Conjugated Dienes

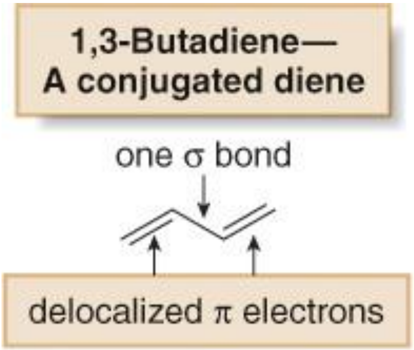
Chapter 14
Organic Chemistry, *8th Edition*
John E. McMurry

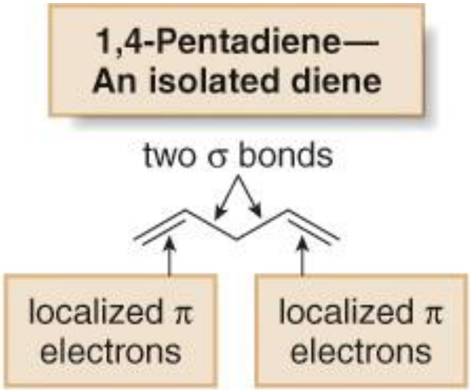
Dienes

- Propadiene (allene) is a cumulated diene.
- 1,3-Butadiene is a conjugated diene.
- 1,4-Pentadiene is an isolated diene.

Allene –
A cumulated diene

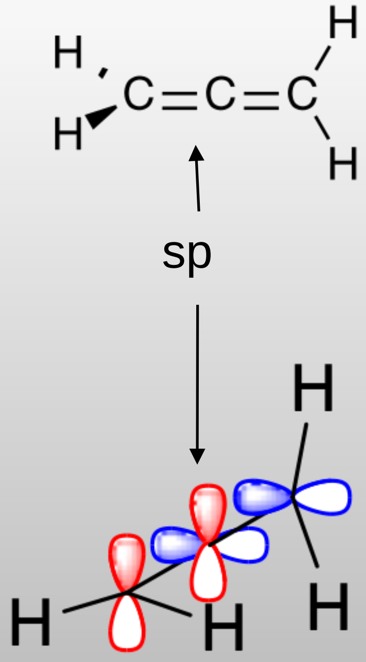
$H_2C=C=CH_2$



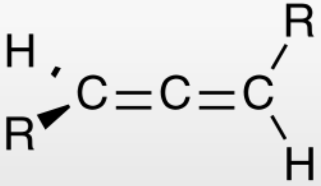


Allenes

Bonding



Stereochemistry



- Chiral
- 1,3 disubstituted allenes have no plane of symmetry
- Axial chirality

Energetics

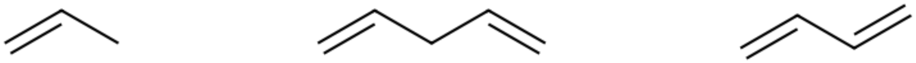
	$\Delta H_f°$ (Kcal/mol)
$H_2C{=}C{=}CH_2$	45.5
$HC{\equiv}C{-}CH_3$	44.2

modelli 3D

Conjugated Dienes

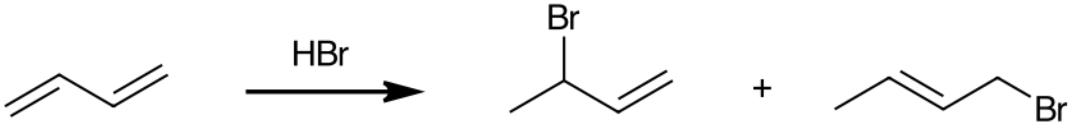
- The C—C single bond joining the two double bonds is unusually short.

- Conjugated dienes are more stable than similar isolated dienes.



ΔH_{hydrog} (kcal/mol)	- 30	- 60	- 56

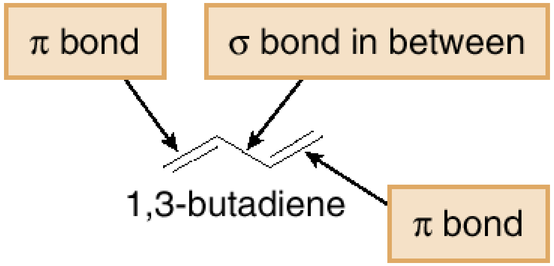
- Some reactions of conjugated dienes are different than reactions of isolated double bonds.



- Conjugated dienes absorb light at longer wavelengths than alkenes.

Delocalisation, Resonance, and Dienes

Delocalisation occurs whenever *p* orbitals can overlap on three or more adjacent atoms.

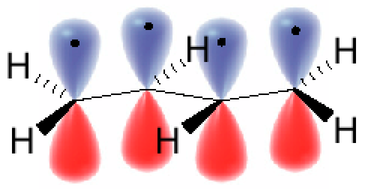


π bond

σ bond in between

π bond

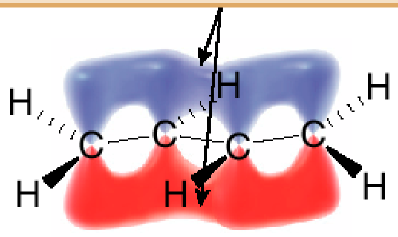
1,3-butadiene



four adjacent *p* orbitals

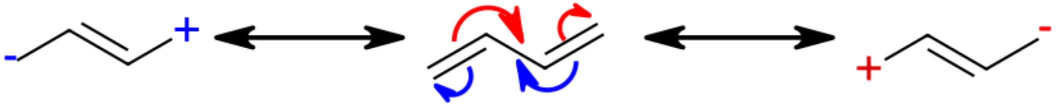
Each C is sp^2 hybridized and has a *p* orbital containing one electron.

overlap of adjacent *p* orbitals



The electron density in the two π bonds is delocalized.

