Conjugated Dienes

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

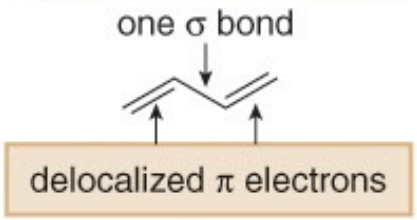
Dienes

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

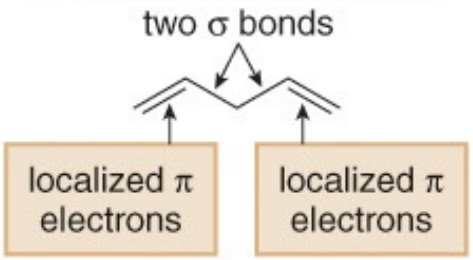
Allene –
A cumulated diene

$H_2C=C=CH_2$

1,3-Butadiene—
A conjugated diene

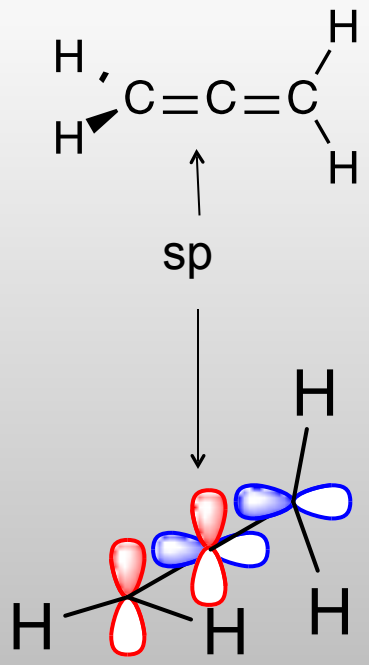


1,4-Pentadiene—
An isolated diene

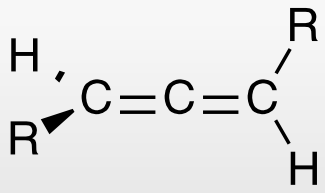


Allenes

Bonding



Stereochemistry



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

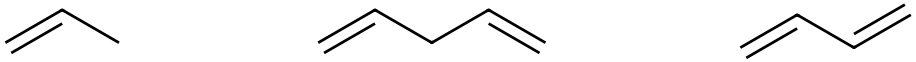
Energetics

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

Conjugated Dienes

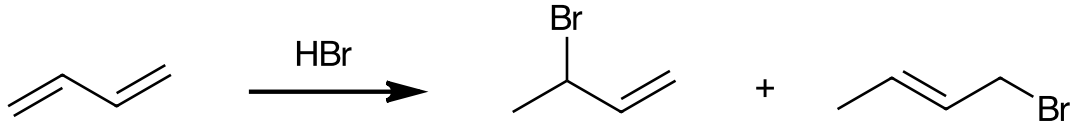
- The C—C single bond joining the two double bonds is unusually short.

- Conjugated dienes are more stable than similar isolated dienes.



ΔH_{hydrog} (kcal/mol)	- 30	- 60	- 56

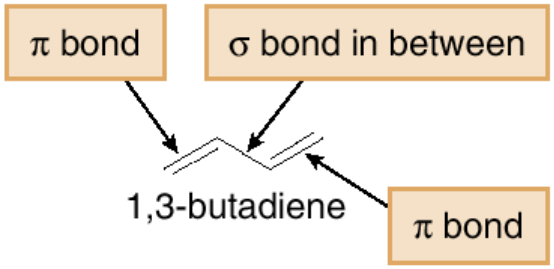
- Some reactions of conjugated dienes are different than reactions of isolated double bonds.

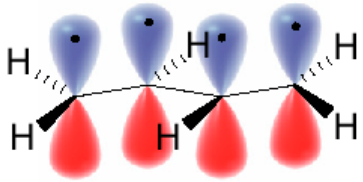


- Conjugated dienes absorb light at longer wavelengths than alkenes.

Delocalisation, Resonance, and Dienes

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

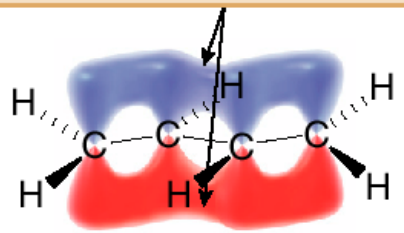




four adjacent *p* orbitals

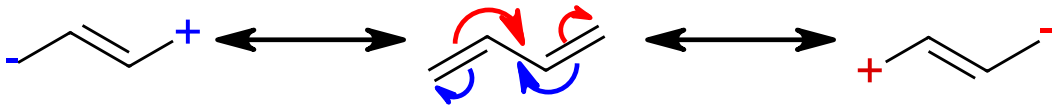
Each C is sp^2 hybridized and has a *p* orbital containing one electron.

overlap of adjacent *p* orbitals



The electron density in the two π bonds is delocalized.

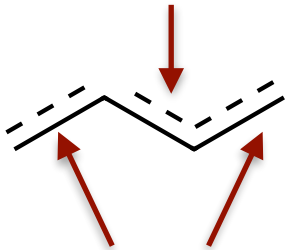
Delocalisation, Resonance, and Dienes



charge separation
less stable

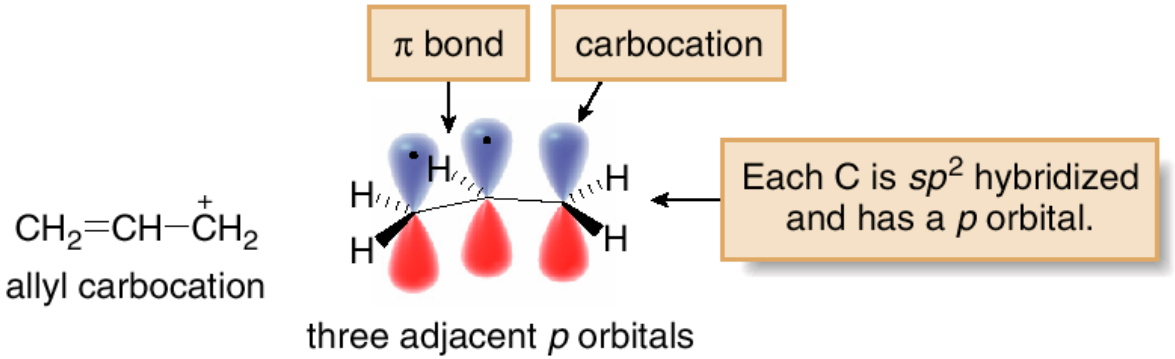
neutral
more stable

charge separation
less stable



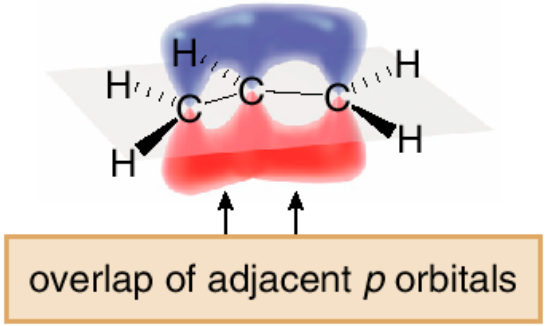
Delocalisation, Resonance, and Dienes

- The allyl carbocation is another example of a conjugated system.



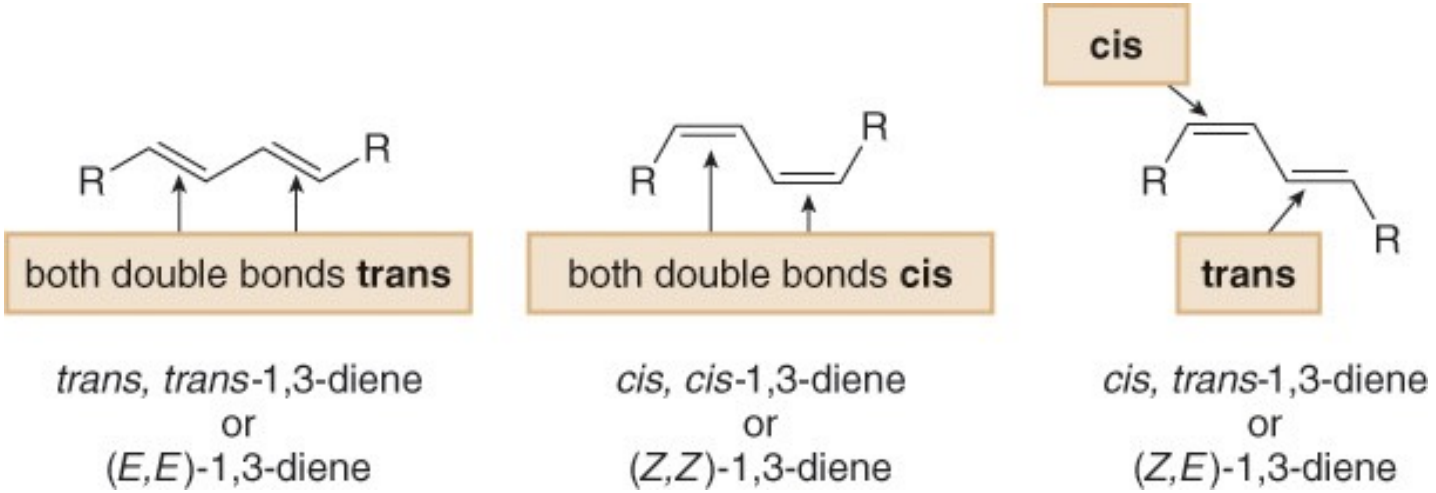
- **Three *p* orbitals on three adjacent atoms, even if one of the *p* orbitals is empty, make the allyl carbocation conjugated.**

- Conjugation stabilizes the allyl carbocation.

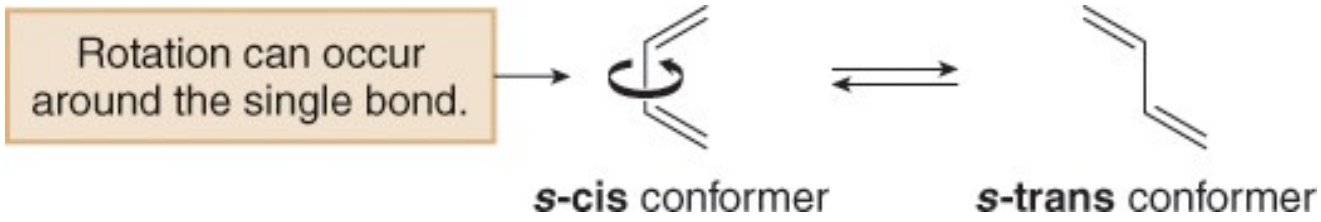


Structure

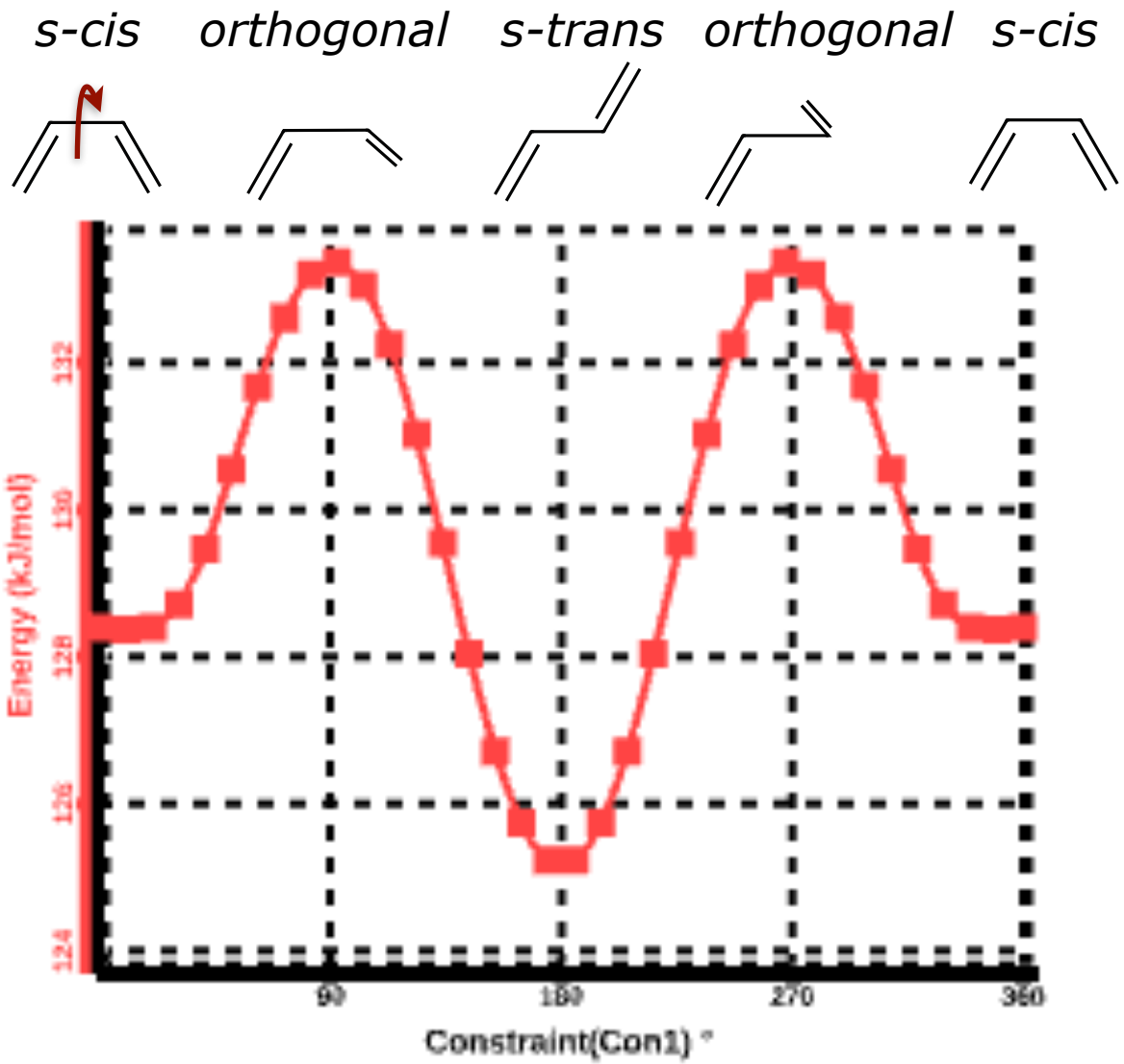
- Three stereoisomers are possible for 1,3-dienes with alkyl groups bonded to each end carbon of the diene.



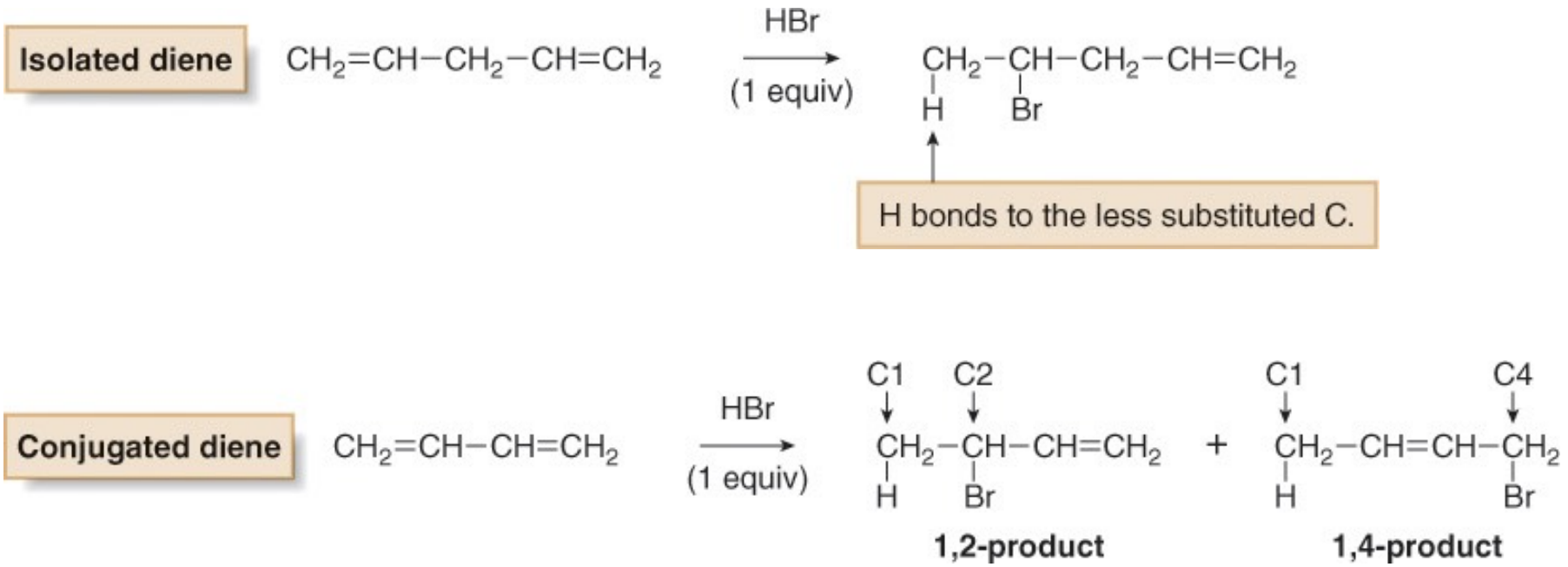
- Two possible conformations result from rotation around the C—C bond that joins the two double bonds.



Conformational Analysis of 1,3-Butadiene

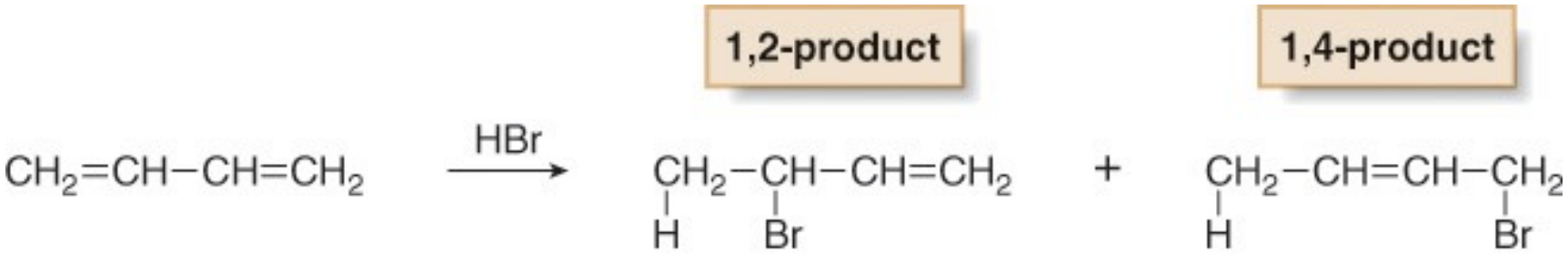


Electrophilic Addition: 1,2- Versus 1,4-Addition



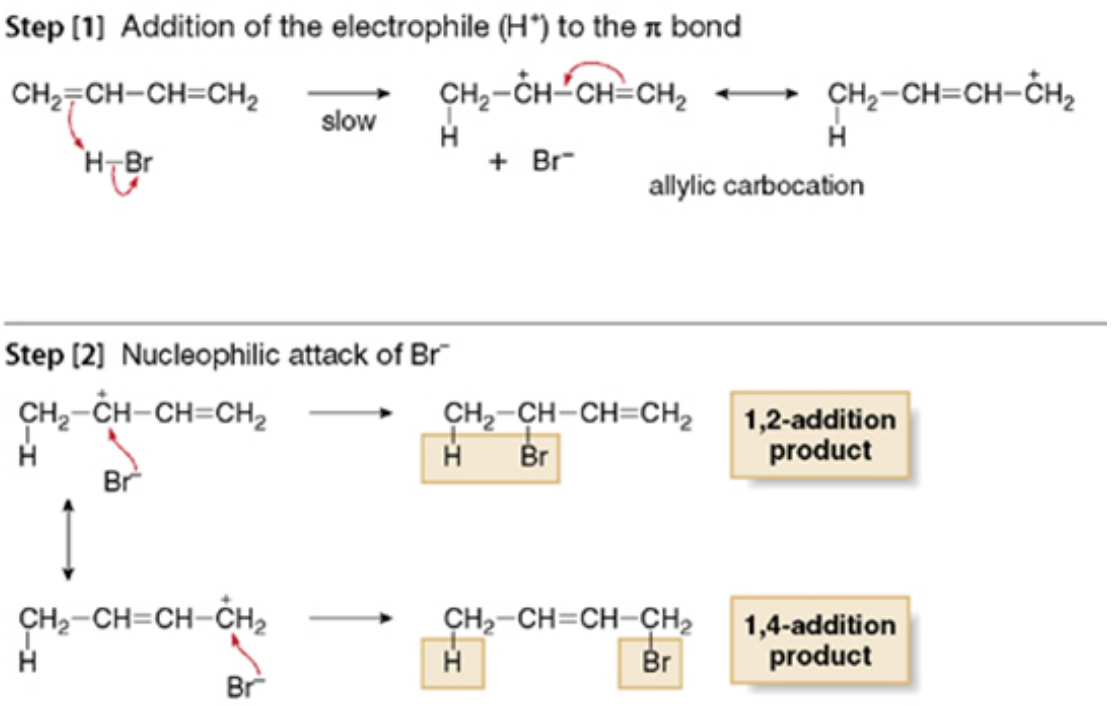
Kinetic Versus Thermodynamic Products

The amount of 1,2- and 1,4-addition products formed in electrophilic addition reactions of conjugated dienes depends greatly on the reaction conditions.



0 °C	71%	29%
40 °C	15%	85%

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

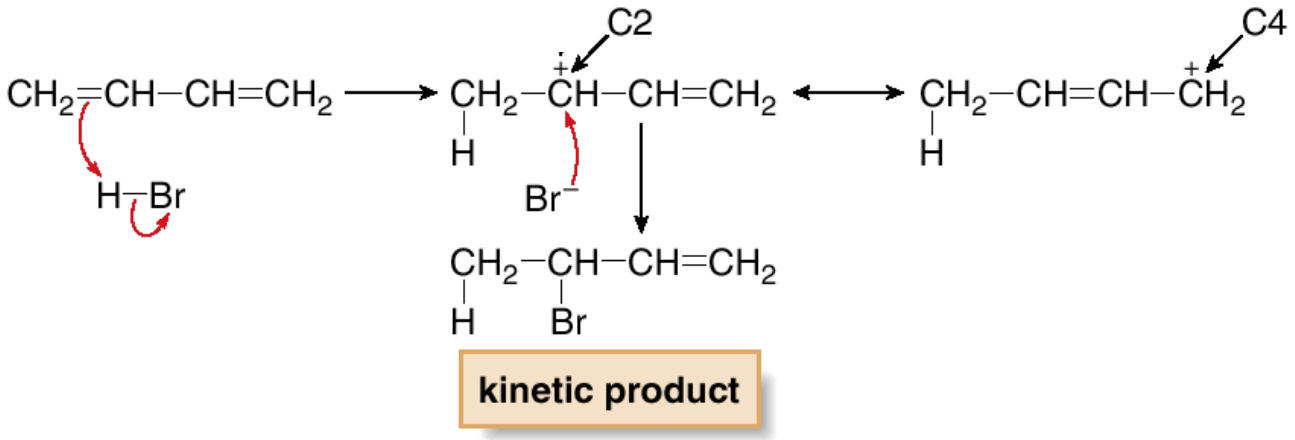


Kinetic Versus Thermodynamic Products

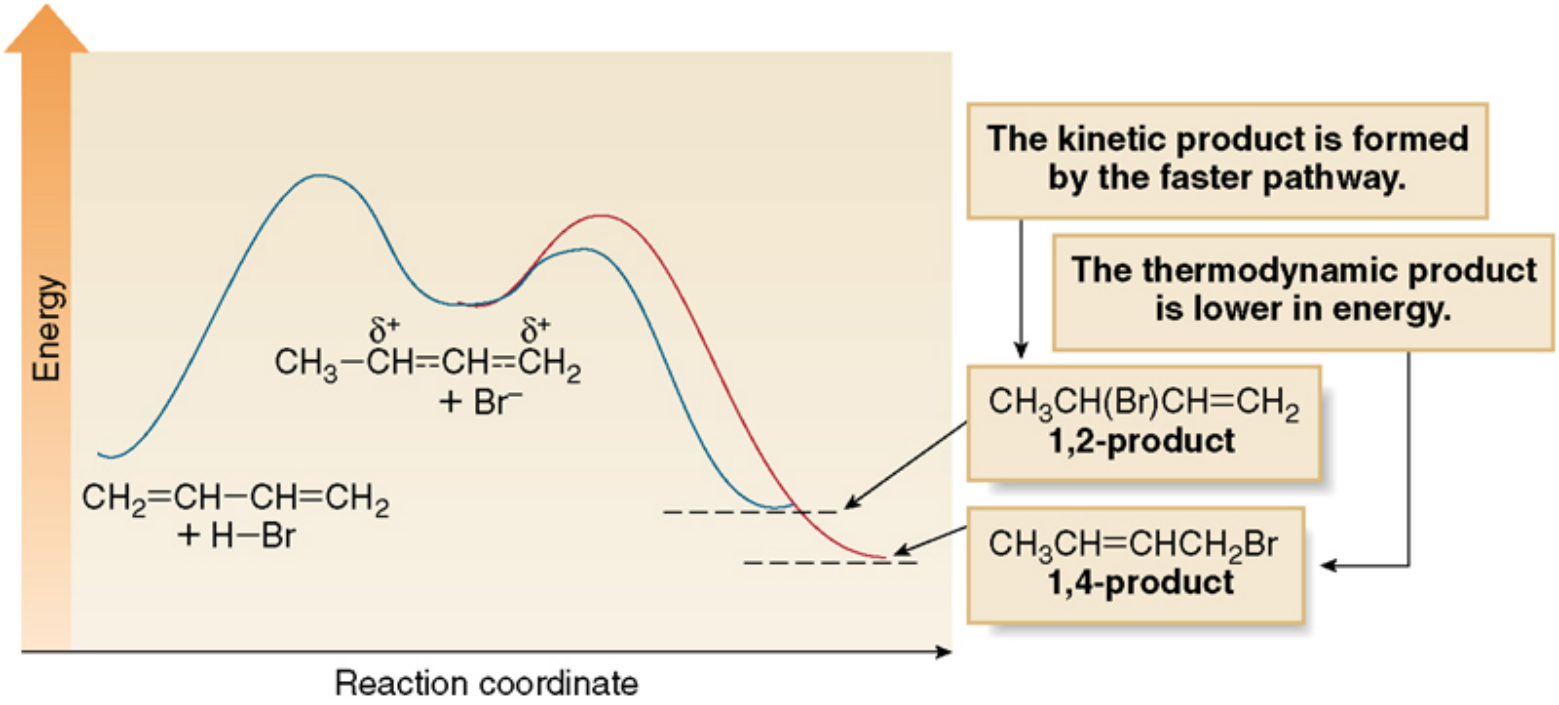
The 1,2-product is the kinetic product because:

a) the charge on C2 is higher

b) a proximity effect.

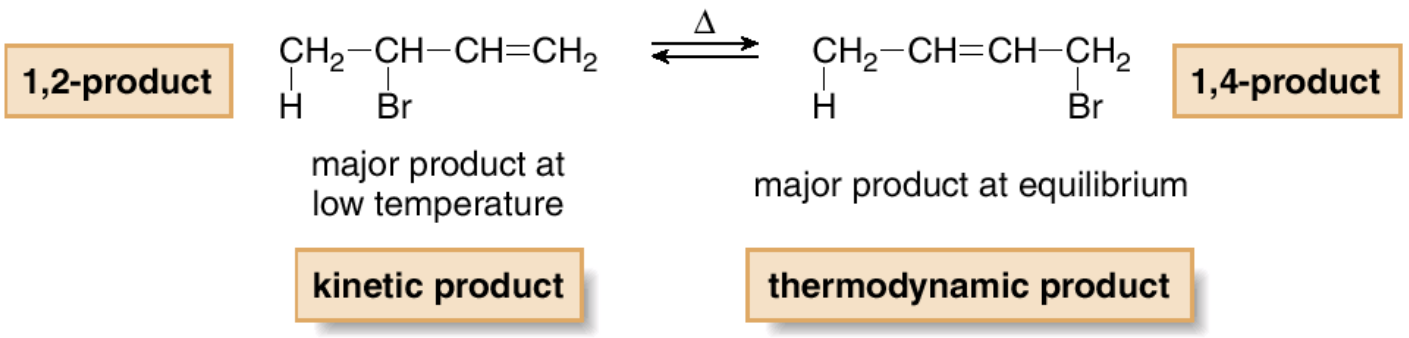


Kinetic Versus Thermodynamic Products



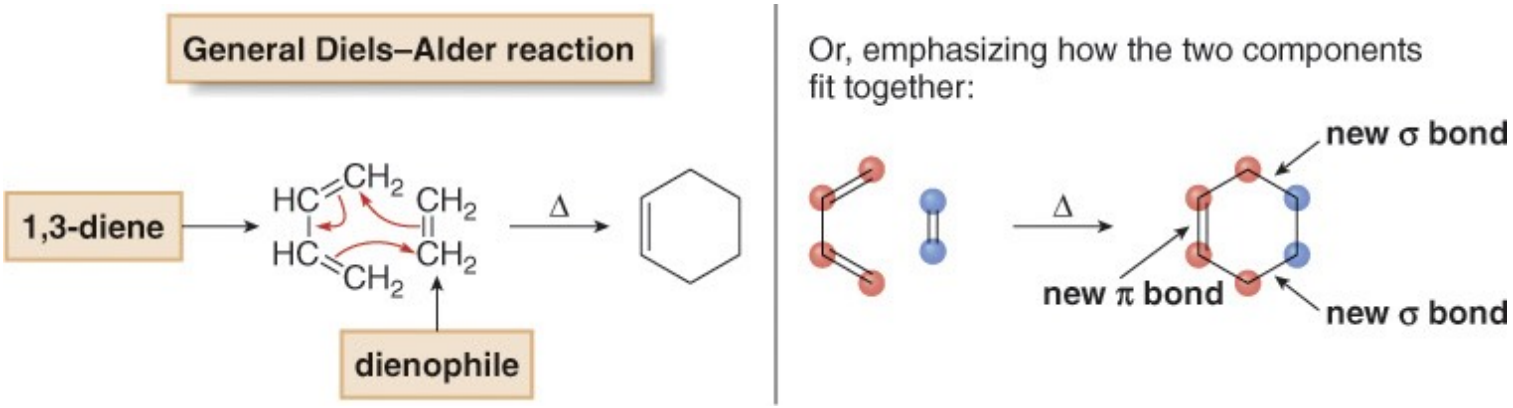
Kinetic Versus Thermodynamic Products

When a mixture containing predominantly the 1,2-product is heated, the 1,4-addition product becomes the major product at equilibrium.



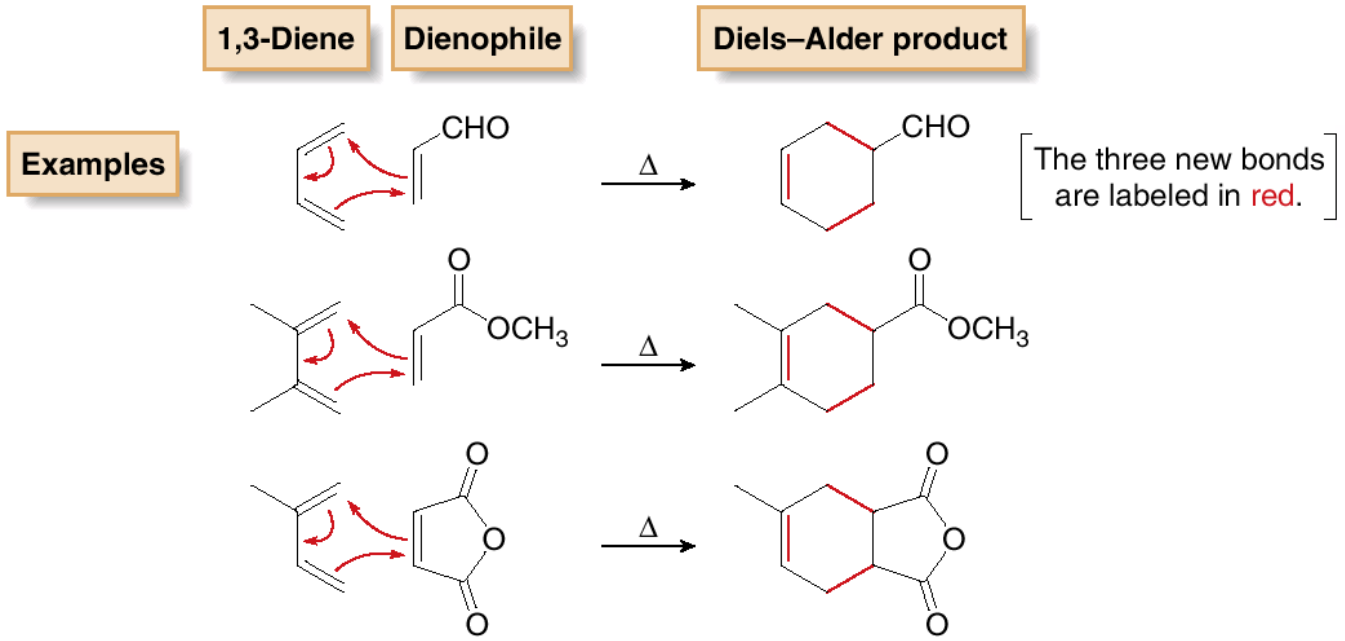
- The 1,2-product is formed faster because it predominates at low temperature. The product that is formed faster is called the *kinetic product.*
- The 1,4-product must be more stable because it predominates at equilibrium. The product that predominates at equilibrium is called the *thermodynamic product.*

The Diels-Alder Reaction



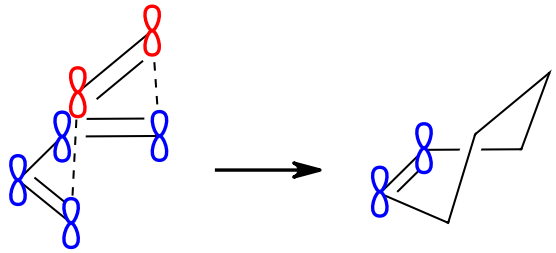
Because each new σ bond is ~20 kcal/mol stronger than a π bond that is broken, a typical Diels-Alder reaction releases ~40 kcal/mol of energy.

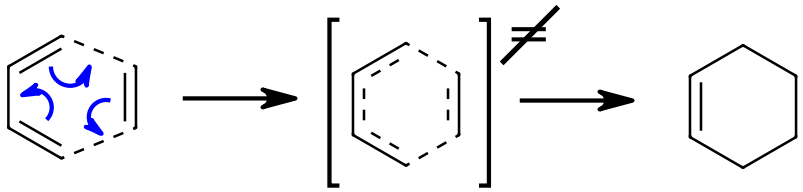
The Diels-Alder Reaction



Mechanism of The Diels-Alder Reaction

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



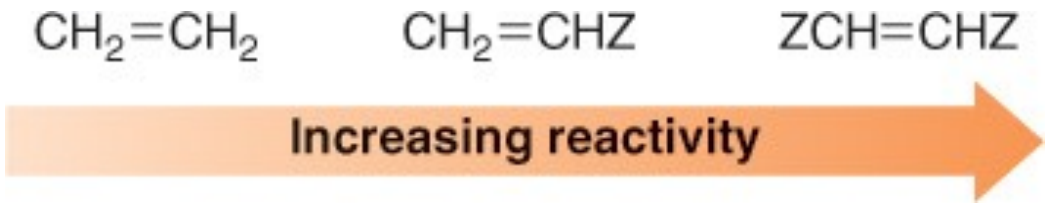


No ions or radicals are involved; 6 electrons are delocalized in the cyclic transition state.
The D.A. cycloaddition is a pericyclic reaction

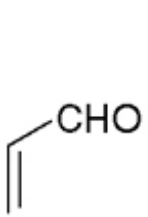
Rules for The Diels-Alder Reaction

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

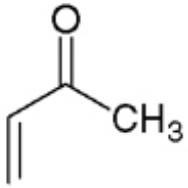
- The diene acts as a nucleophile and the dienophile acts as an electrophile.
- Electron-withdrawing groups make the dienophile more electrophilic



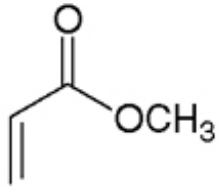
Z : electron-withdrawing group



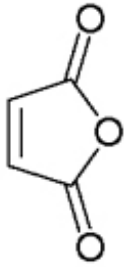
acrolein



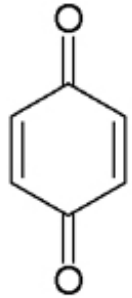
methyl vinyl ketone



methyl acrylate



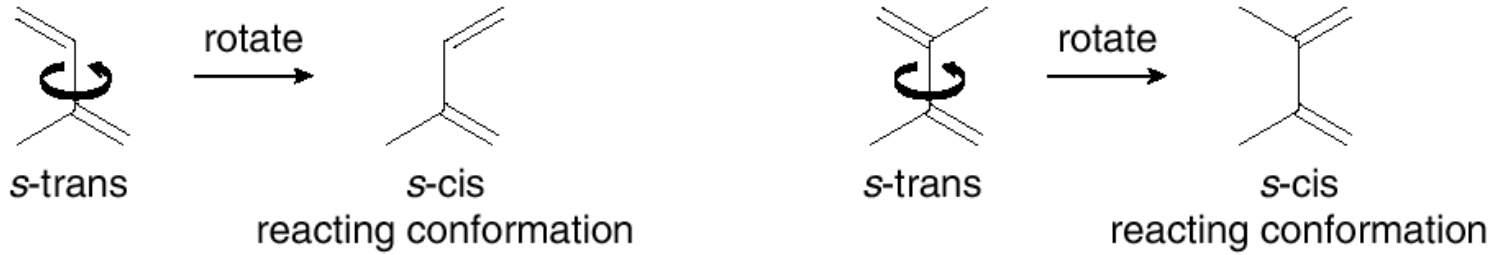
maleic anhydride



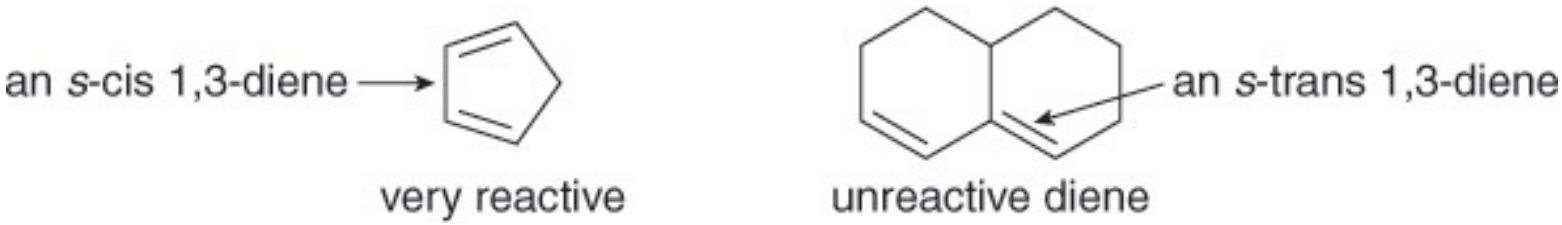
benzoquinone

Rules for The Diels-Alder Reaction

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

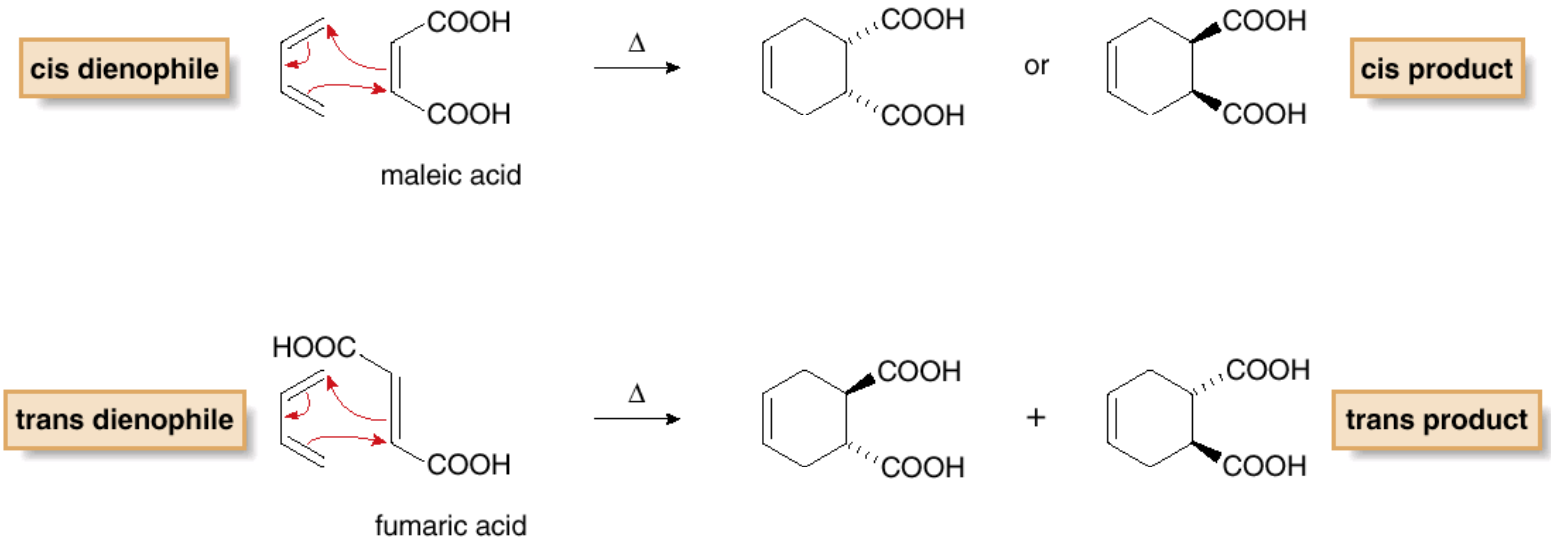


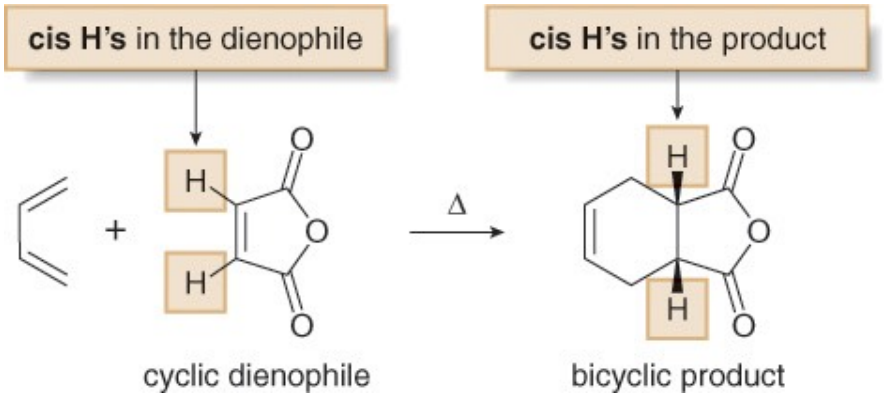
This rotation is prevented in cyclic alkenes.



Rules for The Diels-Alder Reaction

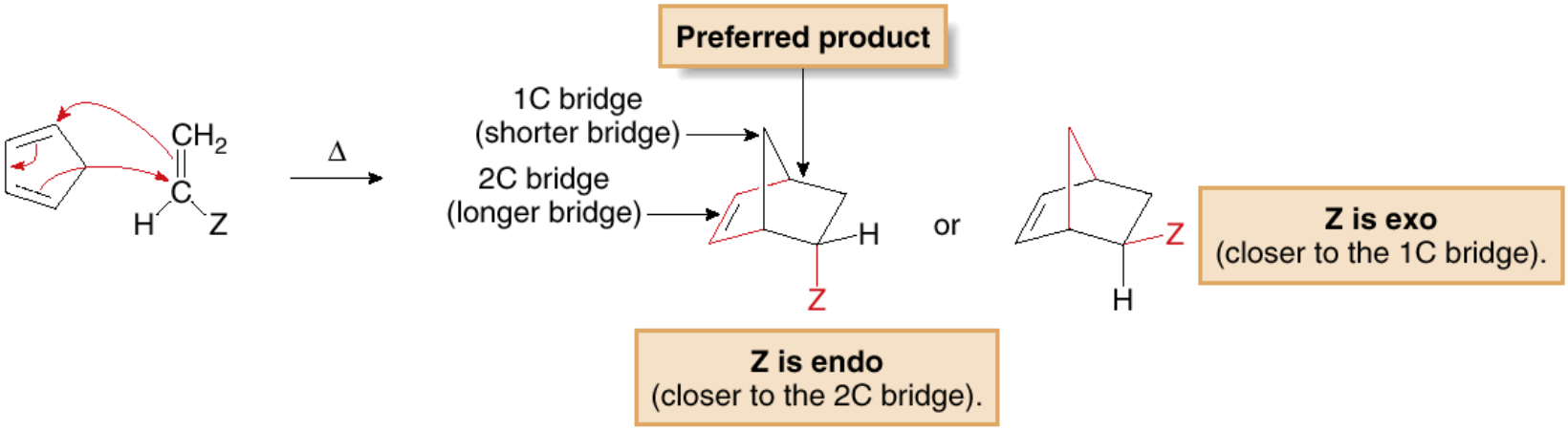
3. The stereochemistry of the dienophile is retained.





Rules for The Diels-Alder Reaction

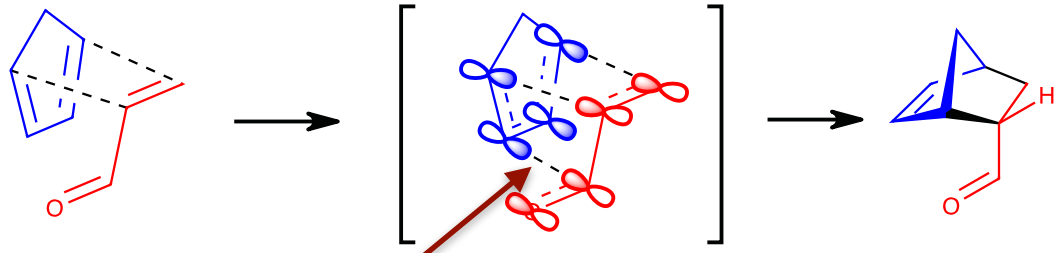
4. When endo and exo products are possible, the endo product is preferred.



