of p-orbitals, thus (these drawings are meant to show p-orbital orientations only — they're not meant to represent actual π -MOs



Dienophile must approach from above or below (not in) plane of diene

cyclohexene is formed in *boat* conformation

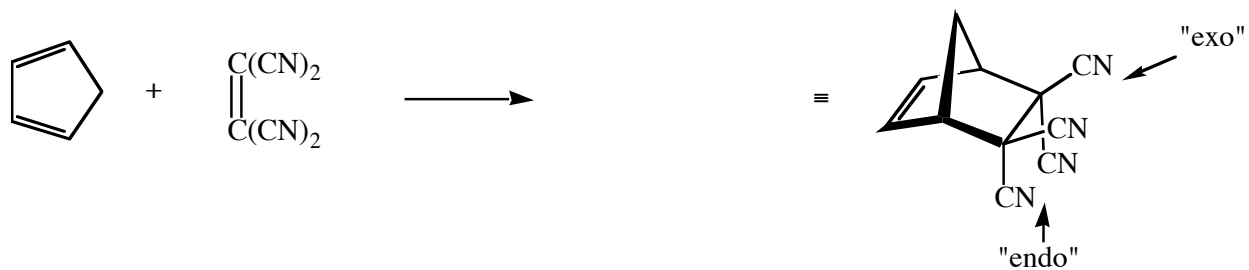
3. Another consequence of concert is that the diene must be *s-cis*, otherwise the reaction cannot occur. Draw the product that would be produced if the diene reacted in its *s-trans* conformation (assuming the dienophile could even *reach* the ends of the diene, which it couldn't do, even if it wanted to, which it doesn't.)



— dienes that cannot be *s-cis* do not react, e.g....
 3-methylenecyclopentene a *cis,cis*-1,4-disubstituted-1,3-butadiene

— and dienes constrained to be *s-cis* react rapidly, e.g....
 1,3-cyclopentadiene 1,2-dimethylenecyclohexane

Of course, a D-A reaction of 1,3-cyclopentadiene produces a bicyclic product



4. In contrast to the Diels-Alder reaction, a "4+2" cycloaddition, neither 2+2 nor 4+4 cycloadditions work. To understand the difference, we need to consider the orbitals of the reacting components —

First, the Diels-Alder in its most basic form —

Butadiene

Ethylene

Now the 2+2 and 4+4 —