



TÁMOP-4.1.1.F-14/1/KONV-2015-0006

SZTE TTIK, KTCS, 1a) Duális és moduláris
képzésfejlesztés a mesterképzéshez

Periciklusos reakciók 1: cikloaddíciók

Pálinkó István, egyetemi tanár

SZÉCHENYI 2020



MAGYARORSZÁG
KORMÁNYA

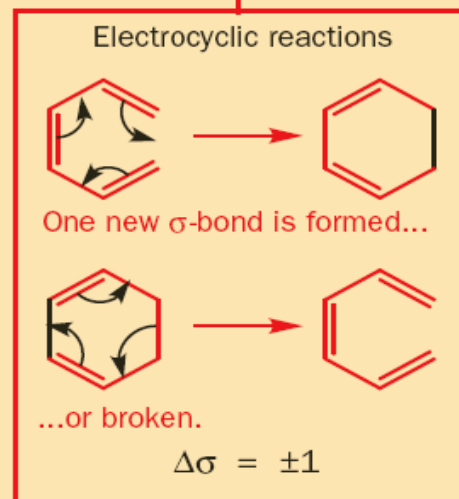
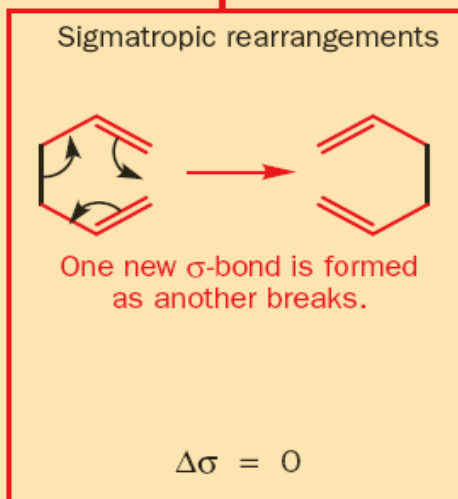
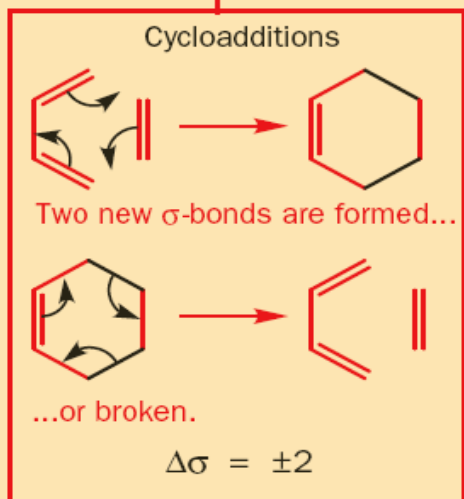
Európai Unió
Európai Szociális
Alap



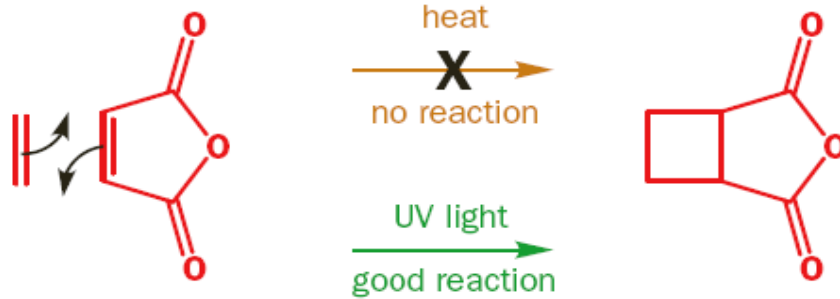
BEFEKTETÉS A JÖVŐBE

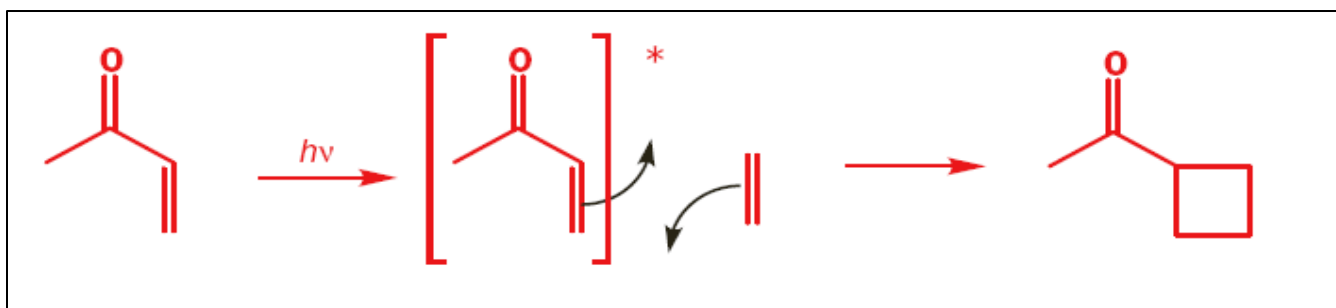
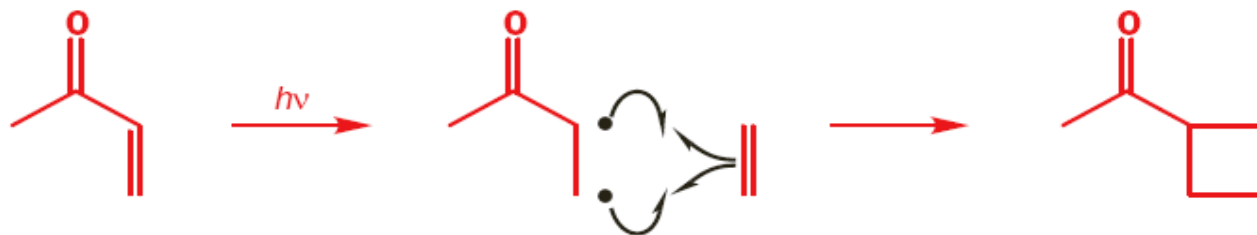
- The types of pericyclic reactions are distinguished by the number of σ bonds made or broken

Types of pericyclic reactions

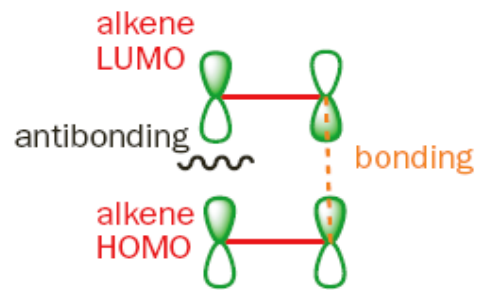


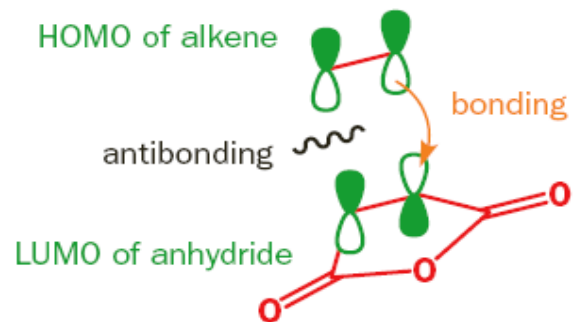
[2+2] cikloaddíciók reakciók

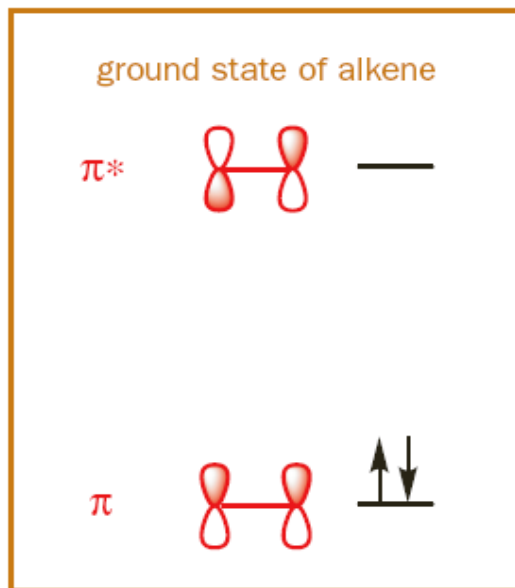




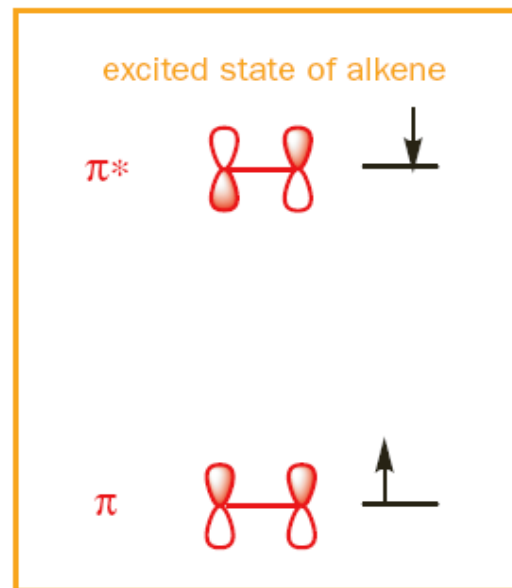

A frontális molekulapálya modell [2+2] cikloaddíciókra





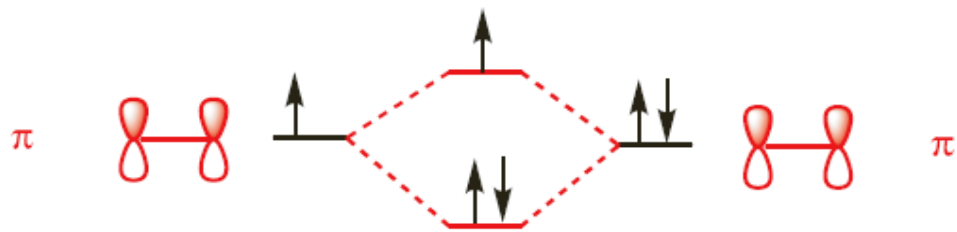
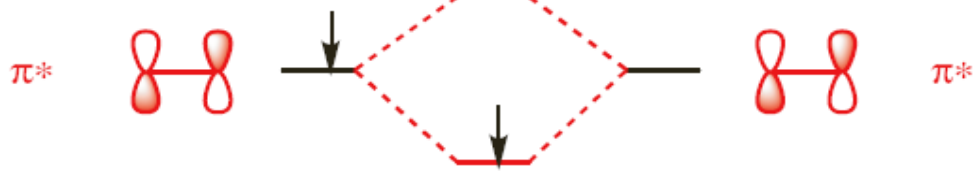


UV light
($h\nu$)

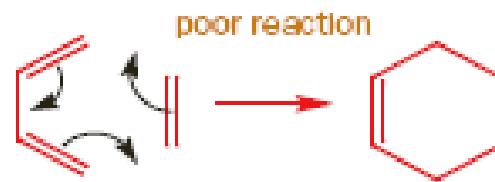


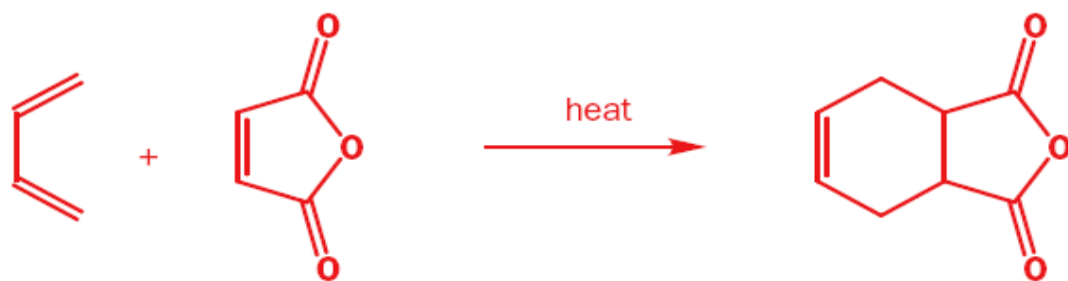
excited state of one alkene

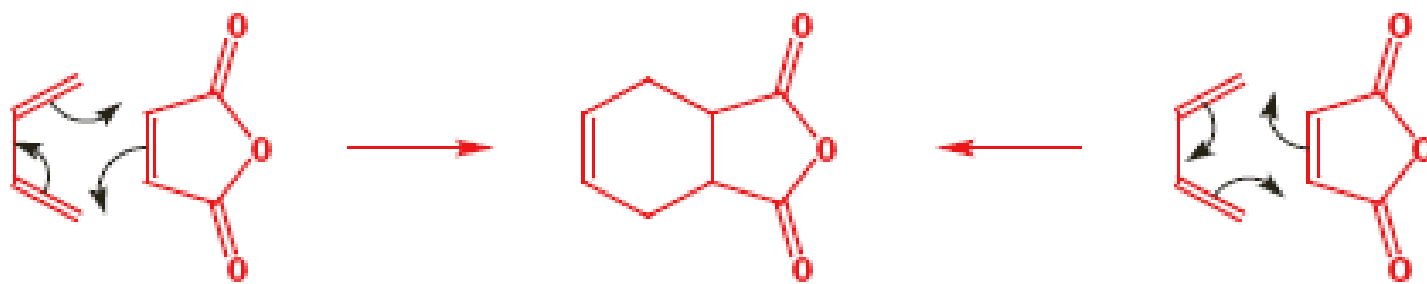
ground state of the other alkene

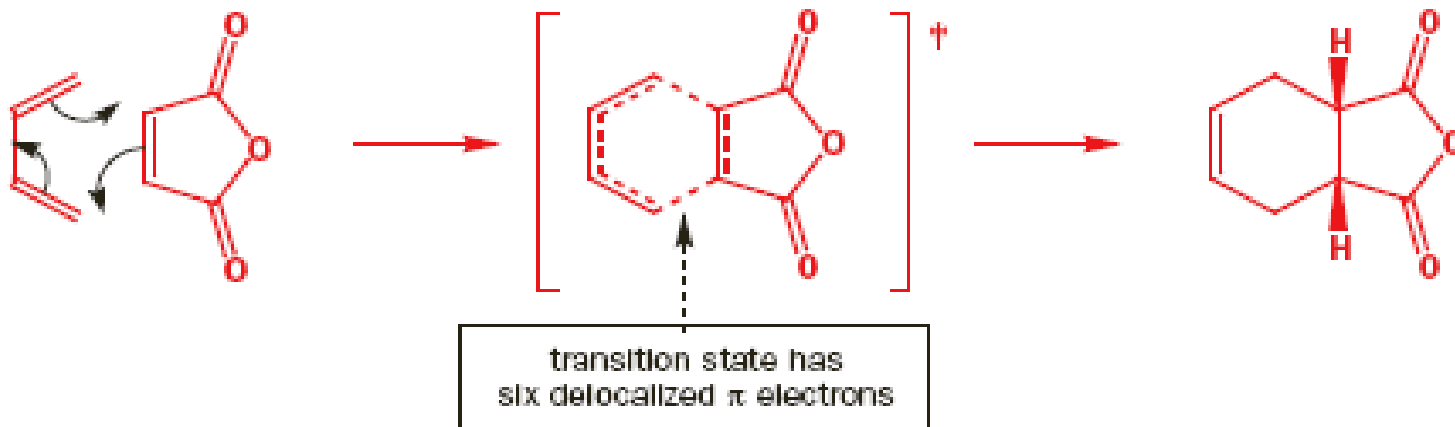


[4+2] cikloaddíciók reakciók (Diels-Alder reakciók)





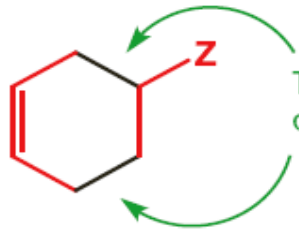




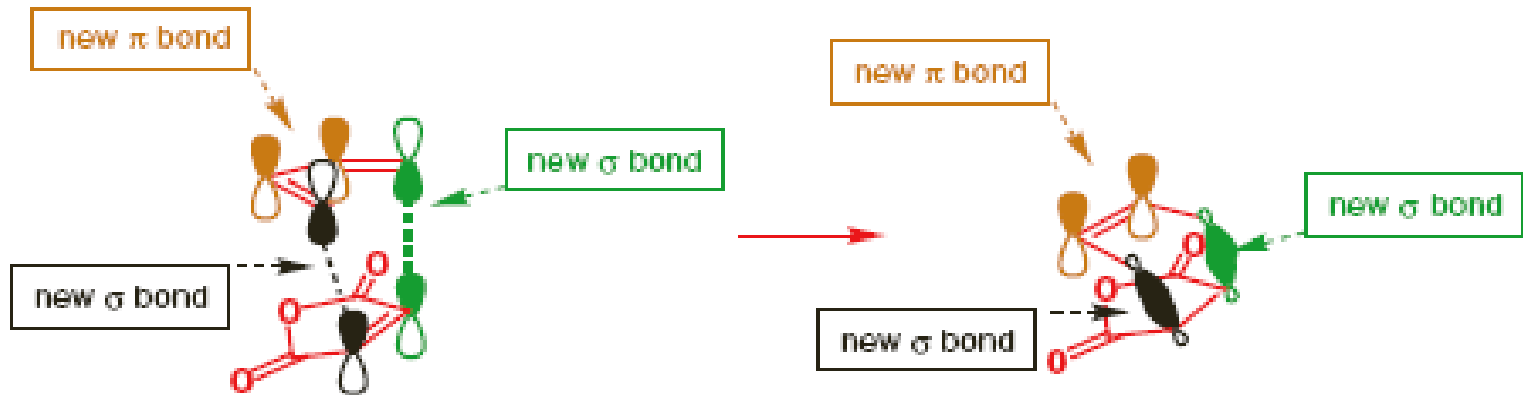
all arrows
start on
 π bonds



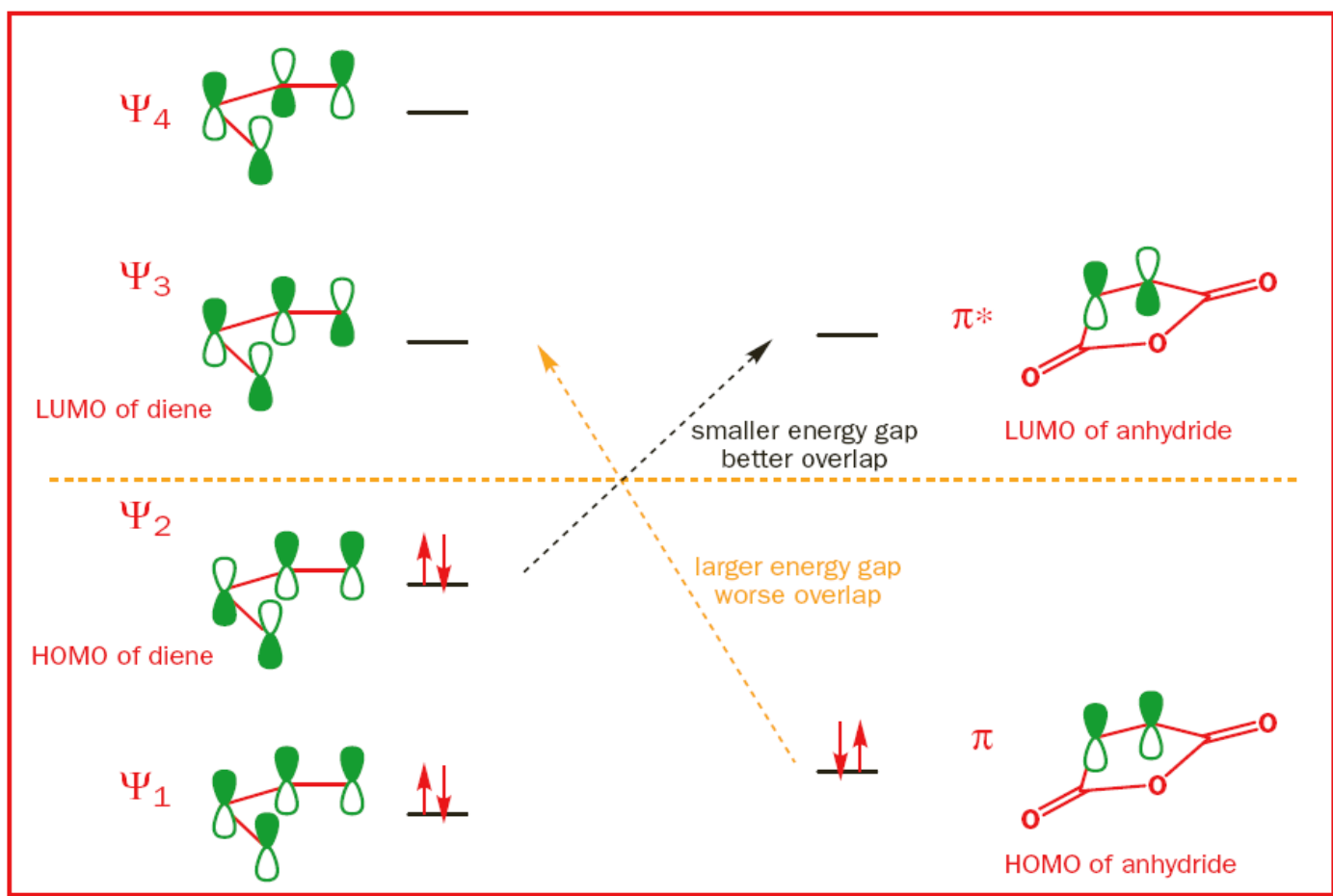
[4 + 2]
cycloaddition

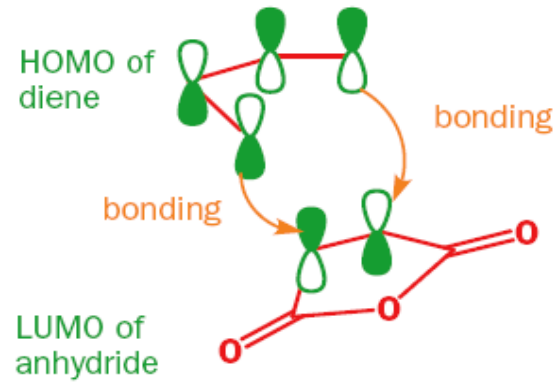


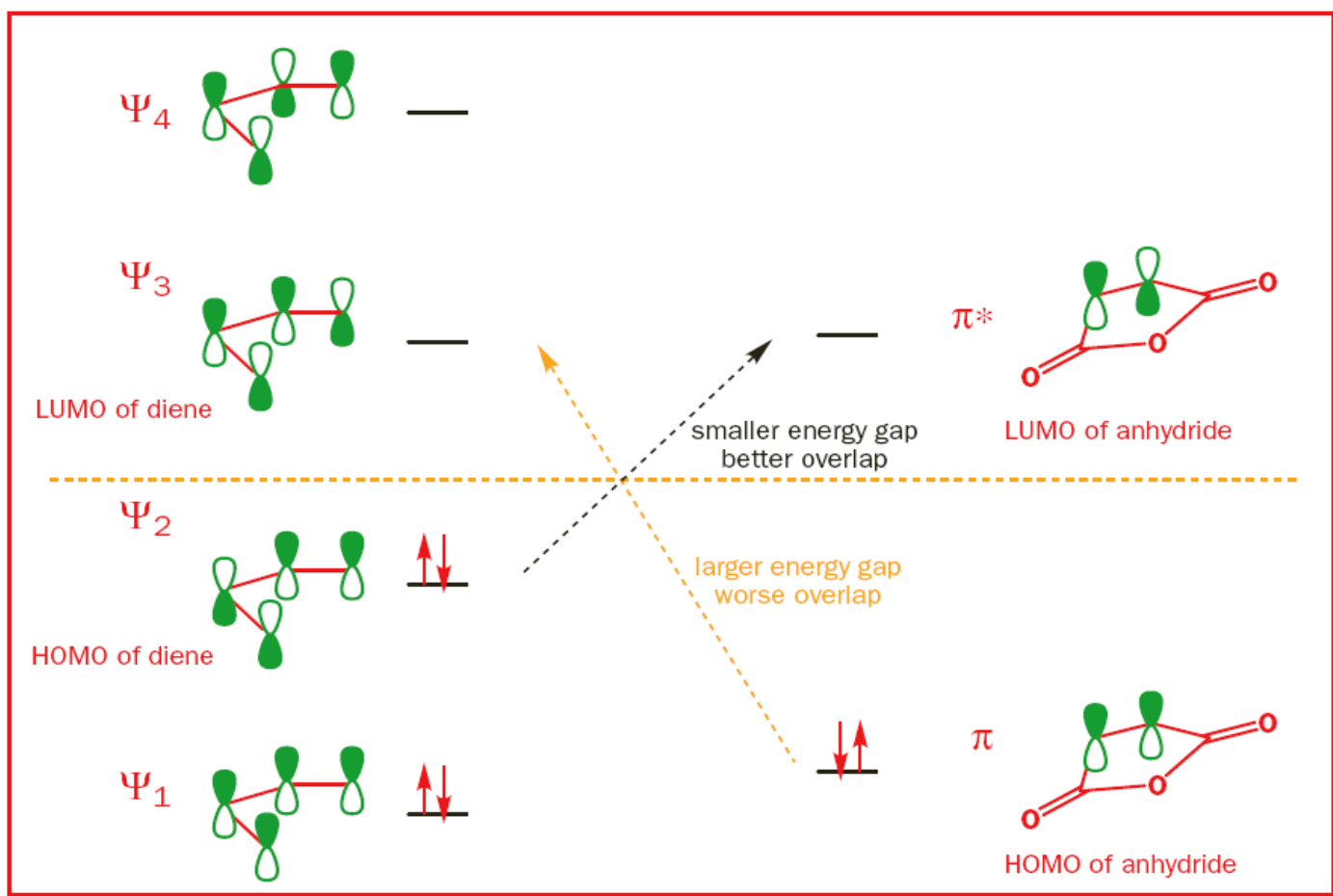
TWO new
 σ bonds

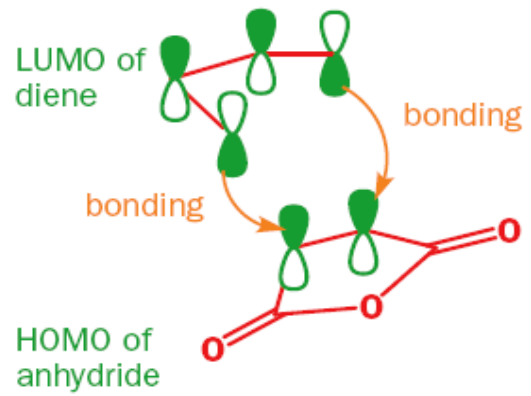


A frontális molekulapálya modell [4+2] ciklizációkra

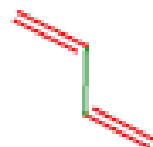






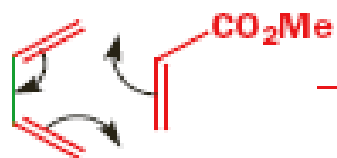


s-trans
conformation

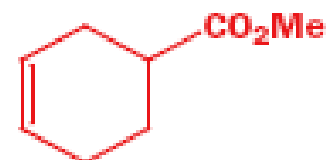


favoured, but
can't do
Diels-Alder

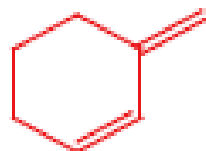
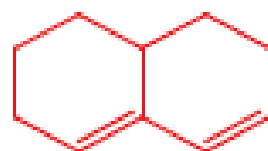
s-ds
conformation

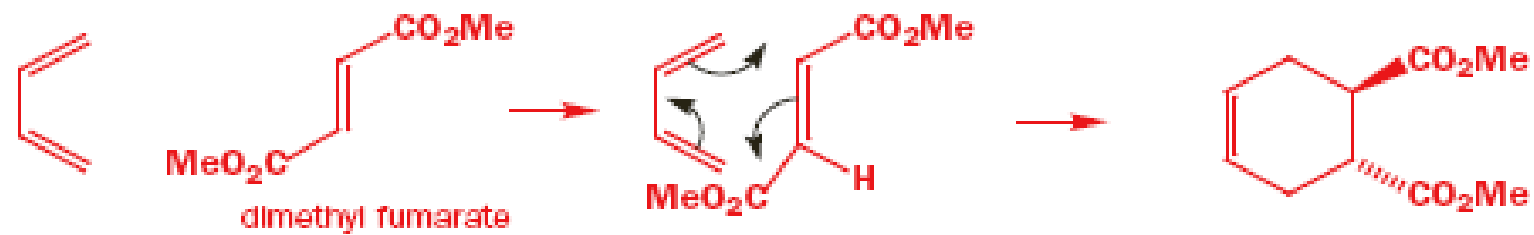
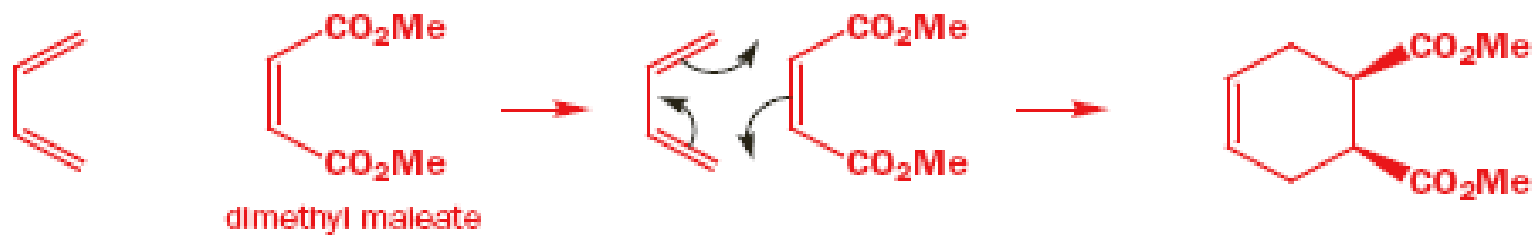


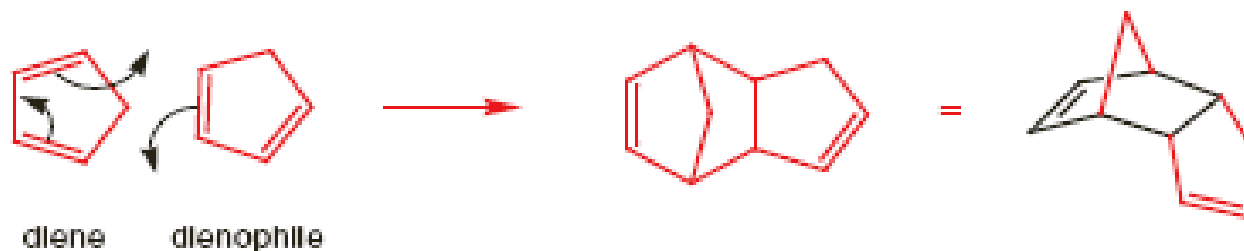
disfavoured; can
do Diels-Alder



dienes permanently in the
s-trans conformation
(cannot do Diels-Alder reactions)

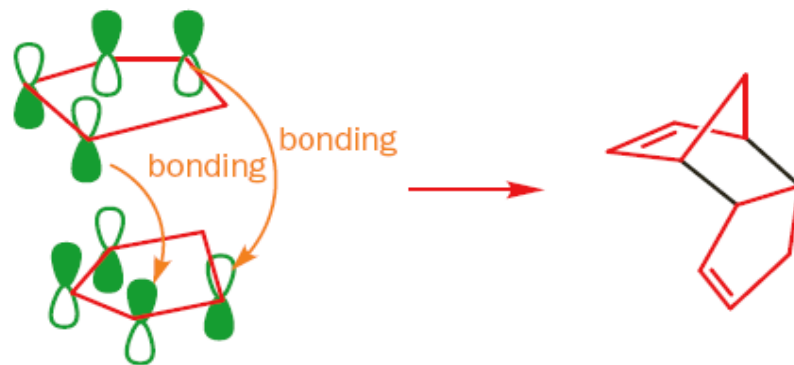




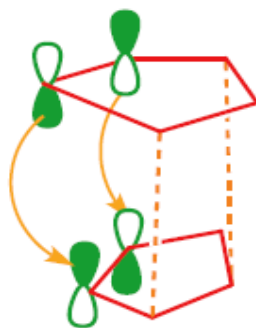


az endo-szelektivitás kinetikai kontrol eredménye – nem egyensúlyi a reakció

ha a reakció egyensúlyi, akkor exo-termék keletkezik (furán reakciója maleinsav anhidriddel)

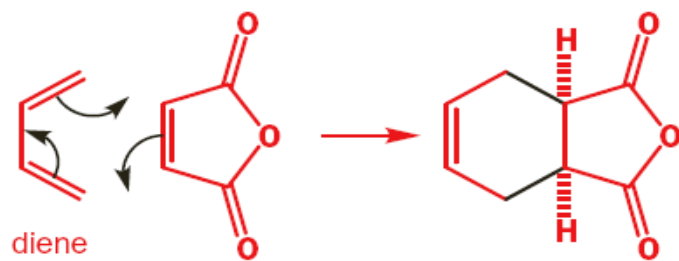


bonding interactions
leading to *endo* product

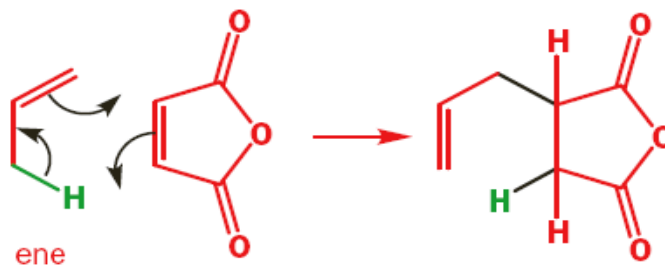


bonding interactions
leading to new σ bonds

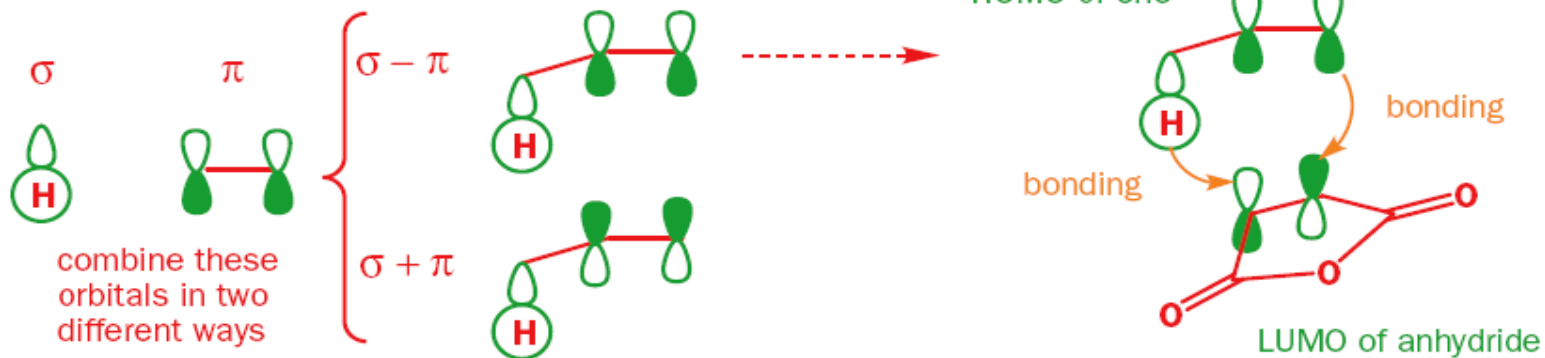
the Diels–Alder reaction



the Alder ene reaction

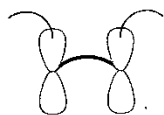


construction of HOMO of ene

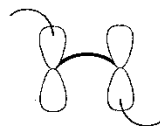


A Woodward-Hoffmann modell [4+2] cikloaddíciónkra

A. π Systems



Suprafacial



Antarafacial

B. σ Systems



Suprafacial



Suprafacial



Antarafacial

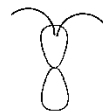


Suprafacial

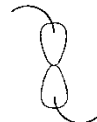


Antarafacial

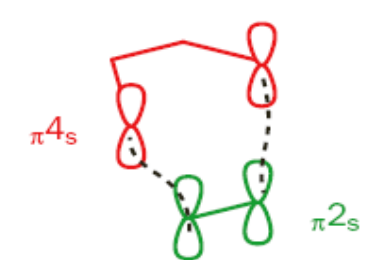
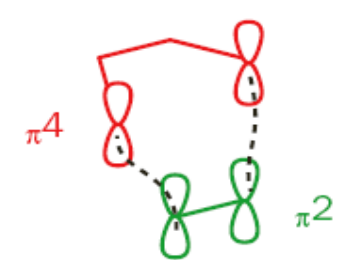
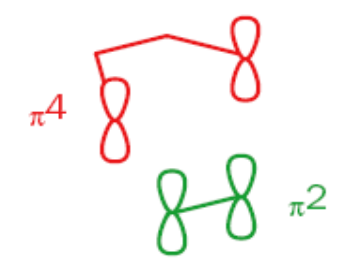
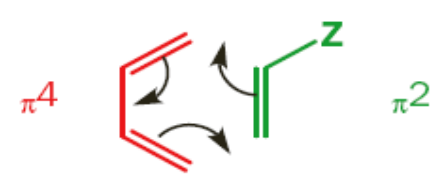
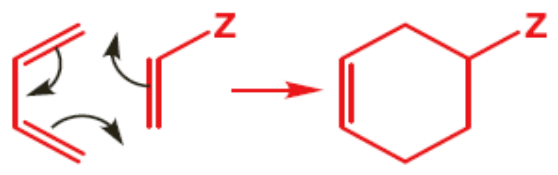
C. Lone pairs (ω)



Suprafacial



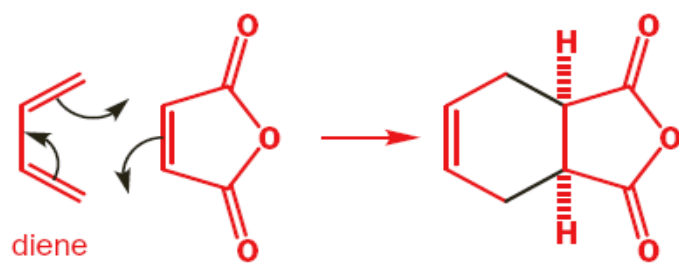
Antarafacial



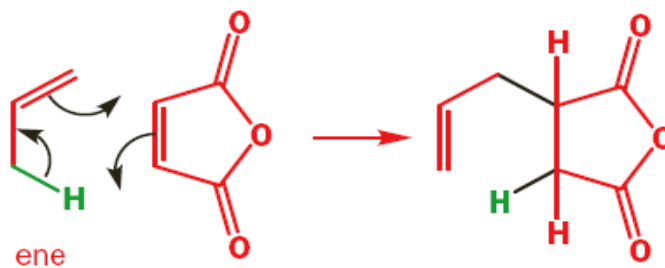
● **Woodward–Hoffmann rules**

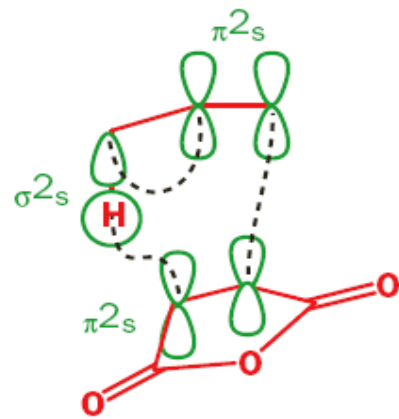
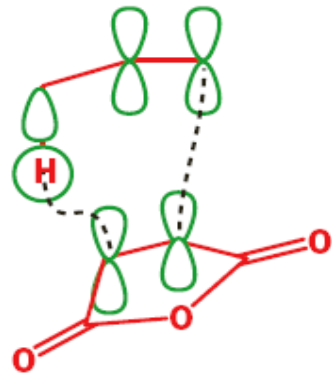
In a thermal pericyclic reaction the total number of $(4q + 2)_s$ and $(4r)_a$ components must be odd.

