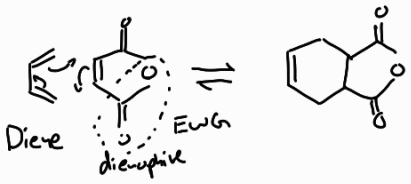
Pericyclic reactions

- Cyclic additions
- Sigmatropic rearrangements

Diels-Alder reactions

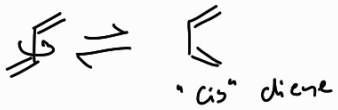
(• Enzymatically observed)

ex



2 requirement

1) diene has to be "cis"

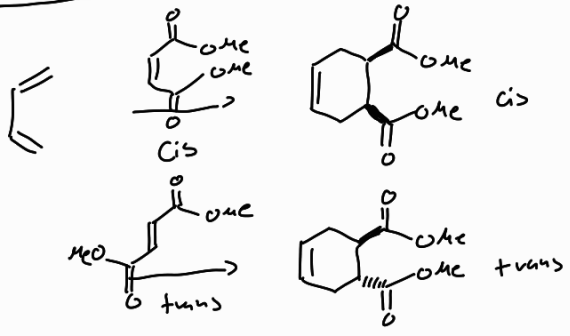


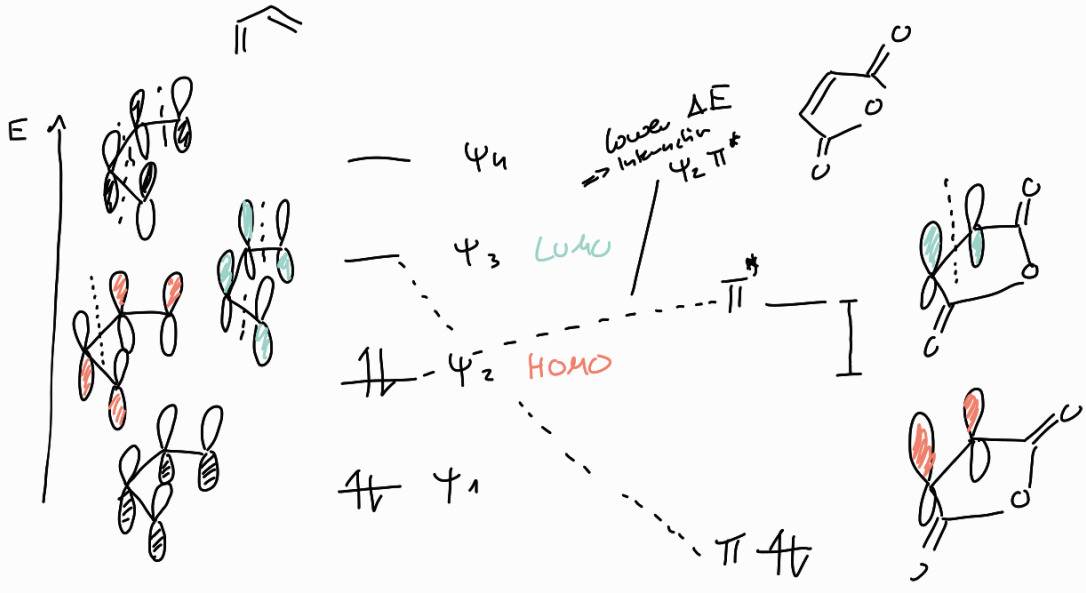
( non reactive)

2) dienophile has to have EWG

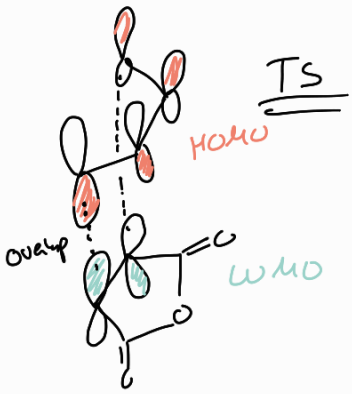
(few exceptions)

Stereospecific reaction:

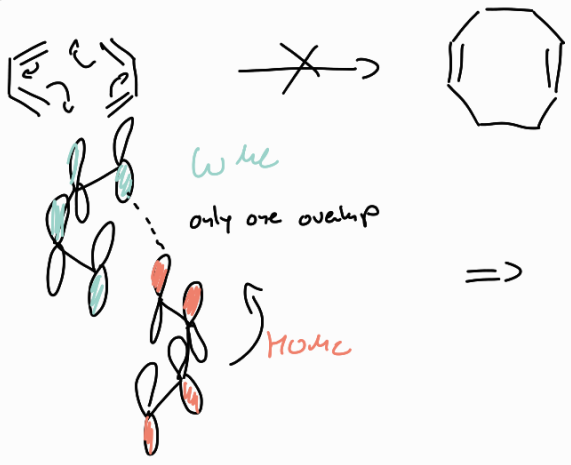




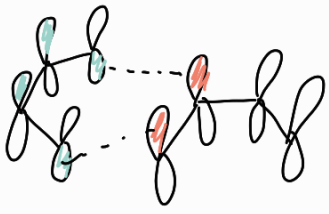
=> EWG lower orbital E



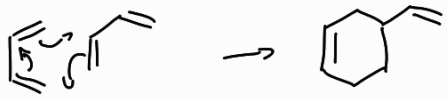
Why not :



=>



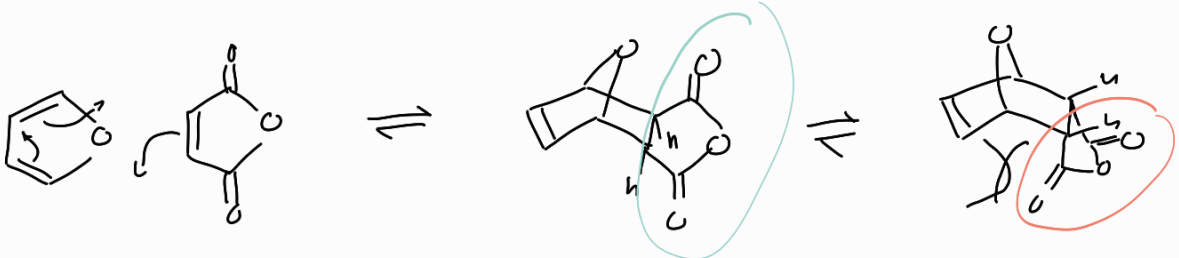
instead



→ but much slower than the other reaction, since there is no EWG lowers the energy of the orbitals.

The Endo rule

ex if reversible DA

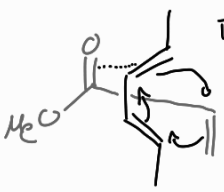


exo
= Ring away from large part of the other ring
thermodynamic product

endo
= Ring close to large part of the other ring
kinetic product

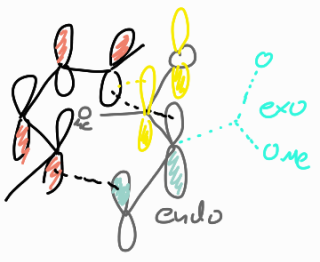
Many DA are high in Activation engy Ea => kinetic endo product is formed