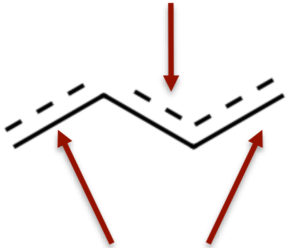
Delocalisation, Resonance, and Dienes



charge separation
less stable

neutral
more stable

charge separation
less stable

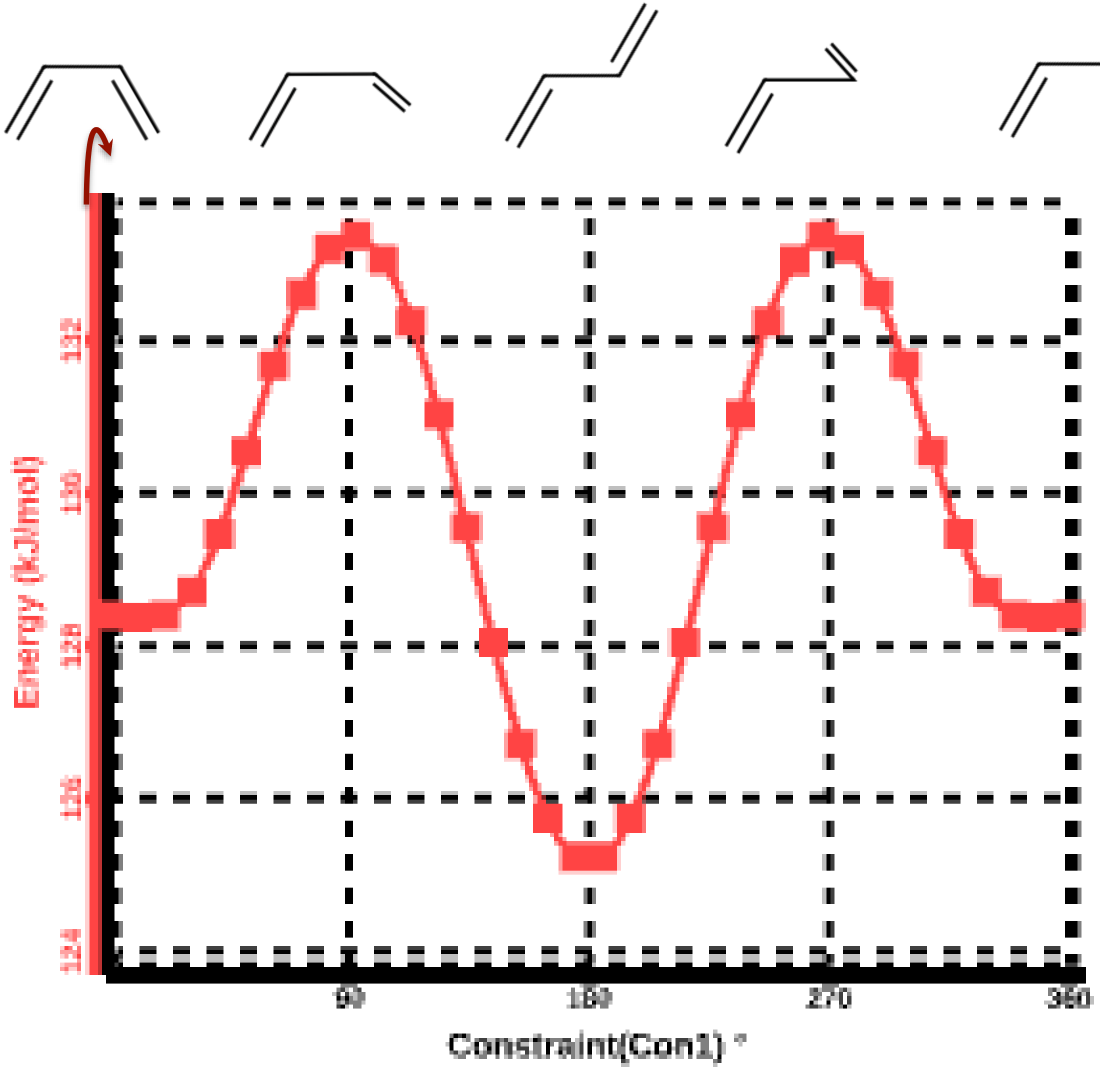


lower π
electron density

higher π
electron density

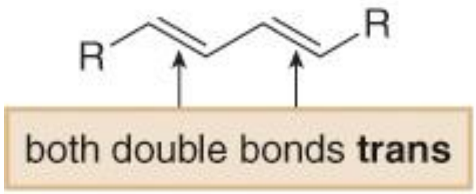
Conformational Analysis of 1,3-Butadiene

