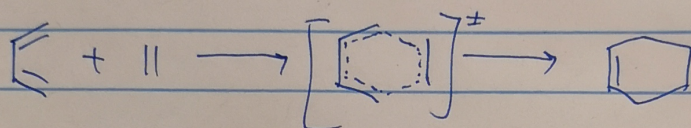


Lecture XXIX = Stereochemistry of Pericyclic Reactions

04-13-2020

Pericyclic reactions are concerted rxns that proceed through a transition state which has a cyclic array of interacting orbitals. The best known example is Diels-Alder reaction:

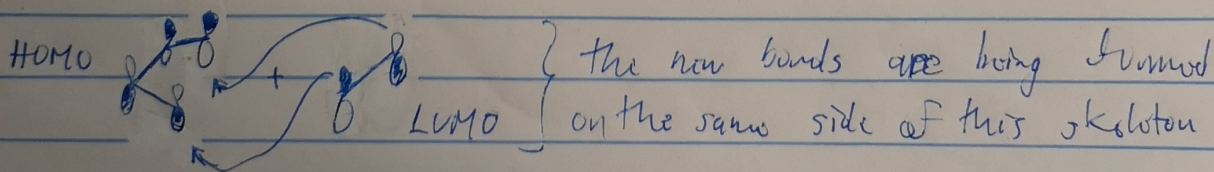
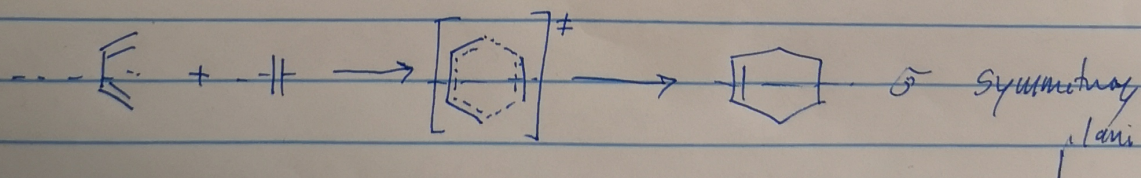


There are four main kinds of pericyclic reactions:

- | | |
|-------------------------|--------------------------------|
| (a) cycloadditions | (c) sigmatropic rearrangements |
| (b) electrocyclizations | (d) cheletropic reactions |

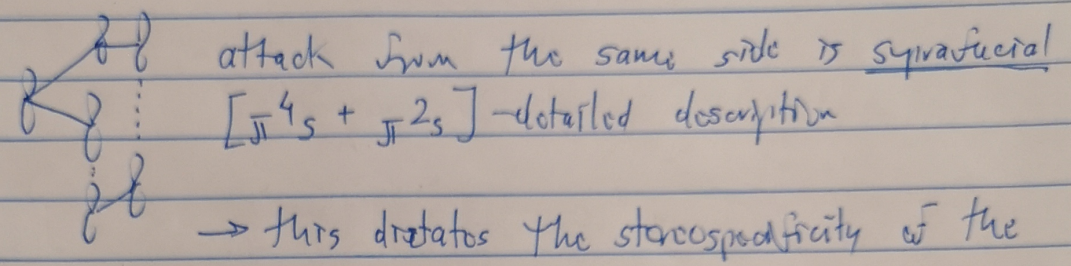
Pericyclic reactions are guided by Woodward-Hoffman rules of orbital symmetry conservation. They say that the starting materials, transition state and products are all connected by a symmetry element—plane or axis—that is maintained throughout the course of this reaction. This symmetry applies to the structures of reactants, but more importantly to their orbitals.

Let's look at the Diels-Alder reaction:

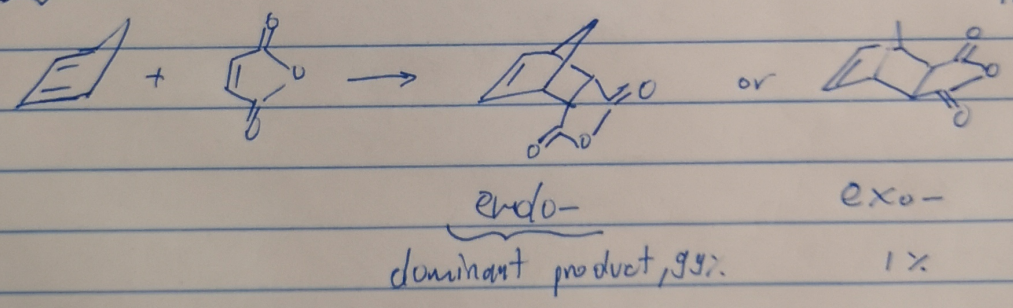
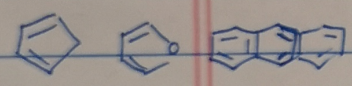
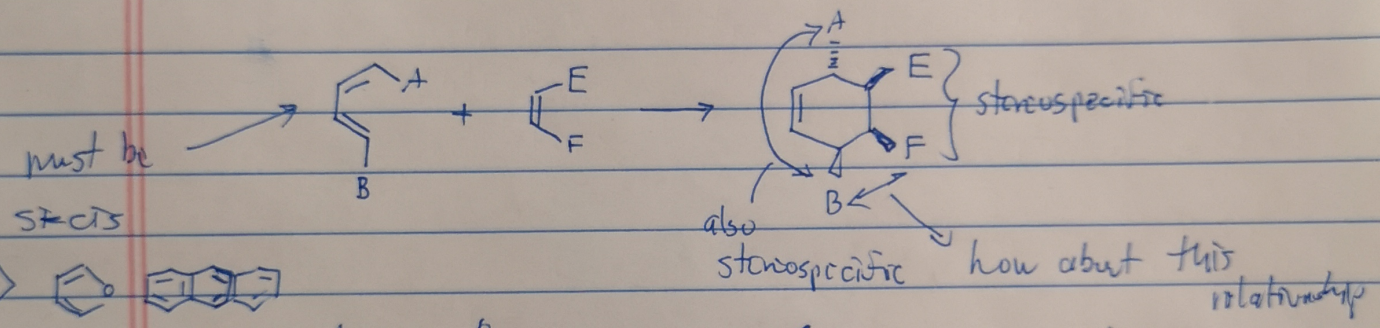


This is a simplified frontier molecular orbital (FMO) treatment of
Fukui

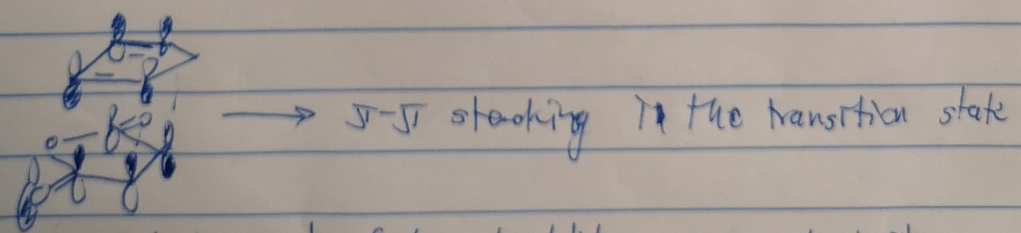
Both HOMO and LUMO are antisymmetric with respect to the σ -plane of the interaction.



Diels Alder reaction:

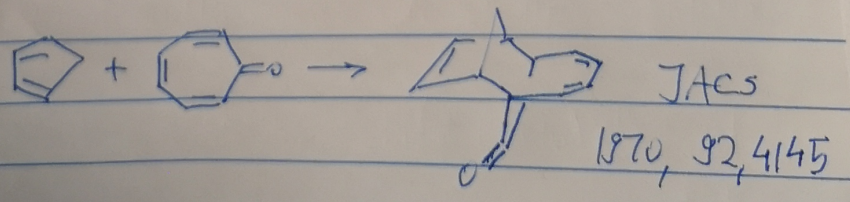


Endo-effect:

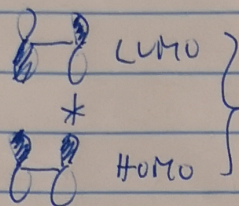


secondary orbital interactions

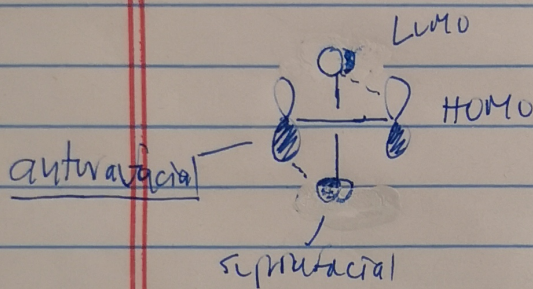
In 6+4 cycloadditions, exo-selectivity is observed.