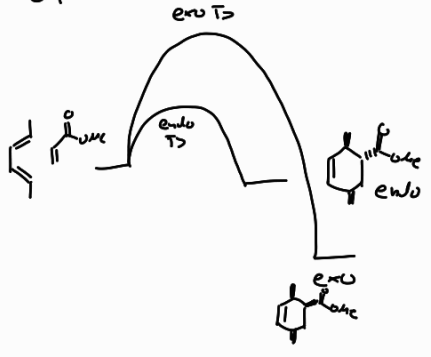
ex



π-π interaction = gain in Engy

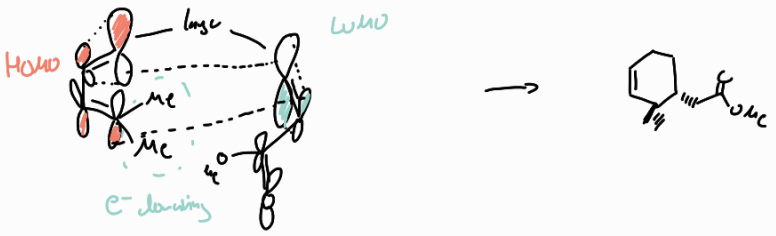
=

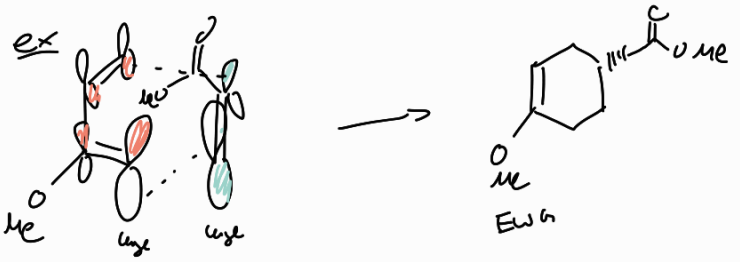




DA Regioselectivity

EWG on dienophile disturb orbital coefficients
EDG on diene

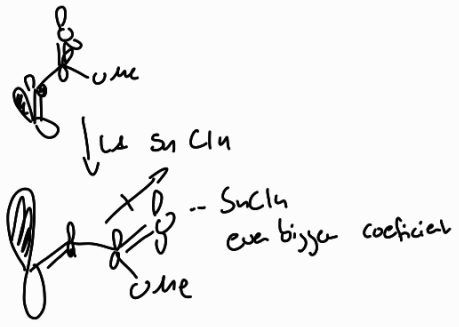


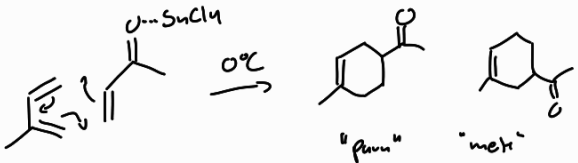


=> Cluider effects of EDG and EWG on where the largest coefficient lies.

=> DA TS is "aromatic-like" => op directing

-> To make the reaction faster, the effect of the EWG should be amplified eg. by Lewis; Proton Acids (Lewis e⁻)
=> DA catalysed by Lewis acid





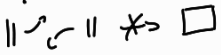
vs. un-catalysed 120°C → 71% 29%

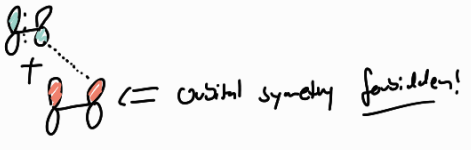
Other Cycloadditions

DA = 2+4 cycloadditions

2+2 cycloadd ?

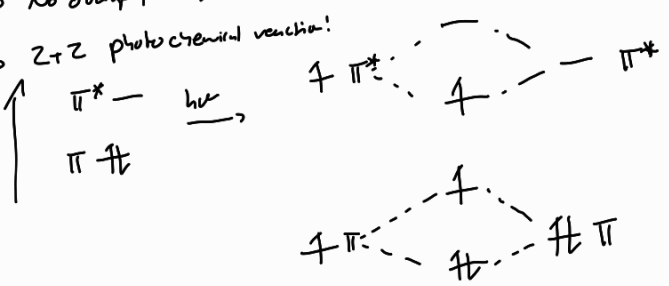
ex ethylene





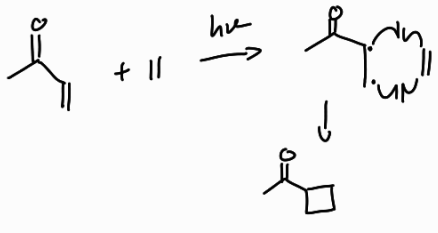
<= orbital symetry forbidden!

=> No overlap, nothing happens
↳ 2+2 photochemical reaction!



1e⁻ goes up in E
3 go down in E

Simplified:



(e⁻ no more in π but anti binding)