s-cis *orthogonal* *s-trans* *orthogonal* *s-cis*

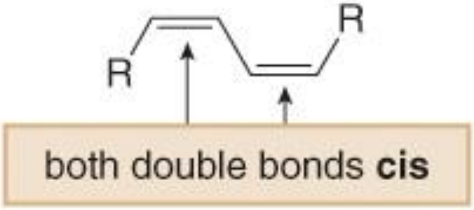


Structure

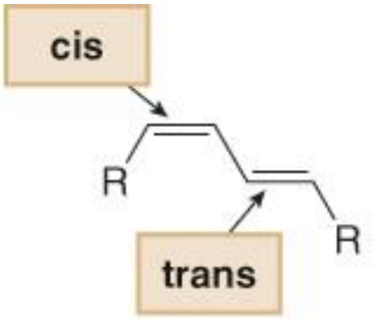
- Three stereoisomers are possible for 1,3-dienes with alkyl groups bonded to each end carbon of the diene.



trans, trans-1,3-diene
or
(*E,E*)-1,3-diene



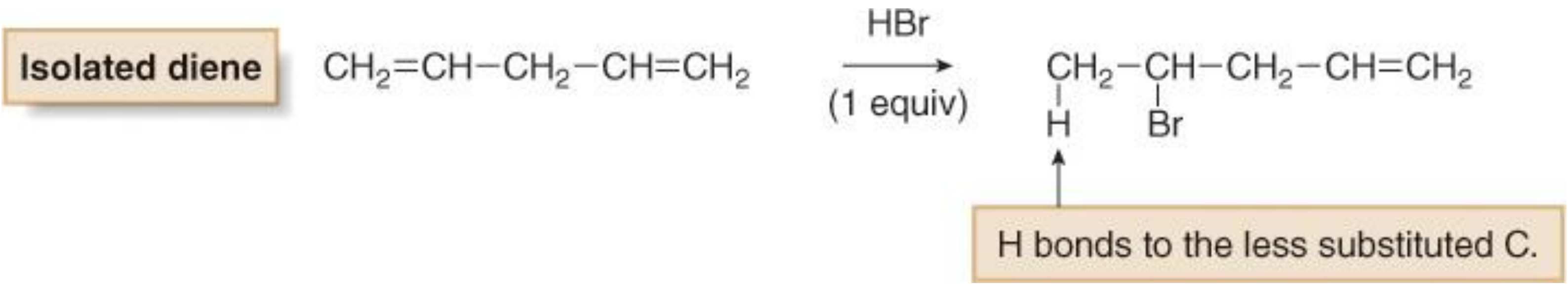
cis, cis-1,3-diene
or
(*Z,Z*)-1,3-diene



cis, trans-1,3-diene
or
(*Z,E*)-1,3-diene

modelli 3D

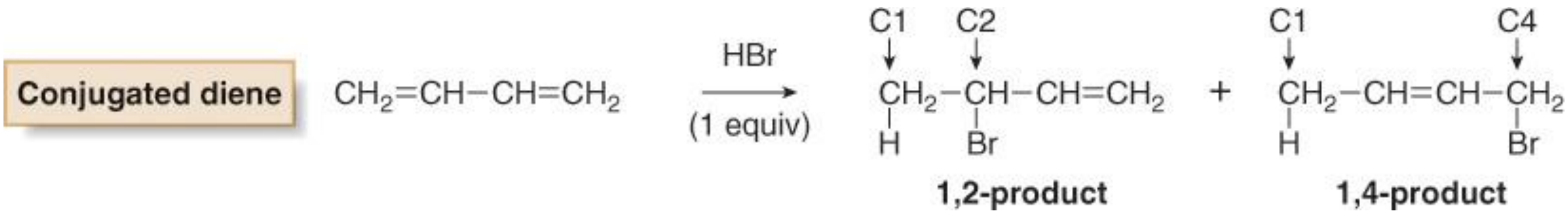
Electrophilic Addition: 1,2- Versus 1,4-Addition



Isolated diene

$$CH_2{=}CH{-}CH_2{-}CH{=}CH_2 \xrightarrow[\text{(1 equiv)}]{HBr} \underset{H}{CH_2}{-}\underset{Br}{CH}{-}CH_2{-}CH{=}CH_2$$

H bonds to the less substituted C.



Conjugated diene

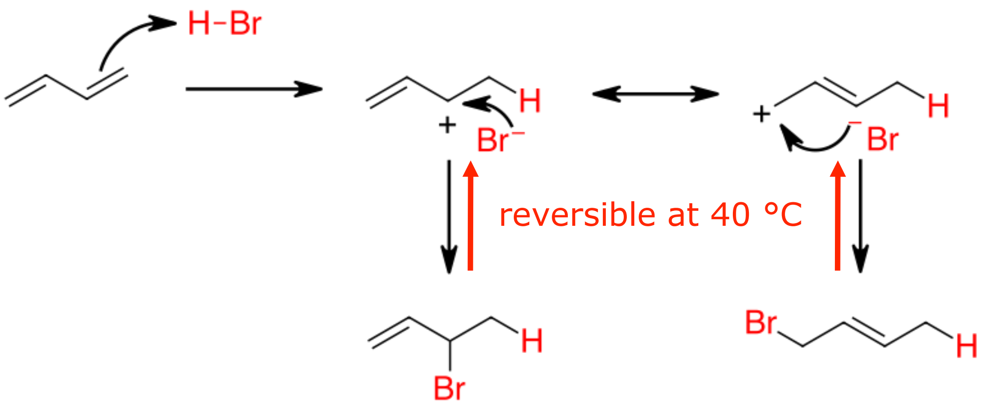
$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[\text{(1 equiv)}]{HBr} \underset{H}{\overset{C1}{CH_2}}{-}\underset{Br}{\overset{C2}{CH}}{-}CH{=}CH_2 + \underset{H}{\overset{C1}{CH_2}}{-}CH{=}CH{-}\underset{Br}{\overset{C4}{CH_2}}$$

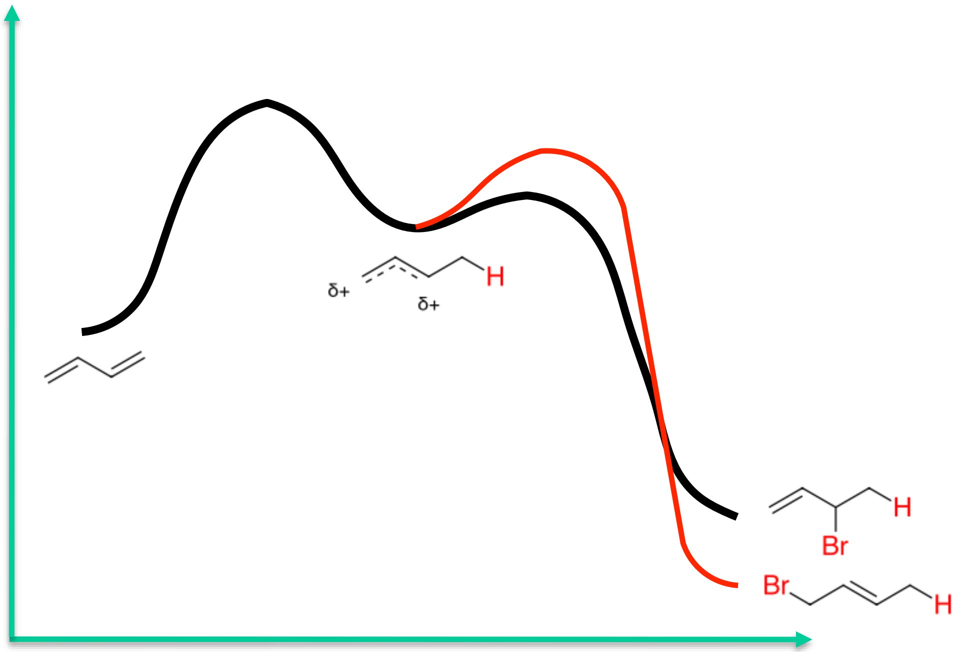
1,2-product **1,4-product**

The amount of 1,2- and 1,4-addition products depends on the reaction conditions.

0 °C	71%	29%
40 °C	15%	85%

Electrophilic Addition: 1,2- Versus 1,4-Addition

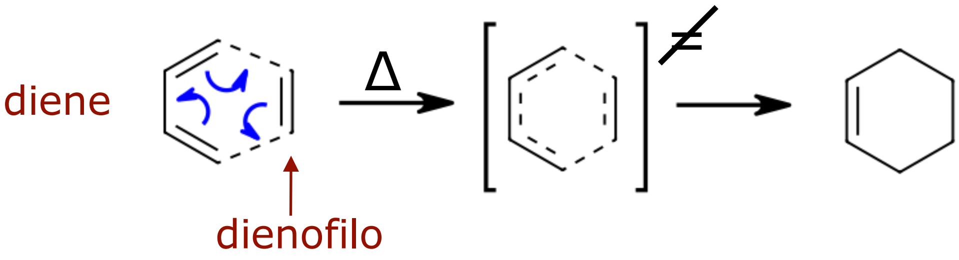




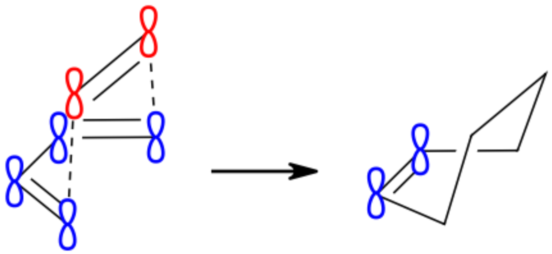
At low temperature the reaction is irreversible (kinetically controlled).
The 1,2-product is **kinetically favoured** by proximity and because the charge on C2 is higher.

At higher temperature the reaction is reversible (thermodinamically controlled).
The 1,4-product is **thermodinamically favoured** because the double bond is more substituted.

The Diels-Alder Reaction



2 new σ bonds are formed simultaneously by interaction of the π orbitals of the diene and dienophile.