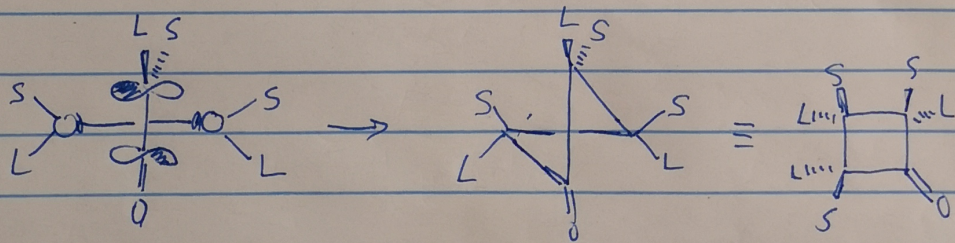
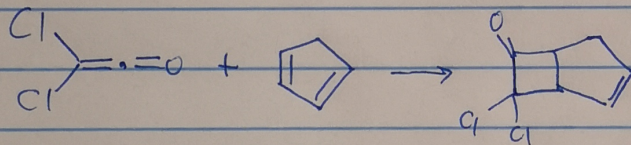
What about [2+2] cycloadditions?



symmetry mismatched \Rightarrow generally forbidden, but a twisted transition state could work



this orientation is quite strained, but can be achieved with small alkenes, such as ketenes:

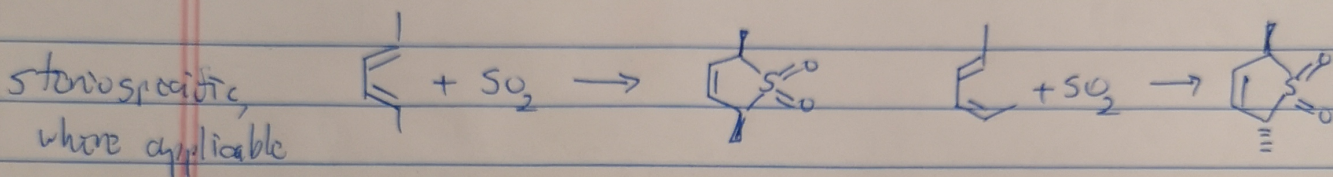
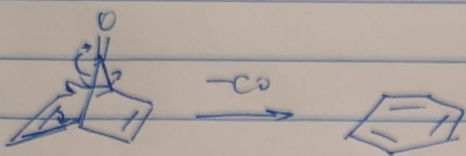


most crowded product!

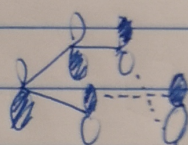
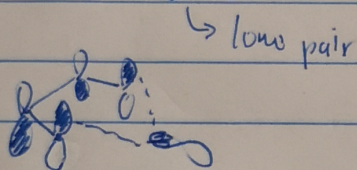
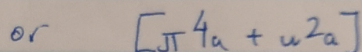
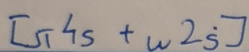
Many [2+2] cycloadditions occur through stepwise radical or zwitterionic intermediates - rules of orbital symmetry conservation do not apply.

Diels Alder: $6 = 4 + 2$ $4n+2$ π electrons \rightarrow allowed, Hückel transition state
 $2+2$: $4n$ π electrons \rightarrow forbidden, but twisted Möbius transition state is allowed

Chelotropic Reactions are a special case of cycloadditions in which 2 electrons reside on a single atom:

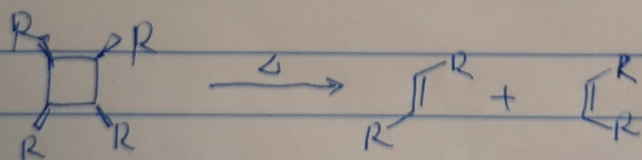
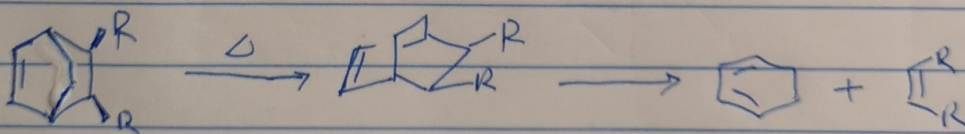


Geometry of attack can be either:



singlet carbene additions to C=C

Cycloversions, such as the e.g. Diels-Alder reaction, proceed with the same stereospecificity:



Next time, we'll look at electrocyclizations and sigmatropic rearrangements. Now, let's construct a detailed orbital correlation diagram for the Diels-Alder reaction:

