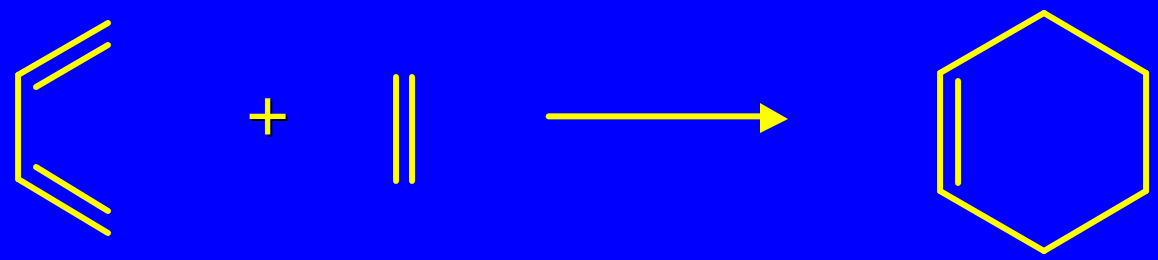
10.12

The Diels-Alder Reaction

Synthetic method for preparing compounds containing a cyclohexene ring

In general...

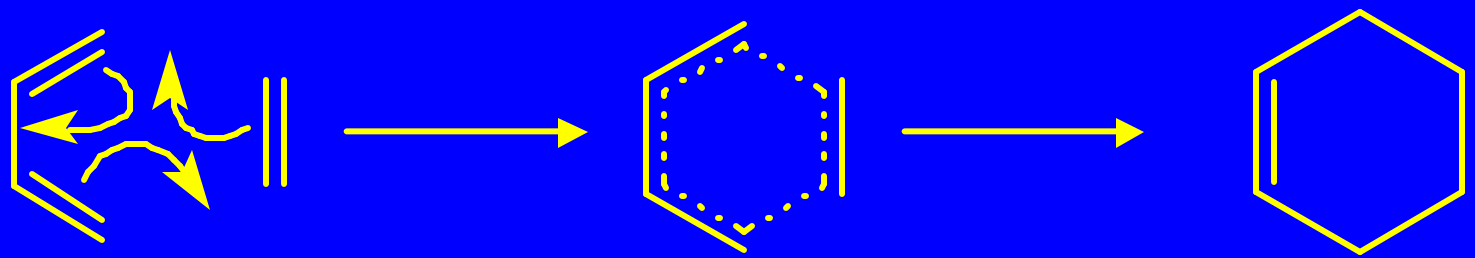


conjugated diene

alkene (dienophile)

cyclohexene

via



transition state

Mechanistic features

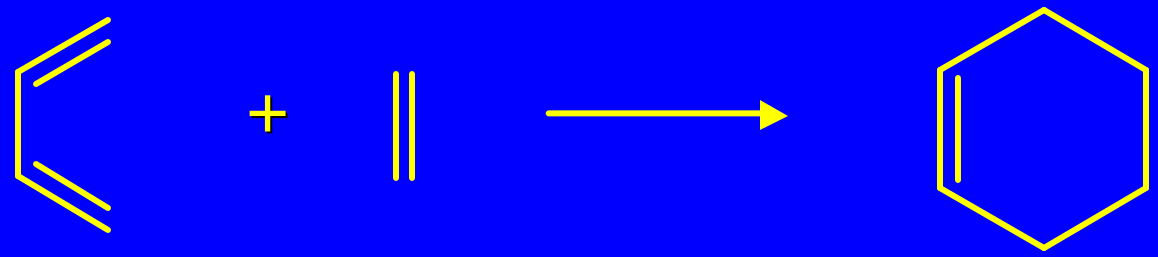
concerted mechanism

cycloaddition

pericyclic reaction

a concerted reaction that proceeds through a cyclic transition state

Recall the general reaction...



conjugated diene

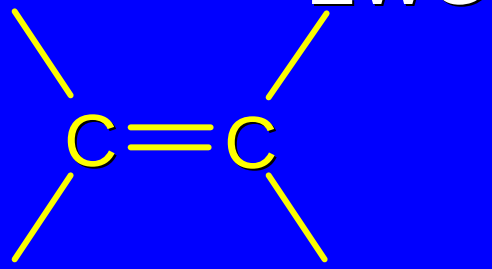
alkene (dienophile)

cyclohexene

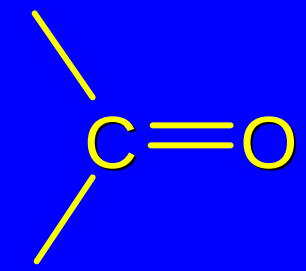
The equation as written is somewhat misleading because ethylene is a relatively unreactive dienophile.

What makes a reactive dienophile?

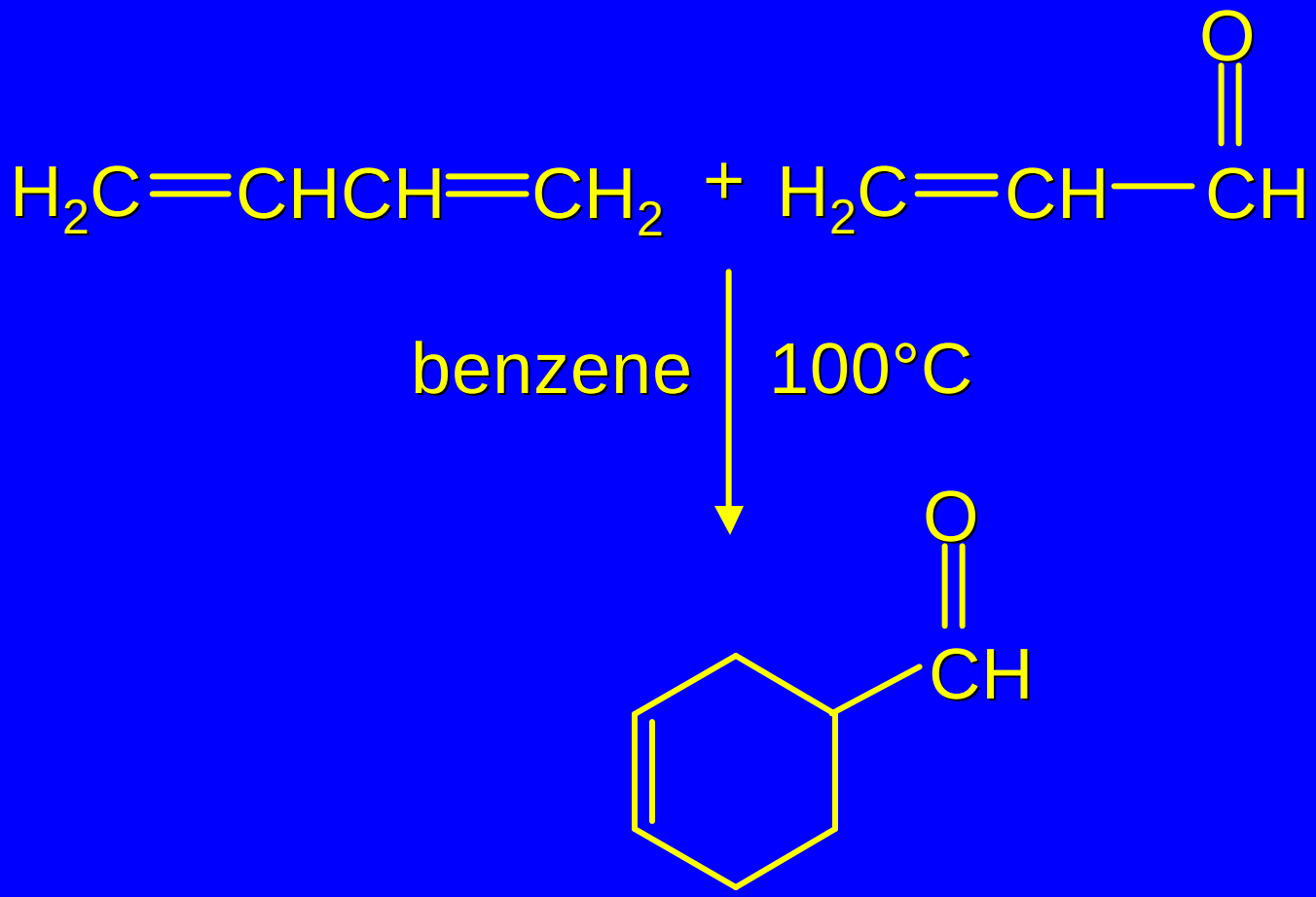
The most reactive dienophiles have an electron-withdrawing group (EWG) directly attached to the double bond.



Typical EWGs

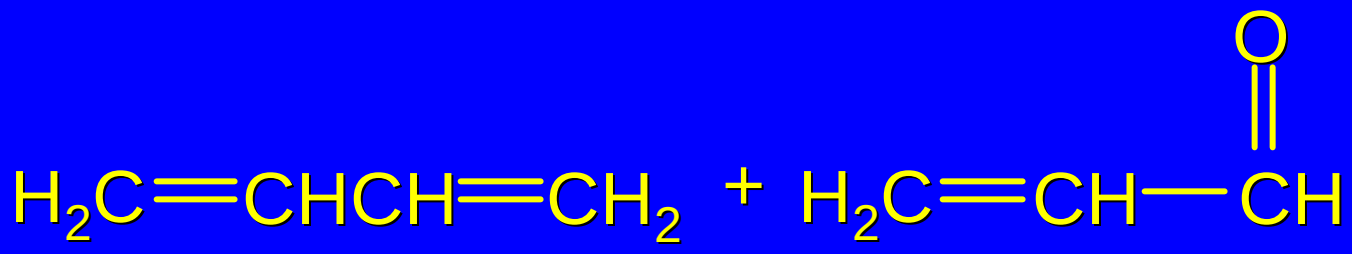


Example



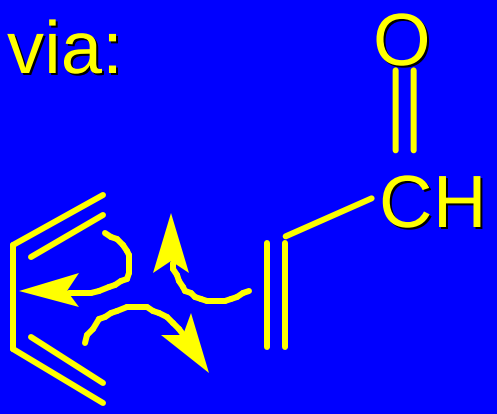
(100%)

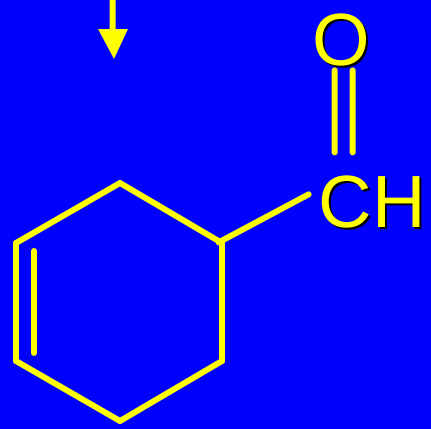
Example



benzene | 100°C

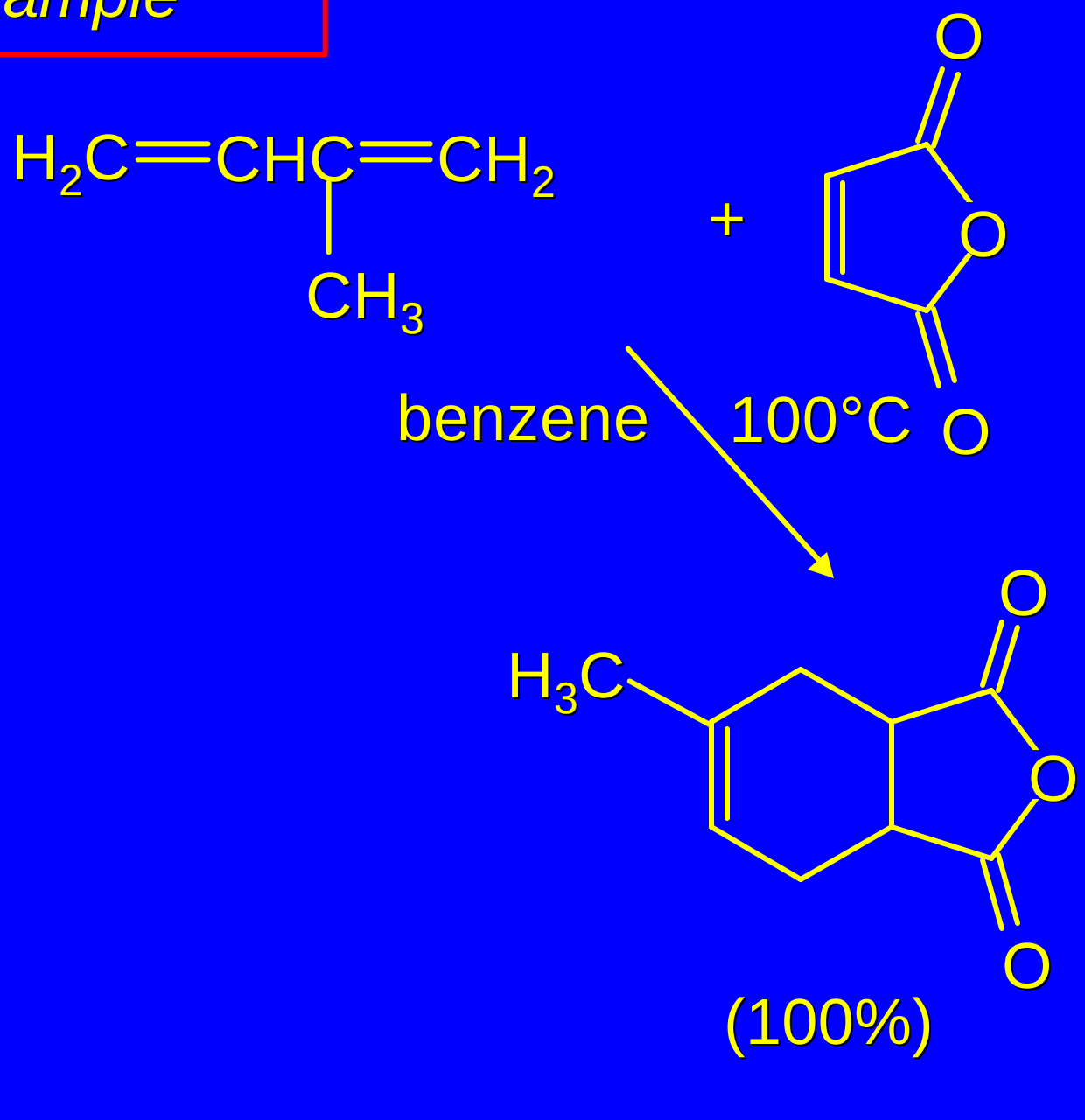
via:



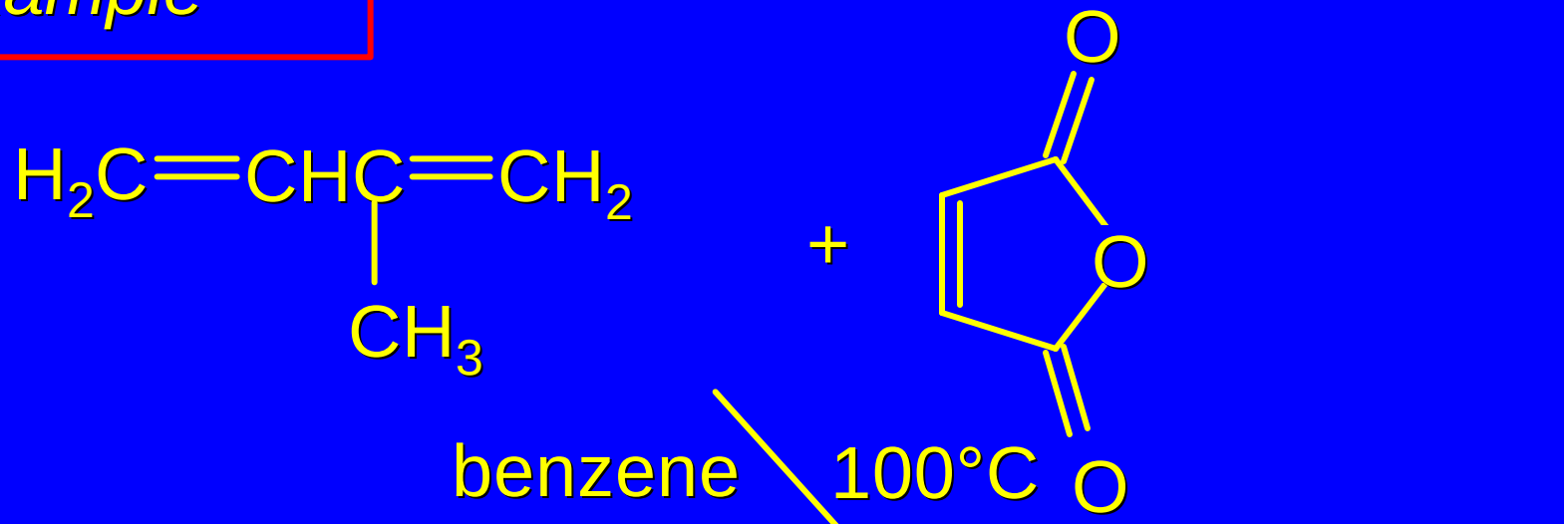


(100%)

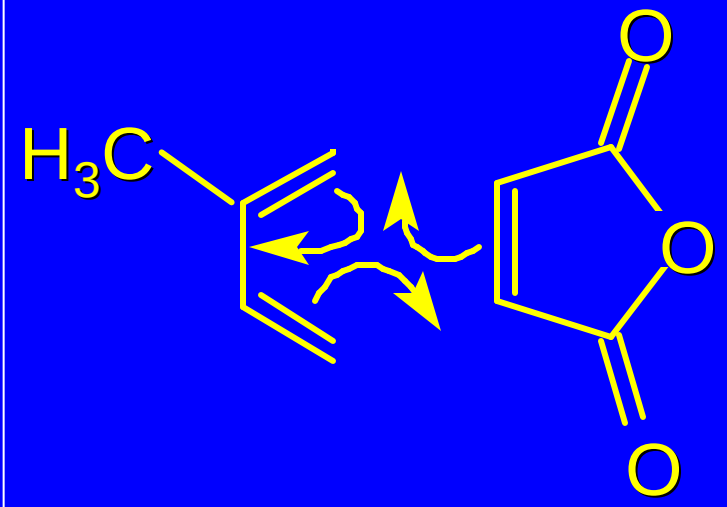
Example

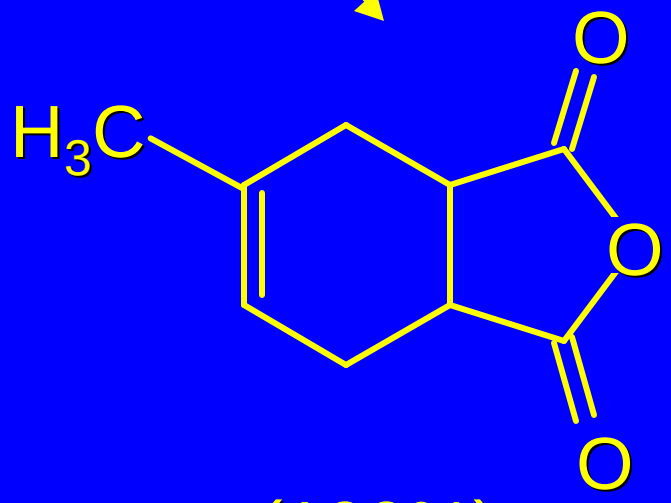


Example



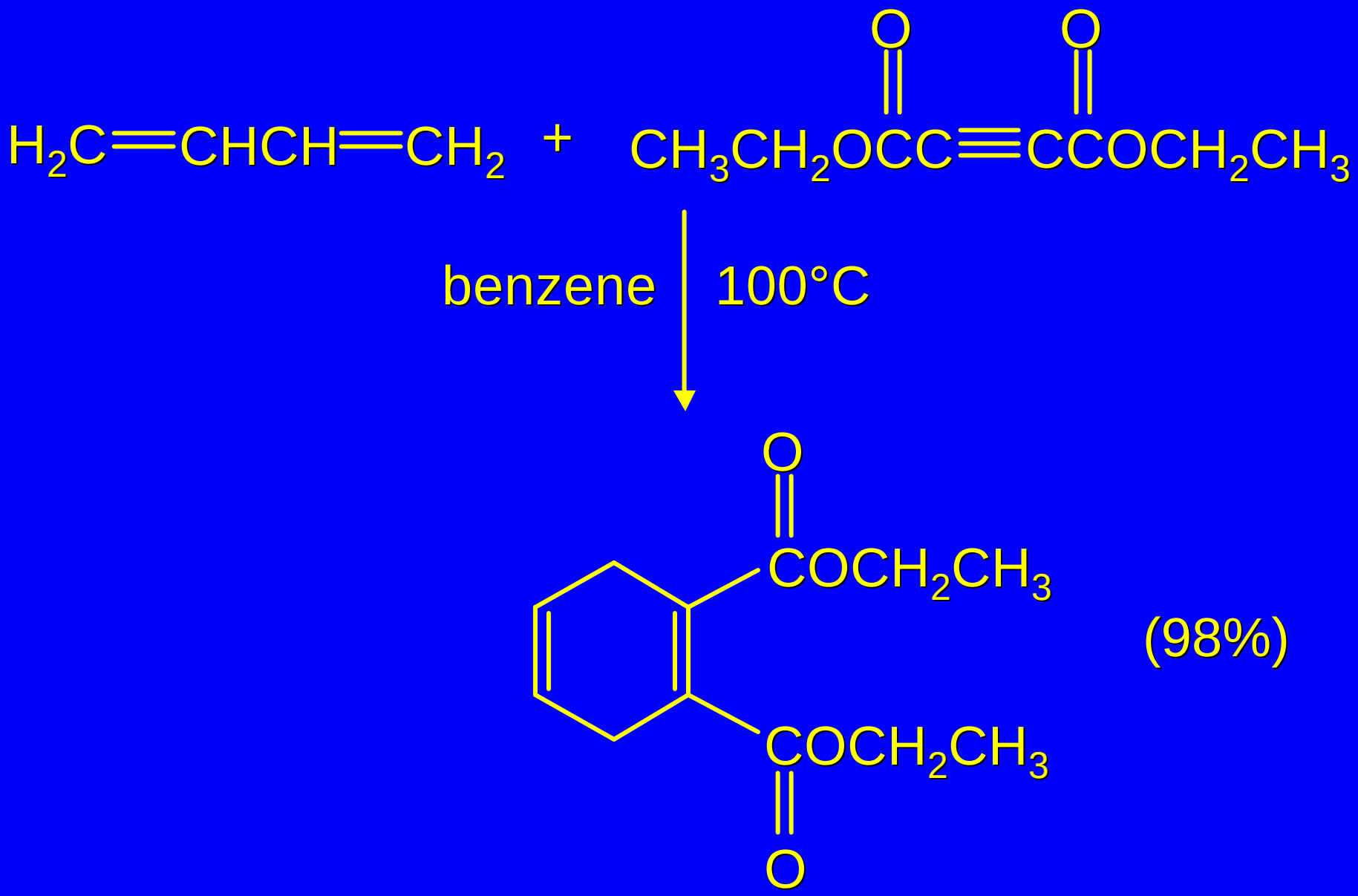
via:





(100%)

Acetylenic Dienophile



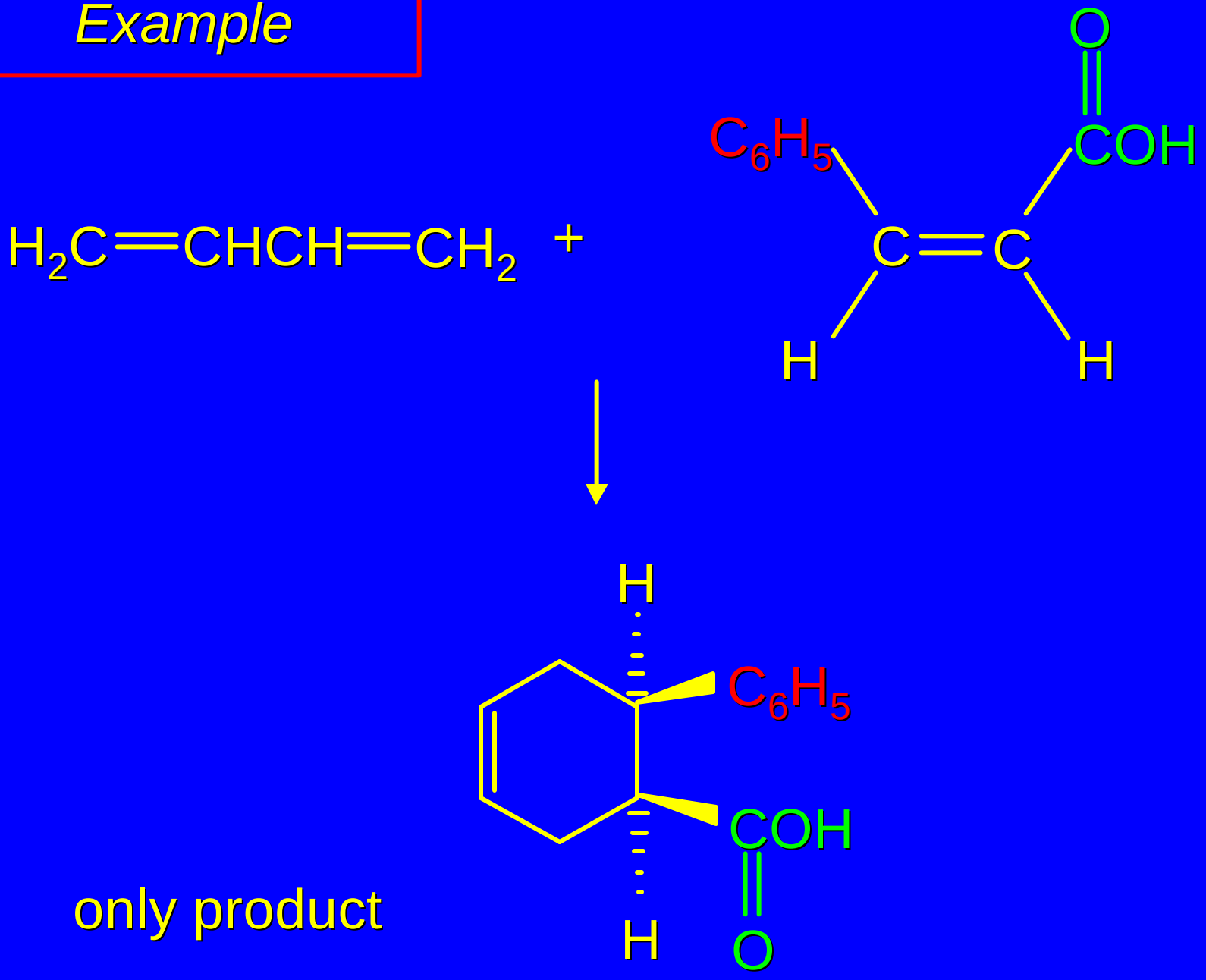
*Diels-Alder Reaction is Stereospecific**

