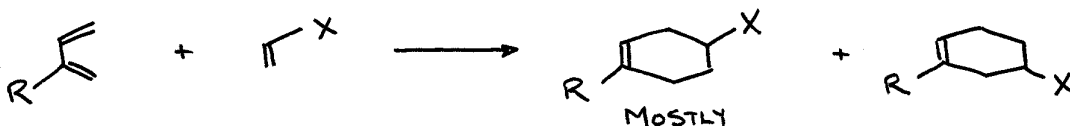


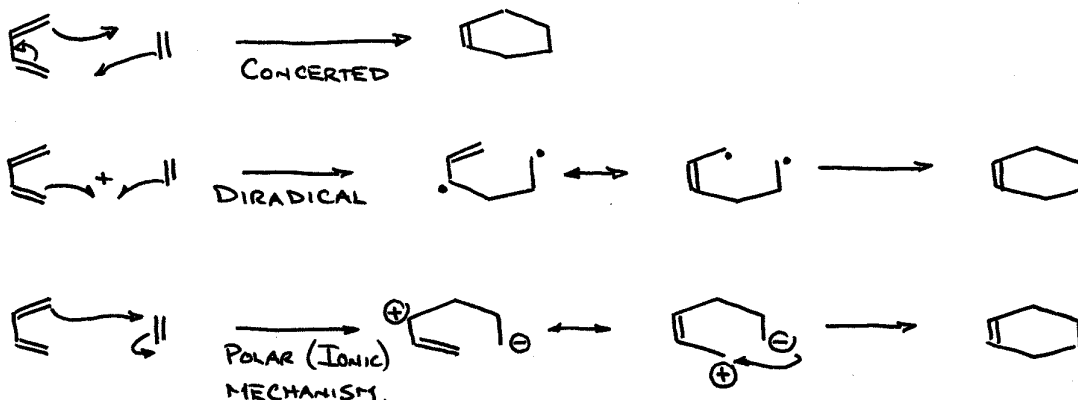
In this case, the indicated regioisomer predominates. If it were a benzene, it would be called the *ortho* product.

Case B- 2-substituted dienes



If this were a benzene, the major product would be called the *para* product. Hence the *ortho/para* rule name. We'll get to why in a bit.

The Mechanism -You could in principle write a concerted mechanisms, a diradical mechanism, or a polar mechanism for the Diels-Alder reaction. The vast majority of the available current evidence supports the **concerted mechanism**, although the diradical mechanism probably operates in some (biased) cases.

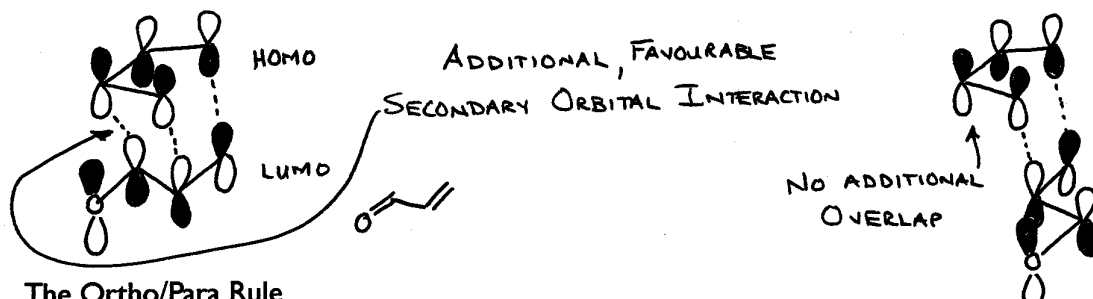


If we accept the contention that the Diels-Alder reaction is a concerted one (and I do), then the reaction characteristics may be explained by examining the frontier molecular orbitals (FMO's) of the diene and dienophile. Since the diene is clearly the more electron rich partner in this reaction, its reactivity will be dominated by its highest occupied molecular orbital (HOMO). Since the dienophile is clearly the electron poor partner, its reaction characteristics should be dominated by its lowest unoccupied molecular orbital (LUMO or LVMO). This is a part of the **Woodward-Hoffmann Rules** or the **Principle of Conservation of Orbital Symmetry**, although we're just touching on this lightly.

Notice then, in the transition state, the positive lobes of the LUMO overlap with the positive lobes of the HOMO, and negative with negative. These are favourable (stabilizing) interactions, and means that the concerted reaction is thermally allowed. So $[4\pi + 2\pi]$ cycloadditions are thermally allowed and common, even if the 4π electron system only has 3 heavy atoms (recall ozone).

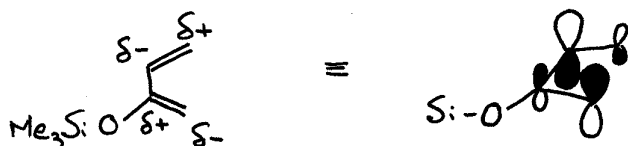
The Endo Rule:

In most dienophiles, there is a -M group conjugated to the diene. That, of course, has a π -system, too, so the LUMO of these dienophiles are slightly more complex. If the -M group's π -system can reach underneath the diene and overlap with another lobe of the HOMO, one can get a secondary, favourable, orbital interaction. This can only occur when the addition occurs in an *endo* fashion. Note also, that this group must have a π -system, so a -I group like CF_3 wouldn't do this.



The Ortho/Para Rule

This can be rationalized using FMO considerations, or by using by considering the relatively electron rich and electron poor sites of the diene and dienophile (this *usually* works). The key is that for the HOMO, the most electron rich atoms (the δ^- ones) almost always have the larger orbital coefficients. In 1-substituted dienes and 2-substituted dienes, that translates as follows.

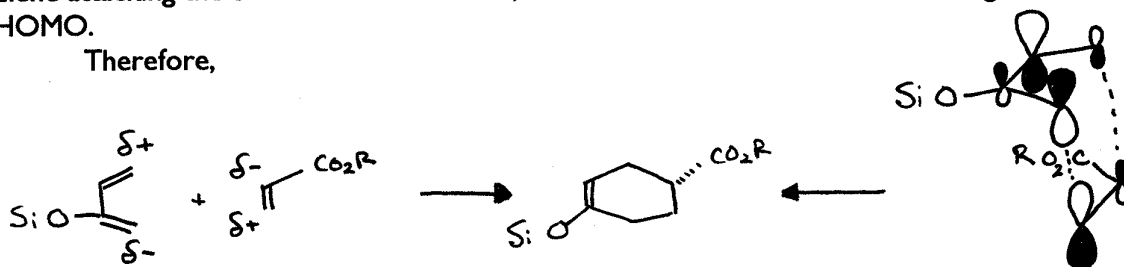


For the LUMO, however, the more electron deficient atoms (δ^+) atoms have the larger orbital coefficients, i.e.,



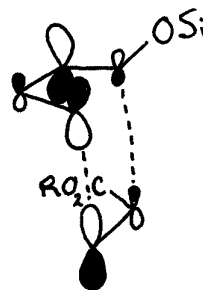
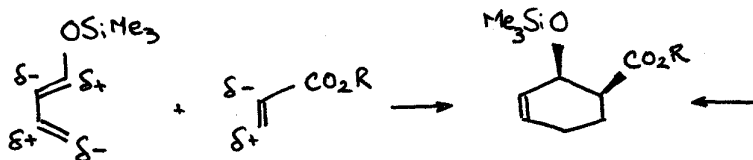
In the transition state for the Diels-Alder, the lowest energy situation occurs where the atoms largest orbital coefficients in the HOMO and LUMO overlap. This corresponds to the δ^- end of the diene attacking the δ^+ atom of the LUMO, and the δ^- end of the LUMO attacking the δ^+ end of the HOMO.

Therefore,



It's probably easier to think of the δ^- / δ^+ way rather than the orbital coefficient approach, although it's somewhat less reliable.

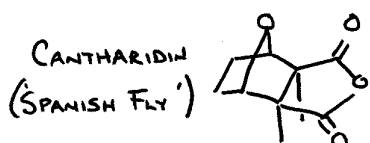
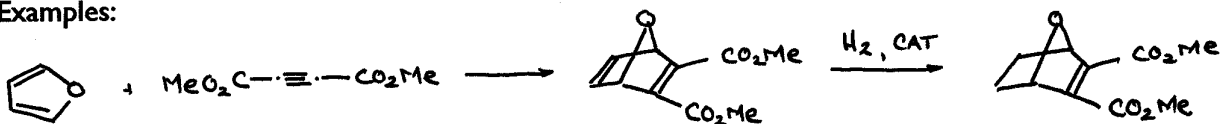
So for the β -substituted dienes



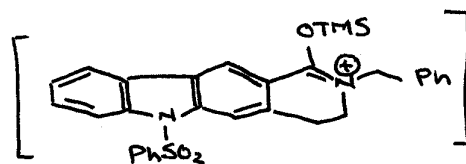
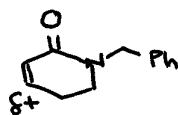
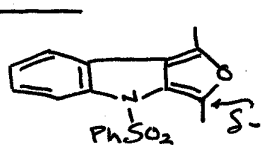
Assorted points:

- 1) The Diels-Alder reaction can often be catalyzed by Lewis acids; sometimes the reaction can be made to go at surprisingly low temperatures.
- 2) Hetero Diels-Alder reactions, where one of the C atoms is replaced by an N or O, are also known.
- 3) Recall that this reaction is reversible: backwards versions (called retro(grade)Diels-Alder reactions) can also occur.
- 4) The Diels-Alder is extremely useful in synthesis due to its
 - a) wide applicability
 - b) known stereochemistry and regiochemistry
 - c) ease of availability of starting materials
- 5) Ketene, $H_2C=C=O$, does not react normally as a dienophile, but tends to participate in [2+2] cycloadditions.

Examples:

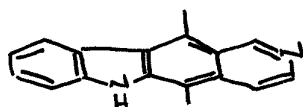


STORK, G. J. AM. CHEM. SOC. 1953, 75, 384

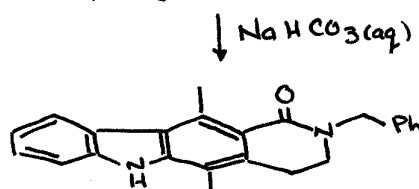


GRIBBLE, G. TETRAHEDRON LETT. 1990, 31, 1081.

ELLIPTICINE
(ANTITUMOUR
ALKALOID)



1) $LiAlH_4$
2) $Pd/C, \Delta$



Nucleophilic Rearrangements

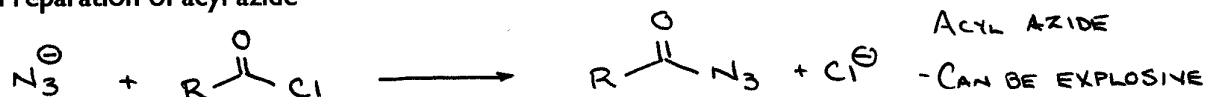
Many rearrangements are highly synthetically useful. A major class of these are caused by rendering an atom severely electron deficient. A carbon based group the migrates with its bonding pair of electrons; in some way, the new electron deficiency created by this is less severe.

There are many of these, but we'll just look at three. By the way, you have already seen two of these in this course.....the Baeyer-Villiger oxidation, and the organoborane to alcohol oxidation reaction.

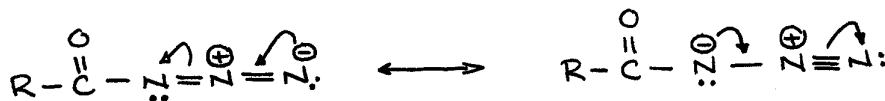
Curtius Rearrangement (March 8-15)

The Curtius rearrangement consists of the decomposition of an acyl azide to give a nitrene (at least in principle), which is severely electron deficient.

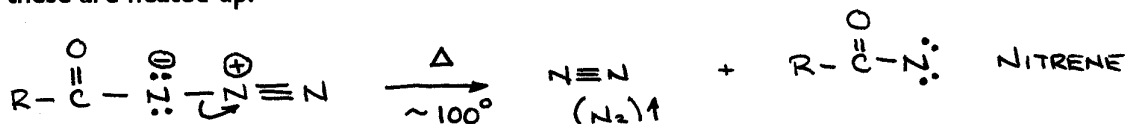
Preparation of acyl azide



Structure



If these are heated up:



A nitrene is a neutral species, which has only six valence electrons at N. Therefore it is very electron deficient and extremely reactive.

Migration of the R group to this electron deficient N atom gives an isocyanate, which is more stable (but still quite reactive). These isocyanates can be isolated in the absence of water or alcohols (or amines). The addition of an alcohol to this isocyanates gives a carbamate (also called a urethane). Treatment of these with acids causes decarboxylation, to give an amine. This can also be done in one step by adding water (usually acidified).