- 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.

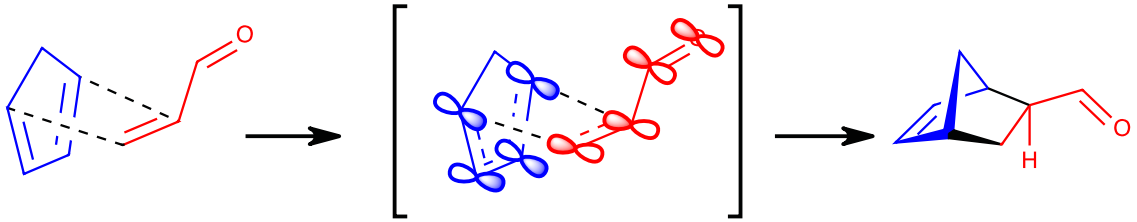
Rules for The Diels-Alder Reaction

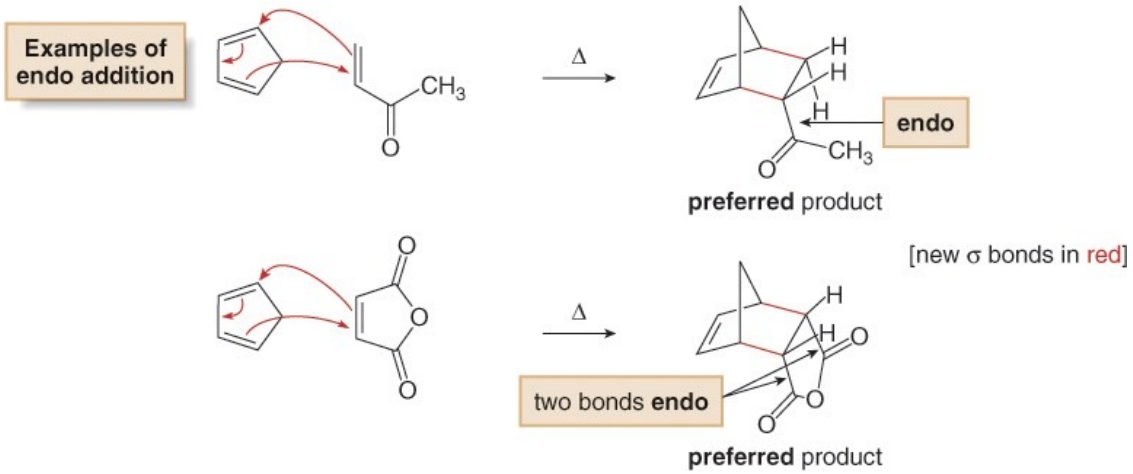
endo



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

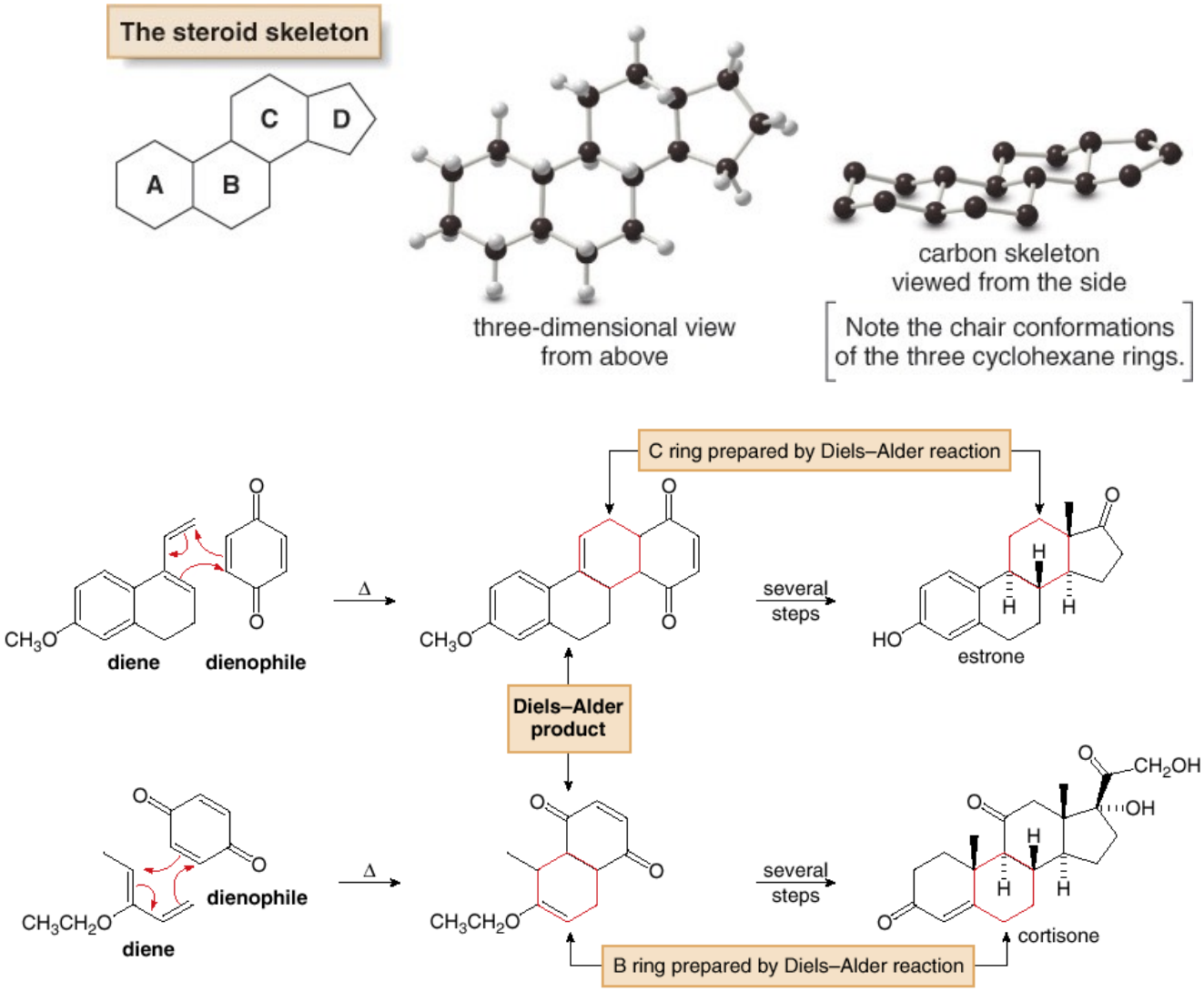
exo





The Diels-Alder Reaction in Organic Synthesis

- Steroids are tetracyclic lipids.



The Diels-Alder Reaction in Organic Synthesis