the Diels–Alder reaction



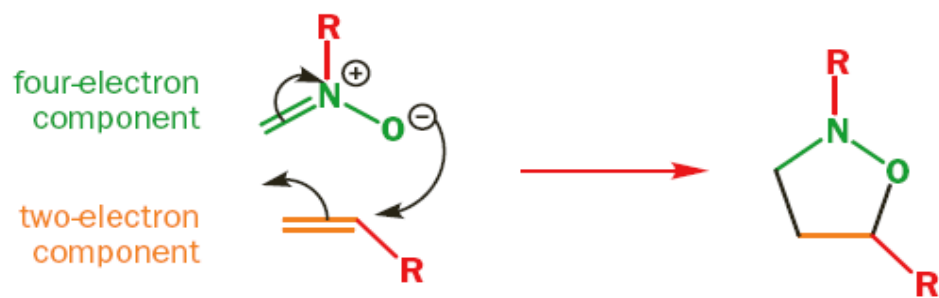
the Alder ene reaction





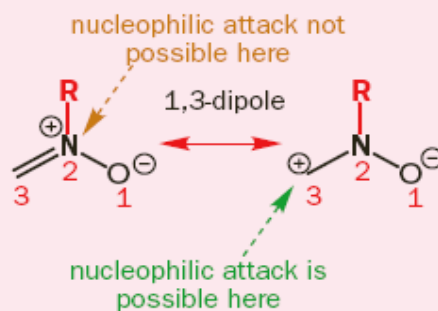
**Öttagú gyűrűt eredményező [3+2] cikloaddíció
(1,3-dipoláris cikloaddíció)**

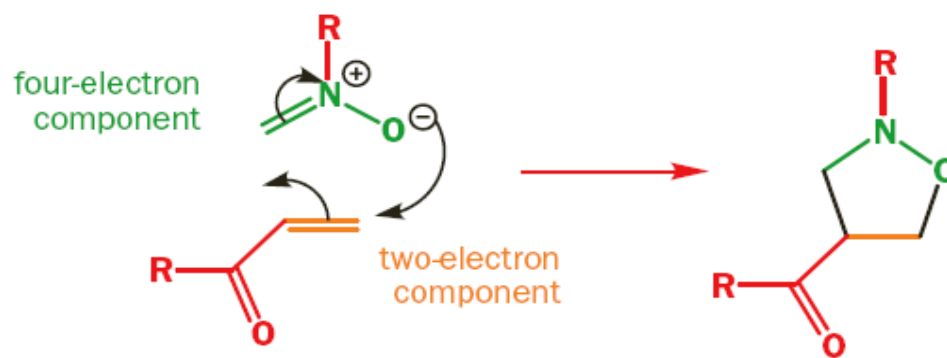
nitron





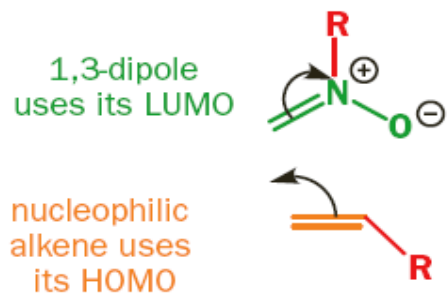
The charges make it look like a 1,2-dipole, but nucleophilic attack on N^+ is impossible.



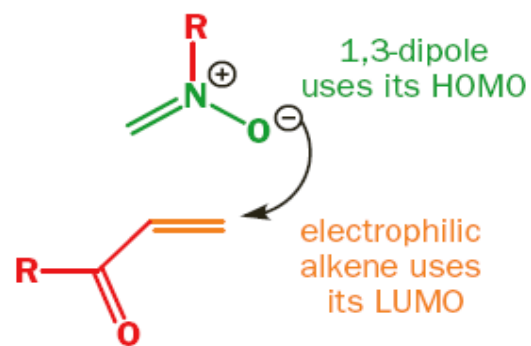


Értelmezés a frontális molekulapálya elmélet segítségével

with an electron-rich dipolarophile



with an electron-poor dipolarophile



a 1,3-dipolar cycloaddition with a nitrile oxide



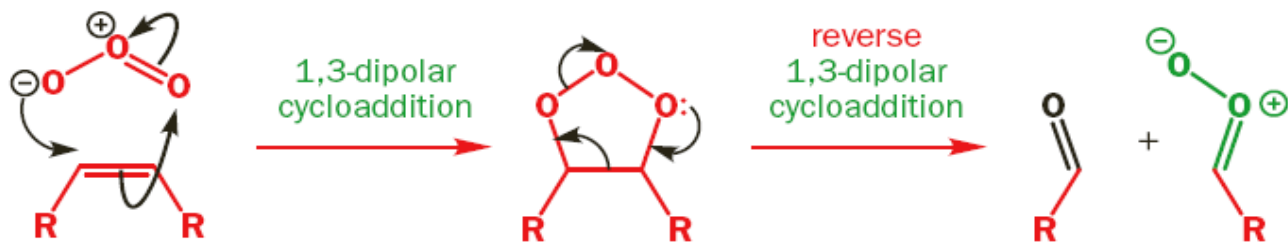
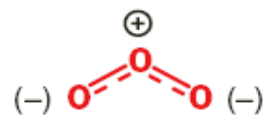
LUMO of nitrile oxide



HOMO of alkene



structure of ozone



KÖSZÖNÖM A FIGYELMET!

SZÉCHENYI  2020



MAGYARORSZÁG
KORMÁNYA

Európai Unió
Európai Szociális
Alap



BEFEKTETÉS A JÖVŐBE