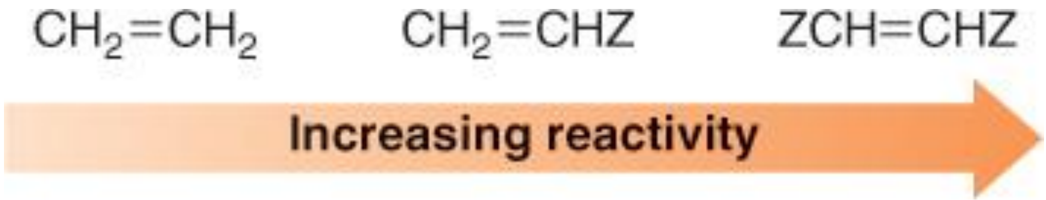
No ions or radicals are involved; 6 electrons are delocalized in the cyclic transition state.
The D.A. cycloaddition is a pericyclic reaction

Because each new σ bond is stronger than the π bond that is broken, a typical Diels-Alder reaction is exothermic (enthalpically favoured).

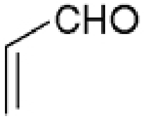
Rules for The Diels-Alder Reaction

1. Electron-withdrawing substituents in the dienophile increase the reaction rate.

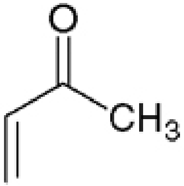
- The diene acts as a nucleophile and the dienophile acts as an electrophile.
- Electron-withdrawing groups make the dienophile more electrophilic



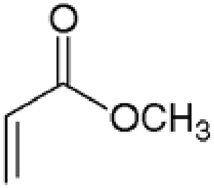
Z : electron-withdrawing group



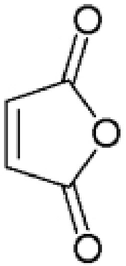
acrolein



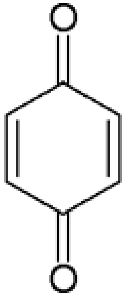
methyl vinyl ketone



methyl acrylate

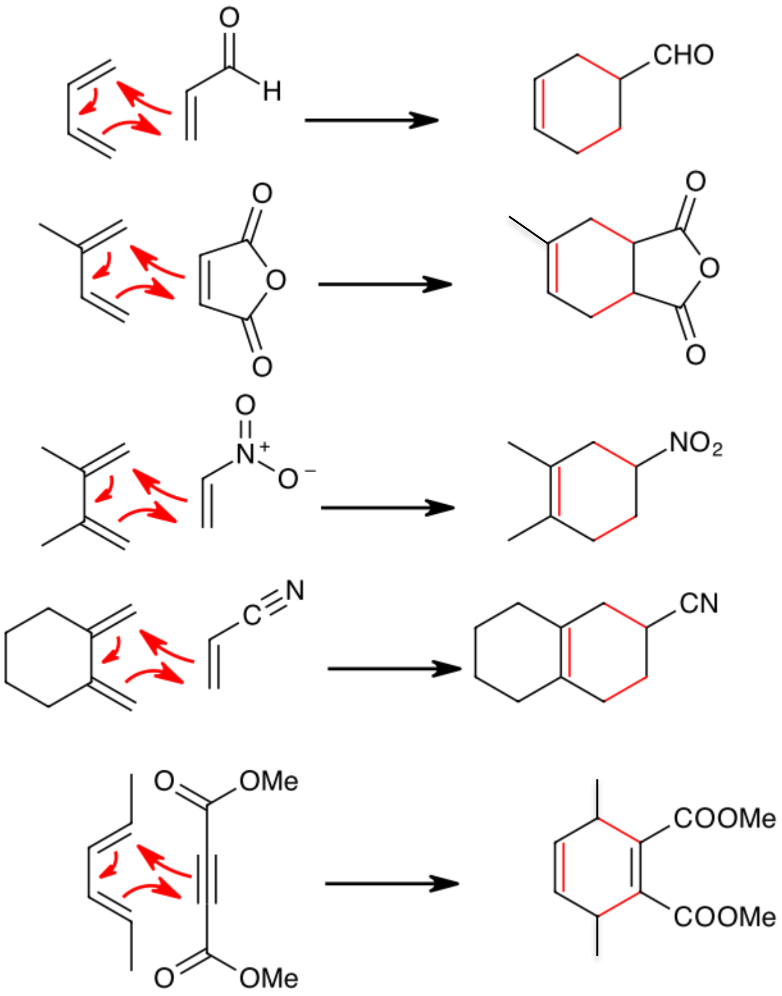


maleic anhydride



benzoquinone

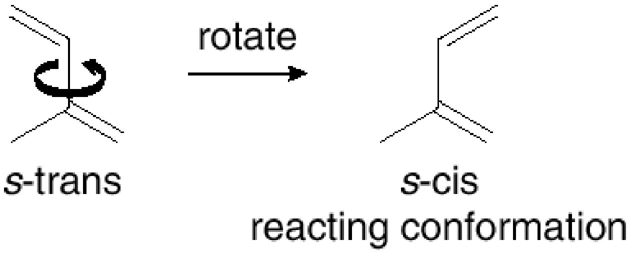
The Diels-Alder Reaction

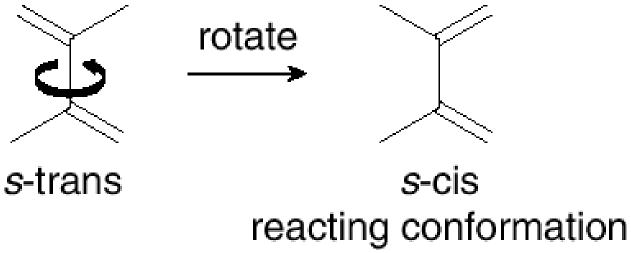


video

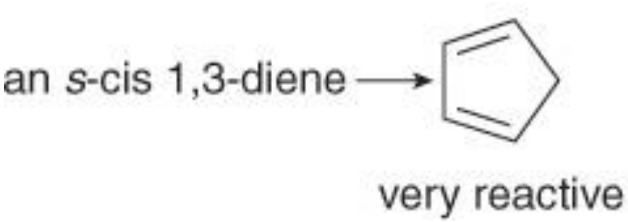
Rules for The Diels-Alder Reaction

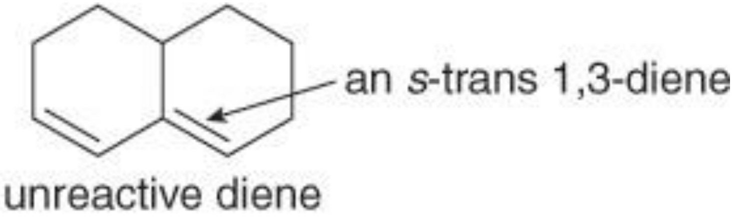
2. The diene can react only when it adopts the *s*-cis conformation.





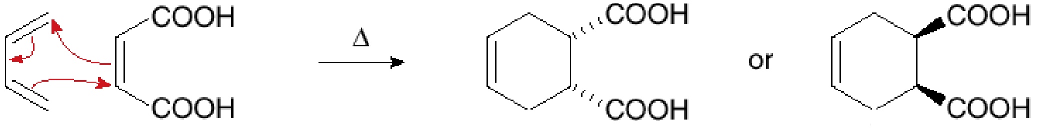
This rotation is prevented in cyclic alkenes.





Rules for The Diels-Alder Reaction

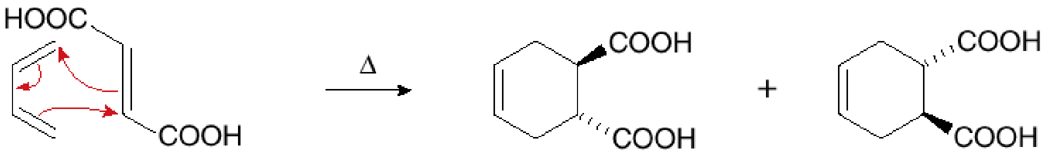
3. The stereochemistry of the dienophile is retained.



cis dienophile

maleic acid

cis product



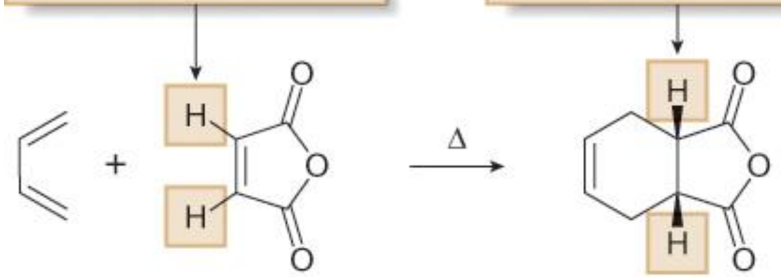
trans dienophile

fumaric acid

trans product

cis H's in the dienophile

cis H's in the product

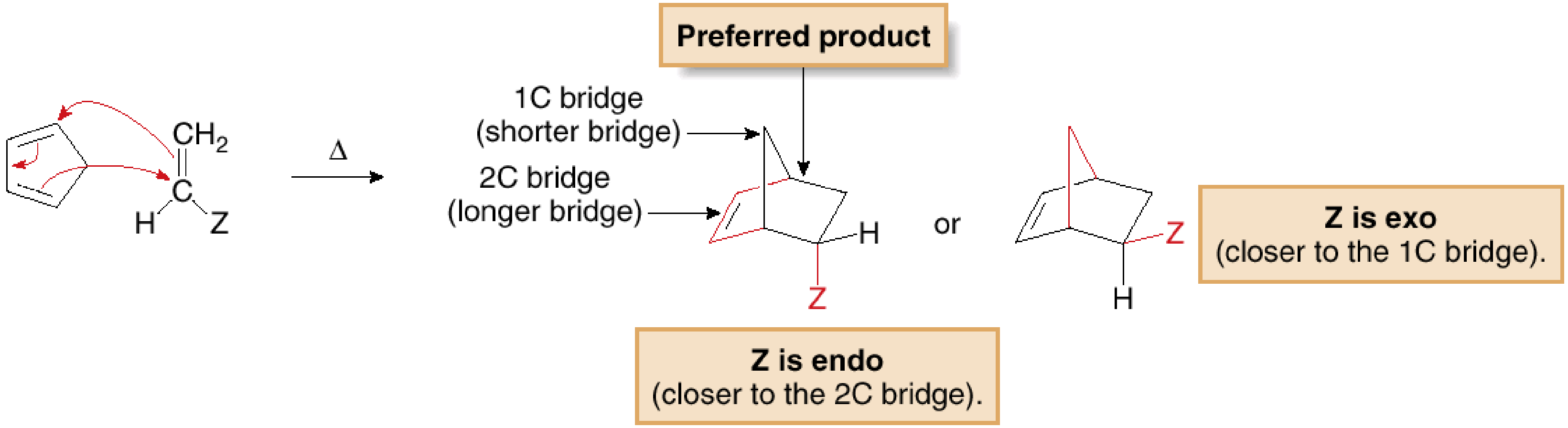


cyclic dienophile

bicyclic product

Rules for The Diels-Alder Reaction

4. When endo and exo products are possible, the endo product is preferred.



Preferred product

1C bridge (shorter bridge)

2C bridge (longer bridge)

Z is endo (closer to the 2C bridge).

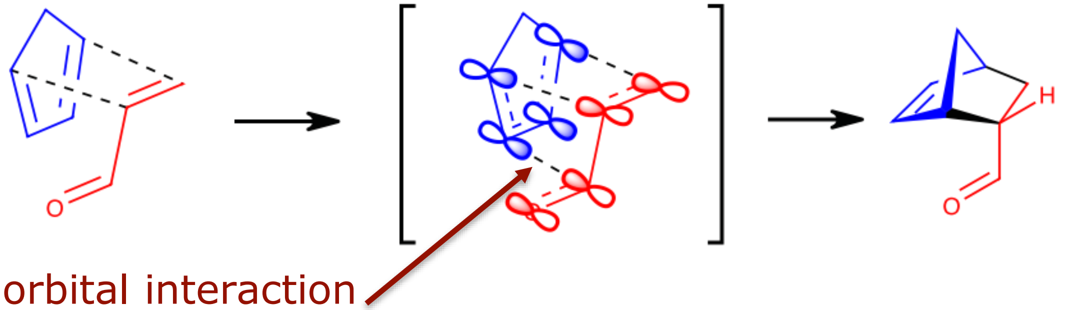
Z is exo (closer to the 1C bridge).

- A substituent on one bridge is *endo* if it is closer to the *longer* bridge that joins the two carbons common to both rings.
- A substituent is *exo* if it is closer to the *shorter* bridge that joins the carbons together.

modelli 3D

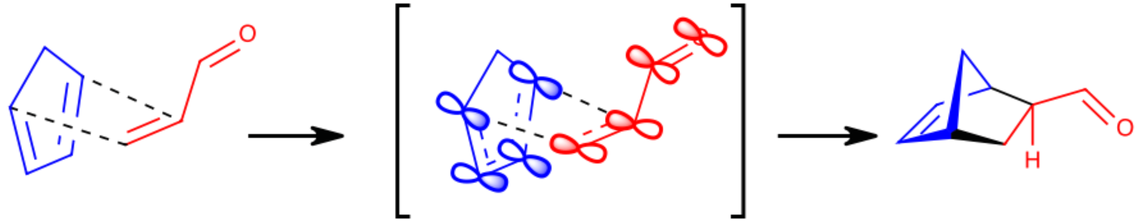
Rules for The Diels-Alder Reaction

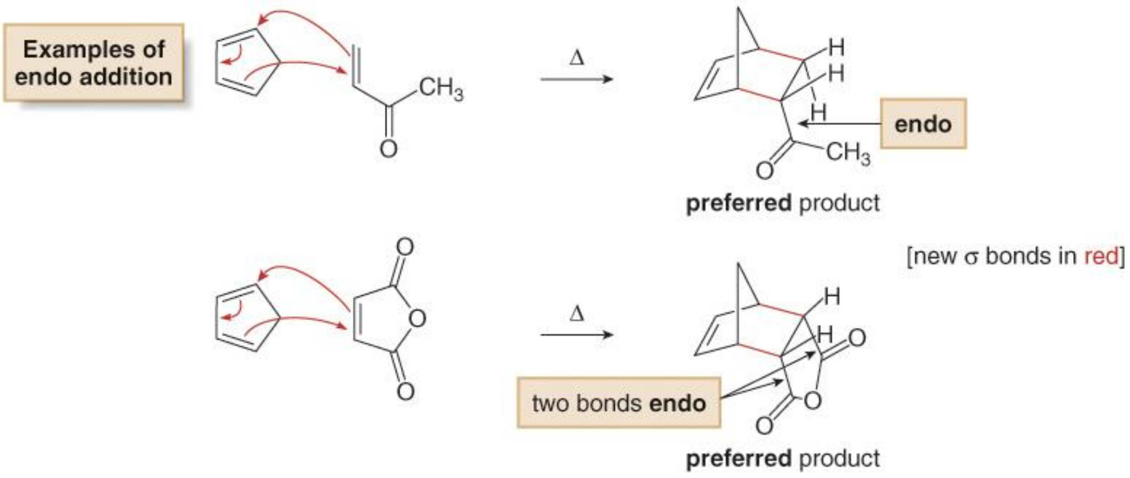
endo



2nd order orbital interaction
(stabilizes the TS but does not lead to bond formation)