syn addition to alkene

cis-trans relationship of substituents on alkene retained in cyclohexene product

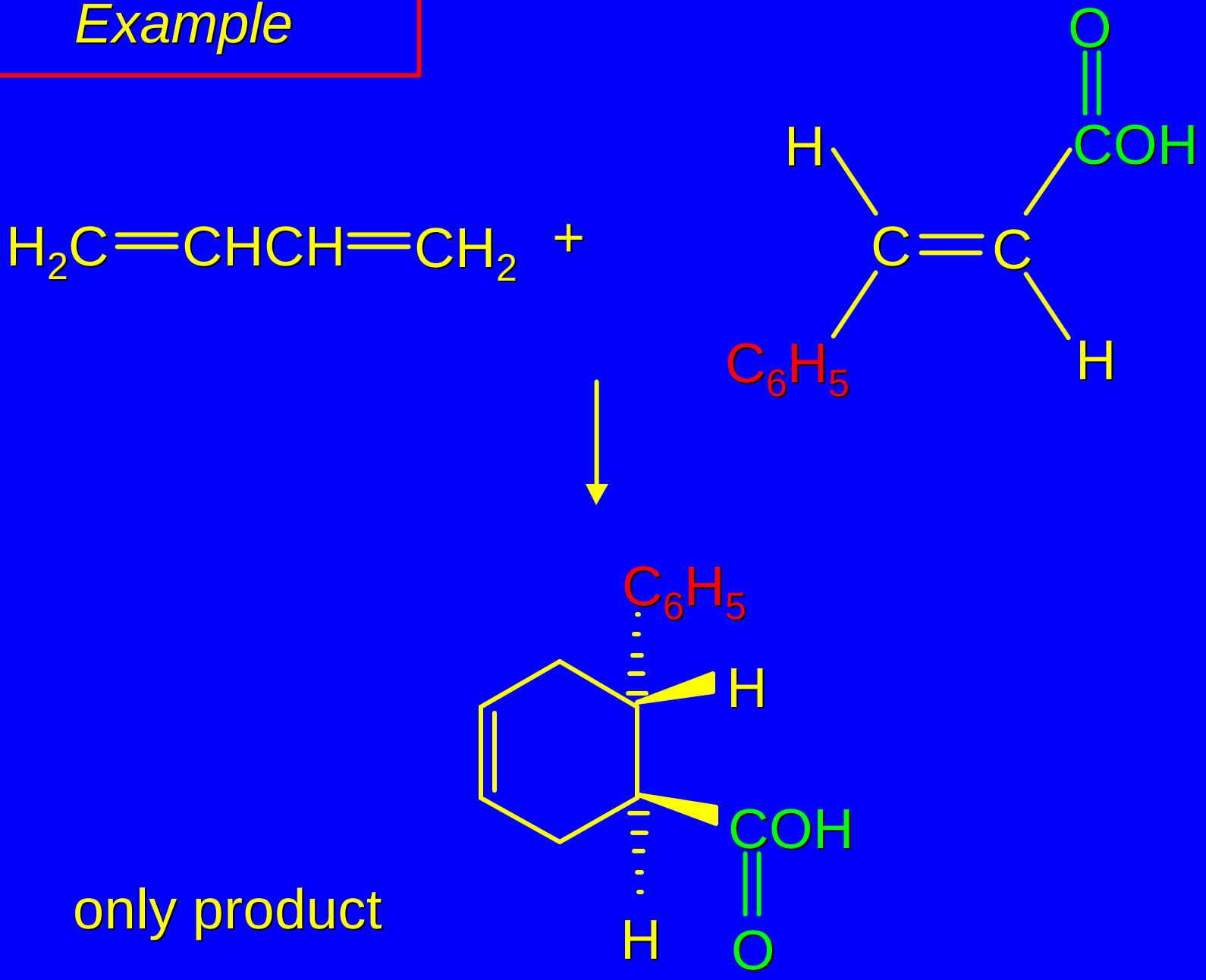
**A stereospecific reaction is one in which stereoisomeric starting materials give stereoisomeric products; characterized by terms like syn addition, anti elimination, inversion of configuration, etc.*

Example



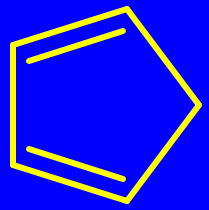
only product

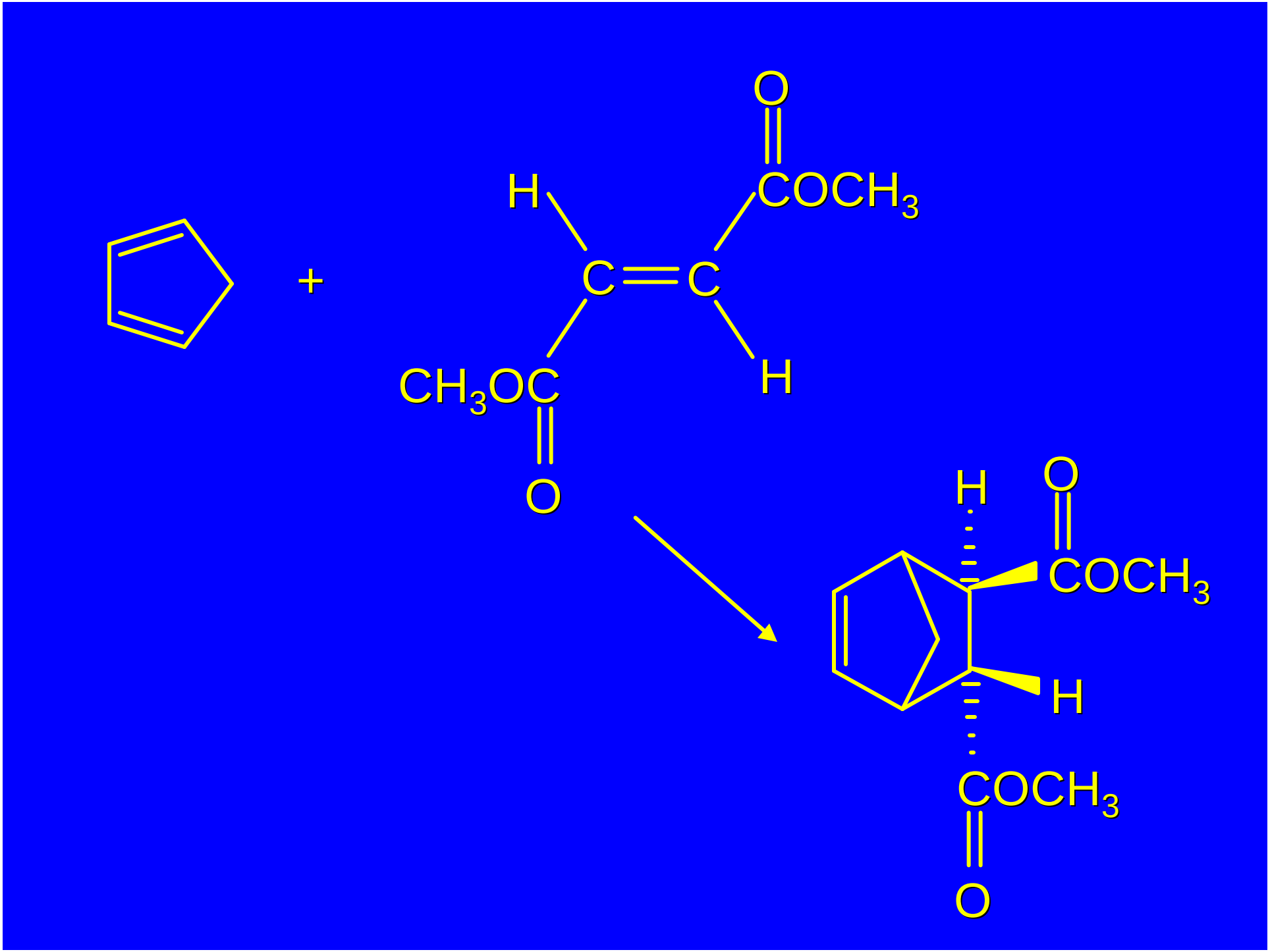
Example

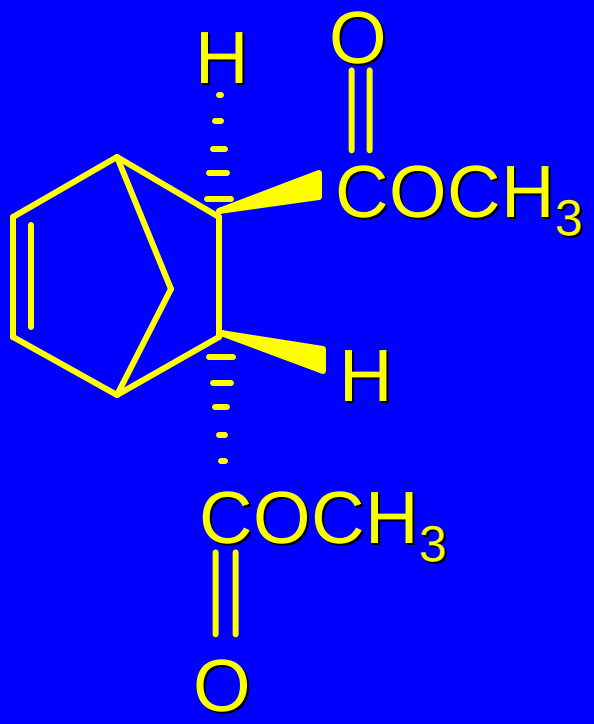


only product

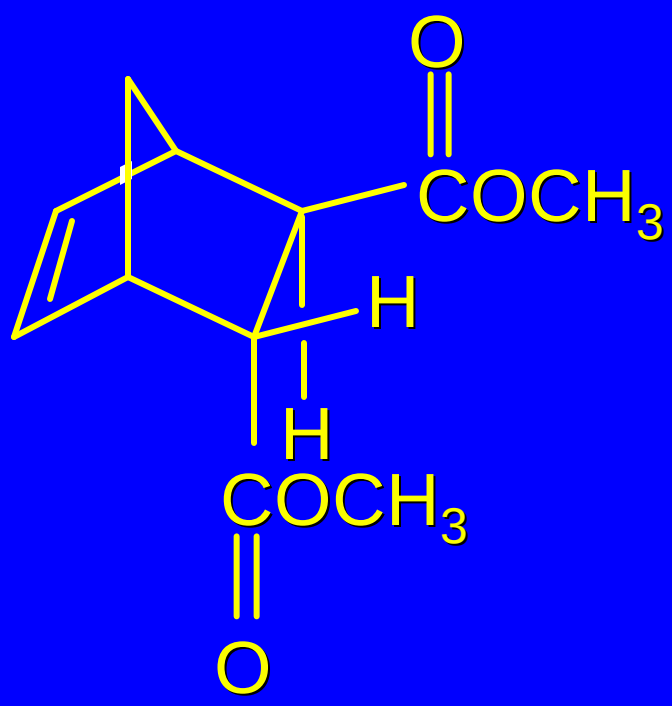
Cyclic dienes yield bridged bicyclic Diels-Alder adducts.




+
O
COCH3
H
C
C
H
CH3OC
O
H
O
COCH3
H
COCH3
O



is the same as



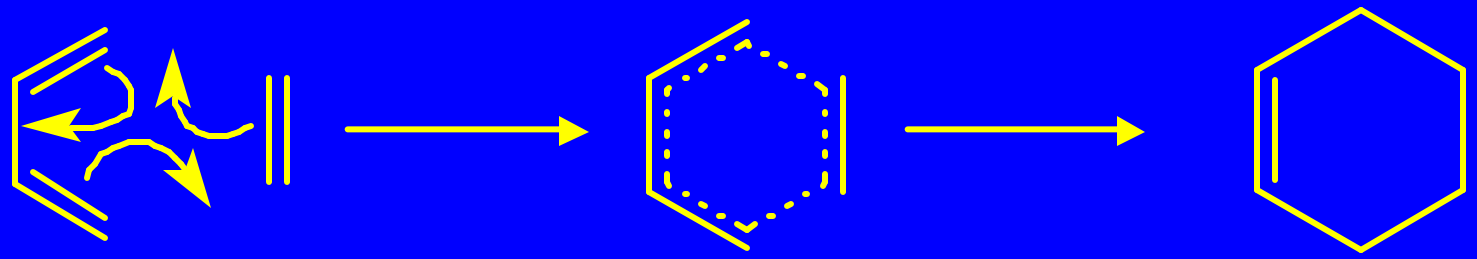
10.13
The π Molecular Orbitals
of
Ethylene and 1,3-Butadiene

Orbitals and Chemical Reactions

A deeper understanding of chemical reactivity can be gained by focusing on the *frontier orbitals* of the reactants.

Electrons flow from the highest occupied molecular orbital (HOMO) of one reactant to the lowest unoccupied molecular orbital (LUMO) of the other.

Orbitals and Chemical Reactions



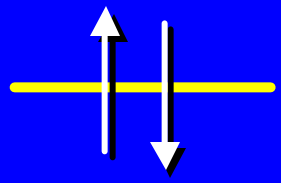
We can illustrate HOMO-LUMO interactions by way of the Diels-Alder reaction between ethylene and 1,3-butadiene.

We need only consider only the π electrons of ethylene and 1,3-butadiene. We can ignore the framework of σ bonds in each molecule.

The p MOs of Ethylene

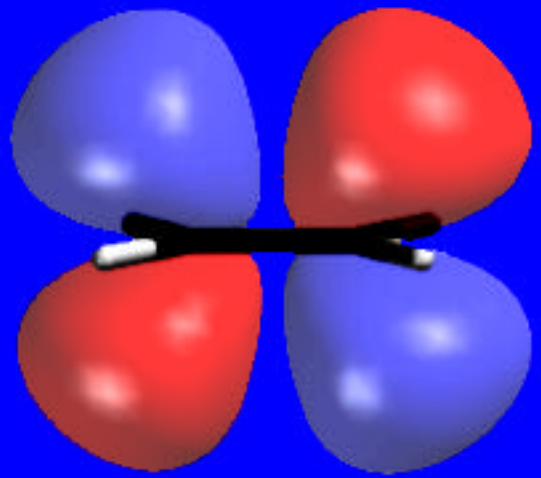
red and blue colors distinguish sign of wave function

bonding π MO is antisymmetric with respect to plane of molecule



Bonding π orbital of ethylene; two electrons in this orbital

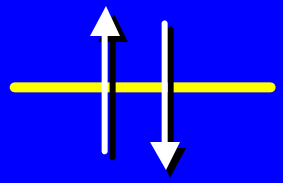
The p MOs of Ethylene



Antibonding π orbital of ethylene;
no electrons in this orbital

LUMO

HOMO



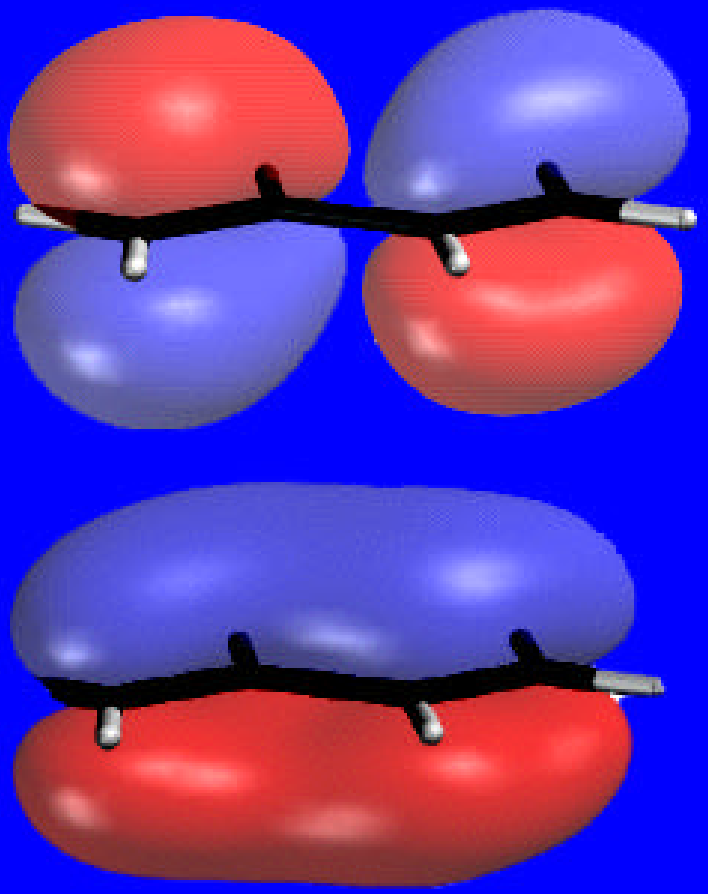
Bonding π orbital of ethylene;
two electrons in this orbital

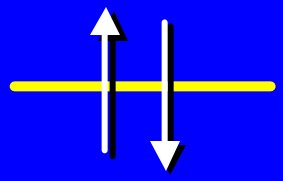
The p MOs of 1,3-Butadiene

Four *p* orbitals contribute to the π system of 1,3-butadiene; therefore, there are four π molecular orbitals.

Two of these orbitals are bonding; two are antibonding.

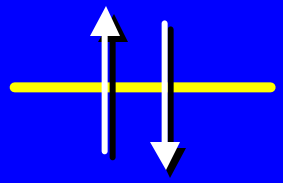
The Two Bonding p MOs of 1,3-Butadiene





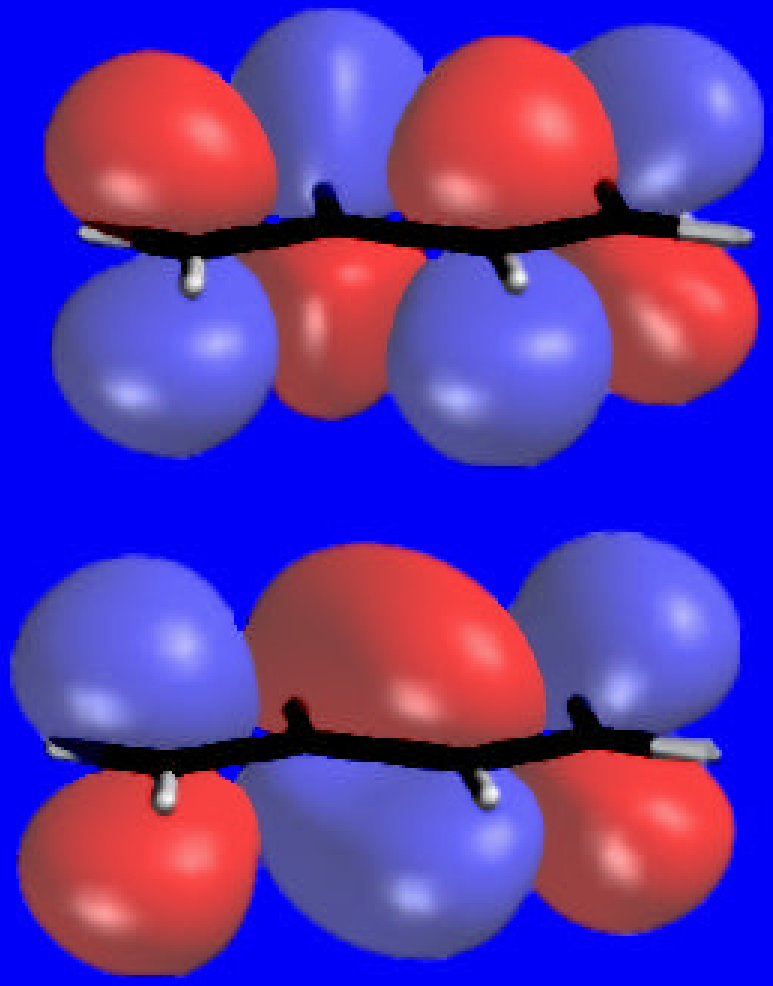
HOMO

4 *p* electrons; 2 in each orbital



Lowest energy orbital

The Two Antibonding p MOs of 1,3-Butadiene



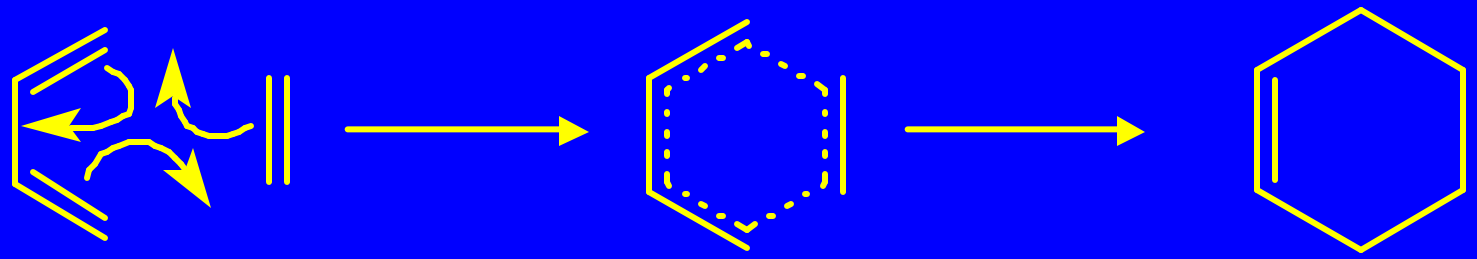
Highest energy orbital

LUMO

Both antibonding orbitals are vacant

10.14
A π Molecular Orbital Analysis of the Diels-Alder Reaction

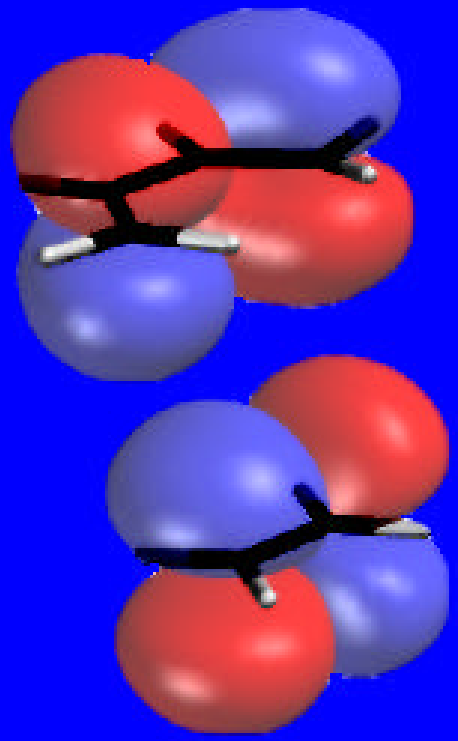
MO Analysis of Diels-Alder Reaction



Inasmuch as electron-withdrawing groups increase the reactivity of a dienophile, we assume electrons flow from the HOMO of the diene to the LUMO of the dienophile.

MO Analysis of Diels-Alder Reaction

HOMO of 1,3-butadiene



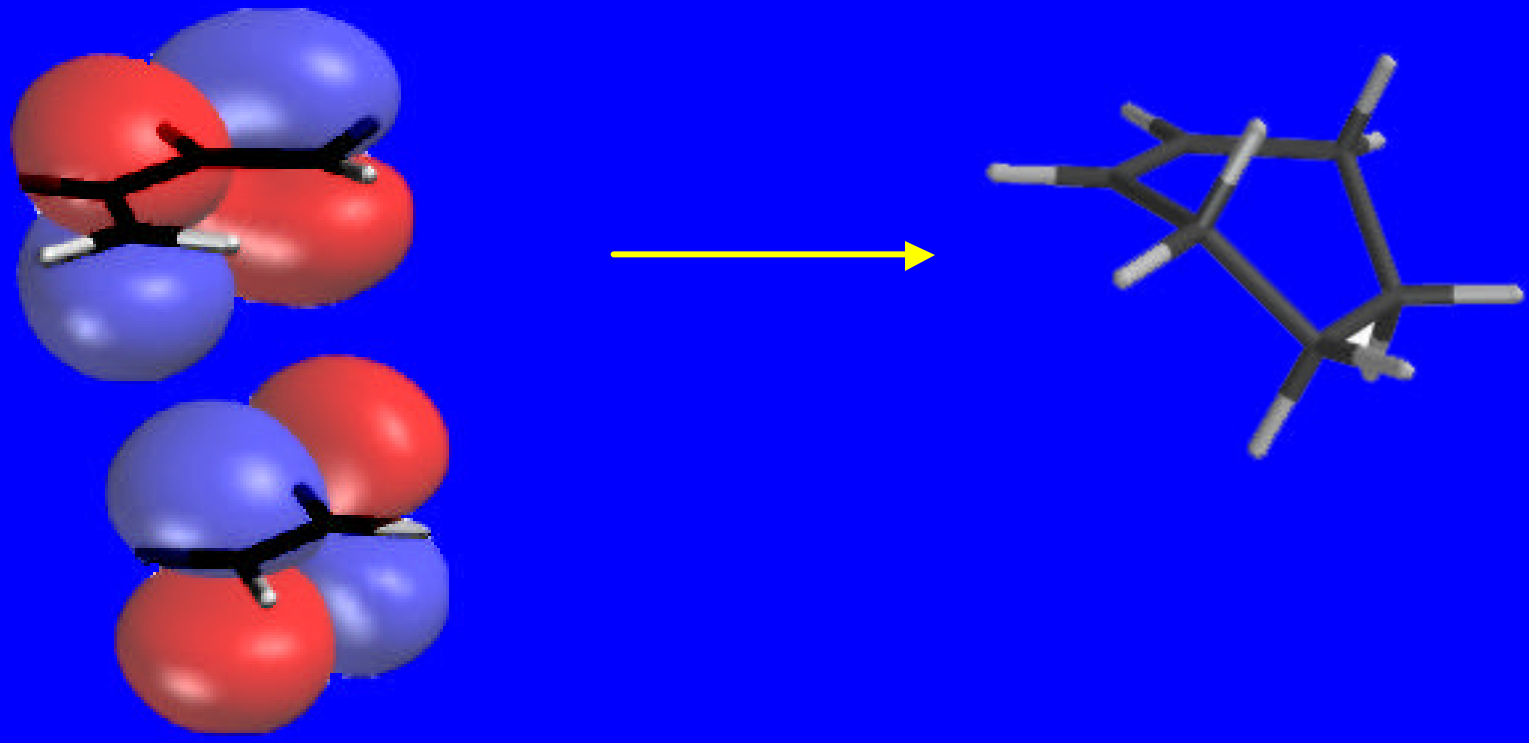
HOMO of 1,3-butadiene and LUMO of ethylene are in phase with one another

allows σ bond formation between the alkene and the diene

LUMO of ethylene (dienophile)

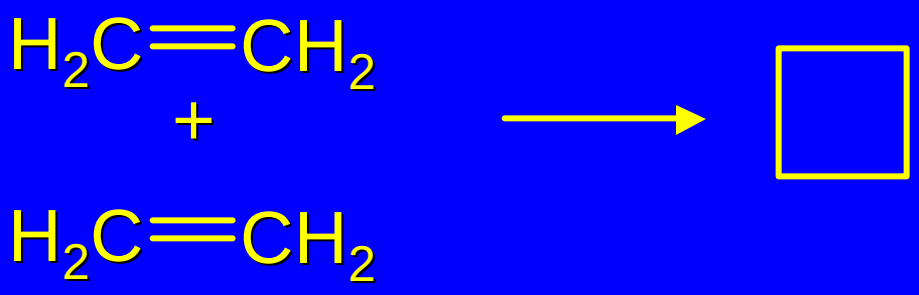
MO Analysis of Diels-Alder Reaction

HOMO of 1,3-butadiene



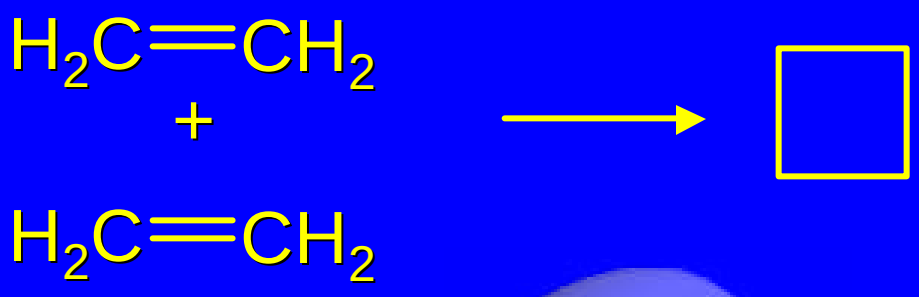
LUMO of ethylene (dienophile)

A "forbidden" reaction

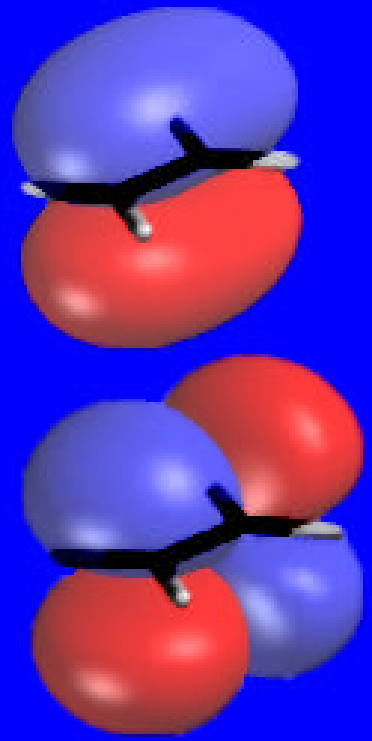


The dimerization of ethylene to give cyclobutane does not occur under conditions of typical Diels-Alder reactions. Why not?

A "forbidden" reaction



HOMO-LUMO mismatch of two ethylene molecules precludes single-step formation of two new σ bonds



HOMO of one ethylene molecule

LUMO of other ethylene molecule