exo





Examples of endo addition

endo

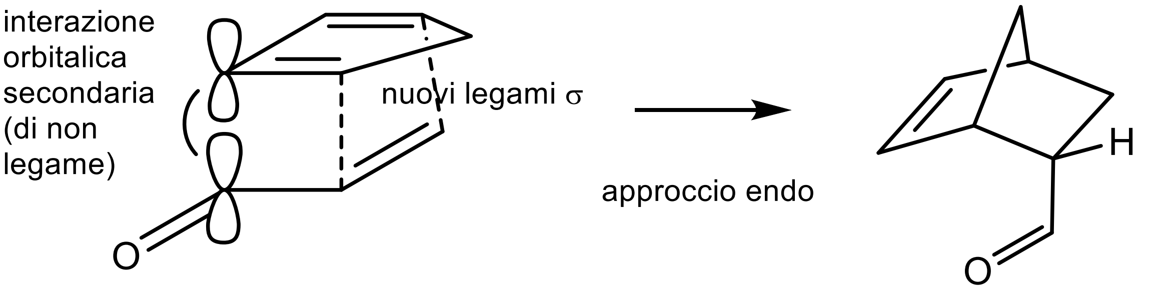
preferred product

[new σ bonds in red]

two bonds **endo**

preferred product

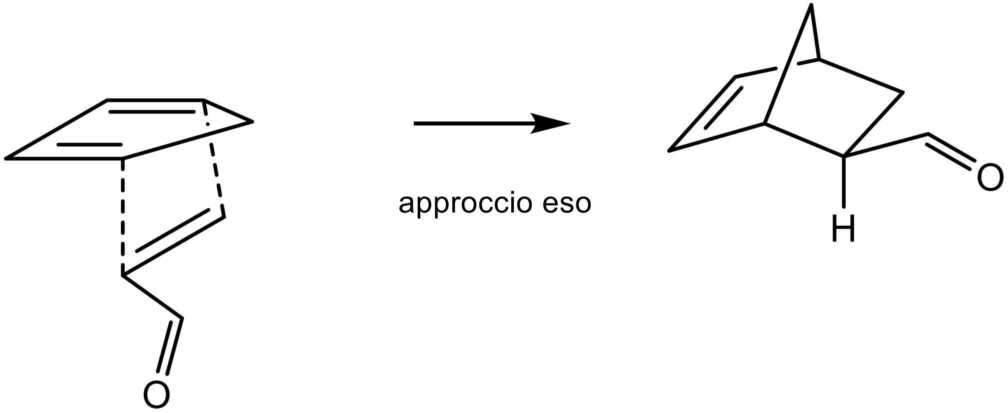
Rules for The Diels-Alder Reaction



interazione orbitalica secondaria (di non legame)

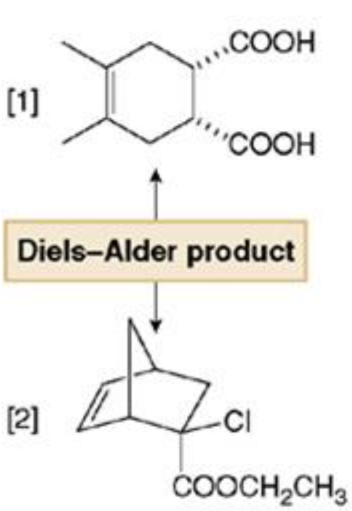
nuovi legami σ

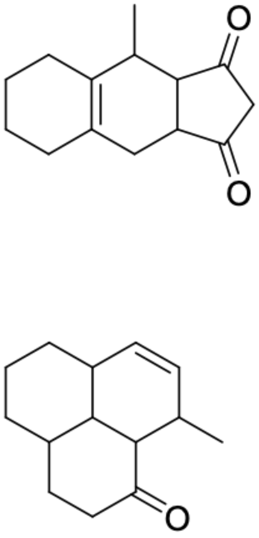
approccio endo



approccio eso

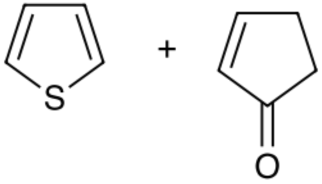
The Diels-Alder Reaction in Organic Synthesis

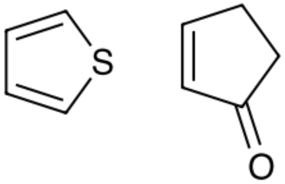




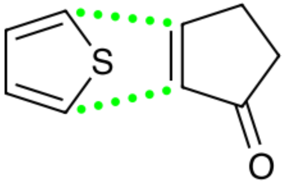
The Diels-Alder Reaction

Indicare il prodotto che si forma nella seguente reazione di cicloaddizione di Diels-Alder

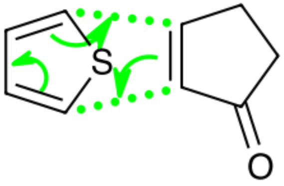




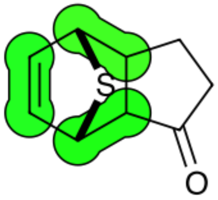
1. Orientare i termini del diene e del dienofilo



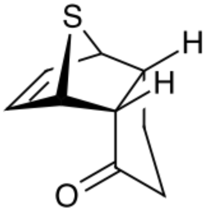
2. Tratteggiare i legami che si formano



3. Applicare il formalismo delle frecce ricurve



4. Scrivere il prodotto nella proiezione planare (evidenziati i nuovi legami σ e π)



5. Aggiustare la stereochimica (cis-endo)