Types of Dienes

I. Conjugated dienes

1,3-butadiene

single bond formed by sp^2–sp^2 overlap

$CH_2{=}CH{-}CH{=}CH_2$

II. Isolated dienes

(behave as alkenes)

1,4-pentadiene

single bonds formed by sp^3–sp^2 overlap

$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$

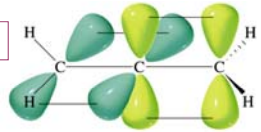
III. Allenes (Cumulated dienes)

hybridization sp^2

hybridization sp

$CH_3CH{=}C{=}CHCH_3$

2,3-pentadiene



Relative Stability of Dienes

I. Conjugated dienes

$CH_2{=}CHCH{=}CHCH_3 + 2\,H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_2CH_3$ ΔH^o = -226 kJ mol^{-1}

1,3-pentadiene

II. Isolated dienes

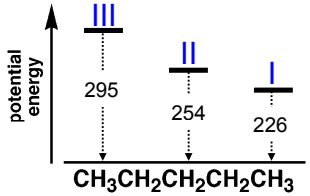
$CH_2{=}CHCH_2CH{=}CH_2 + 2\,H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_2CH_3$ ΔH^o = -254 kJ mol^{-1}

1,4-pentadiene

III. Allenes

$CH_3CH{=}C{=}CHCH_3 + 2\,H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_2CH_3$ ΔH^o = -295 kJ mol^{-1}

2,3-pentadiene



Order of stability

III < II < I

Increasing stability

Molecules with Delocalized Electrons

Heat of hydrogenation:

$CH_3CH_2CH{=}CH_2 + H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3$ $\Delta H^\circ = -30.3$ kcal mol^{-1} (-127 kJ mol^{-1})

$CH_2{=}CHCH_2CH_2CH{=}CH_2 + 2\,H_2 \xrightarrow{Pt} CH_3(CH_2)_4CH_3$ $\Delta H^\circ = -60.5$ kcal mol^{-1} (-253 kJ mol^{-1})

$CH_2{=}CHCH_2CH{=}CH_2 + 2\,H_2 \xrightarrow{Pt} CH_3(CH_2)_3CH_3$ $\Delta H^\circ = -60.8$ kcal mol^{-1} (-254 kJ mol^{-1})

$CH_2{=}CH{-}CH{=}CH_2 + 2\,H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3$ $\Delta H^\circ = -57.1$ kcal mol^{-1} (-239 kJ mol^{-1})

Bond length:

147 pm

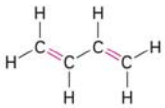
$H_2C{=}CH{-}CH{=}CH_2$

1,3-Butadiene

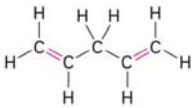
153 pm

$CH_3{-}CH_2{-}CH_2{-}CH_3$

Butane



1,3-Butadiene

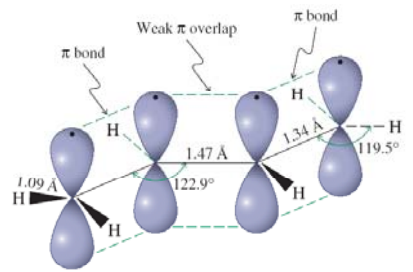


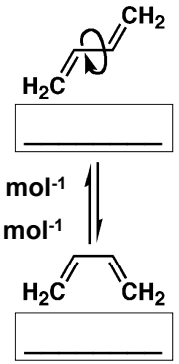
1,4-Pentadiene

alternating double and single bonds:
conjugated

nonalternating double and single bonds:
nonconjugated

Isomerism of Butadiene and Benzene

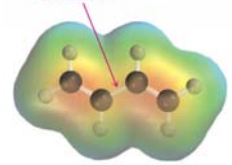


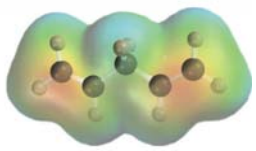


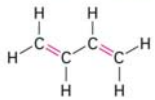
ΔH^o = -12 kJ mol^{-1}

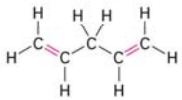
$\Delta G^{\neq}$ = 25 kJ mol^{-1}

Partial double-bond character

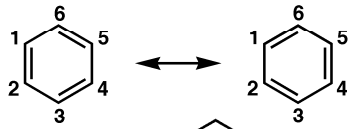






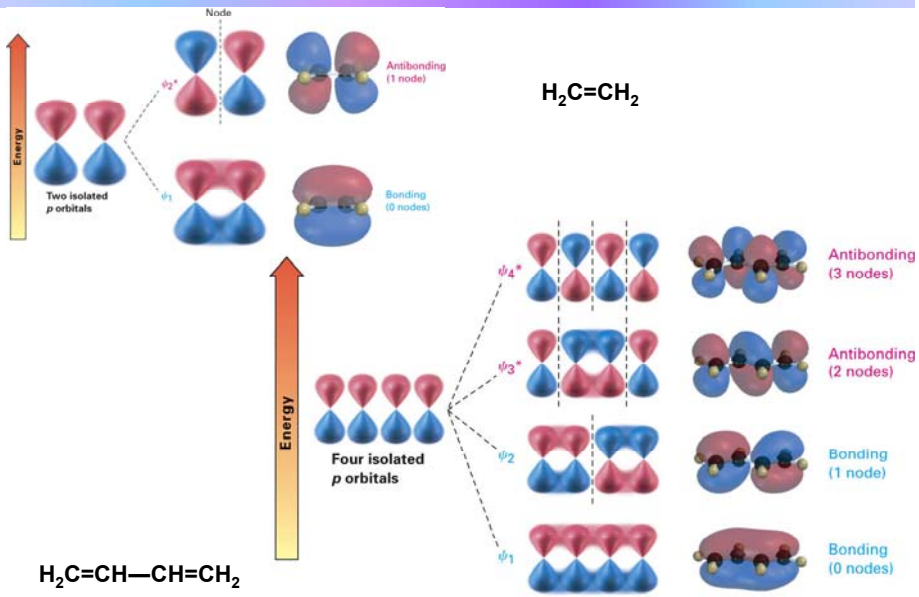


consider benzene:



also represented as

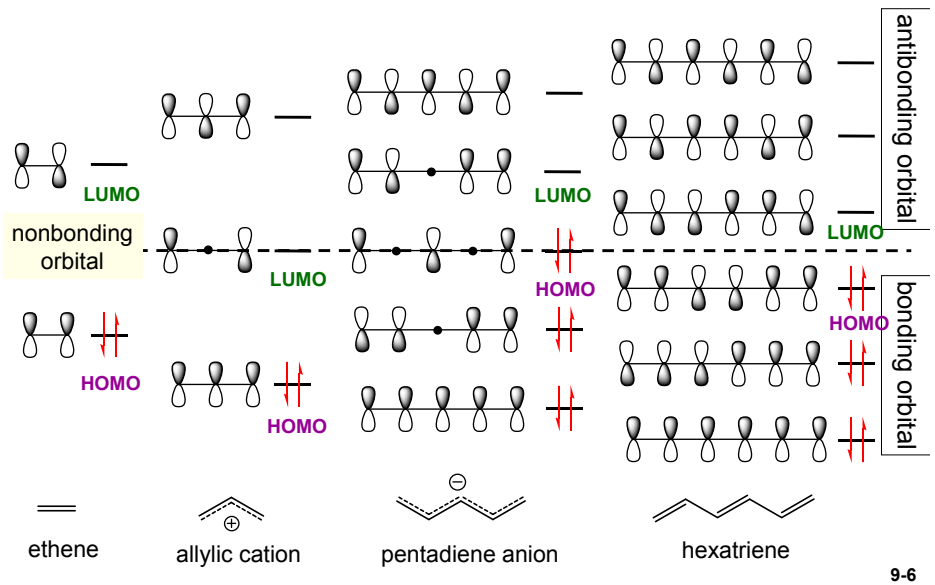
Molecular Orbital Theory



$H_2C{=}CH_2$

$H_2C{=}CH{-}CH{=}CH_2$

Molecular Orbital Theory



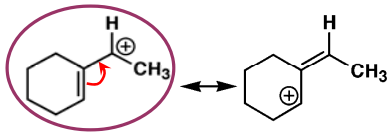
Significance of Resonance Contributors

- Reveal "hidden" reactivity
- Stability of intermediates, TS≠, products:
  The stabilizing energy associated with resonance contributors is resonance energy

The greater the number of important resonance contributors, the greater the resonance energy

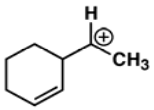
Which is more stable? Why?

Gains stability from resonance energy

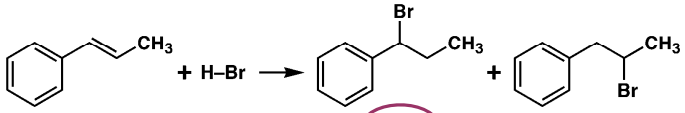


or

No resonance contributors

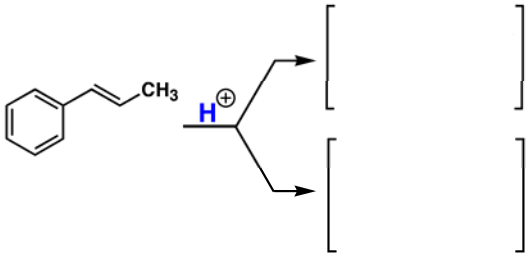


Explain the following with resonance considerations and energy diagrams

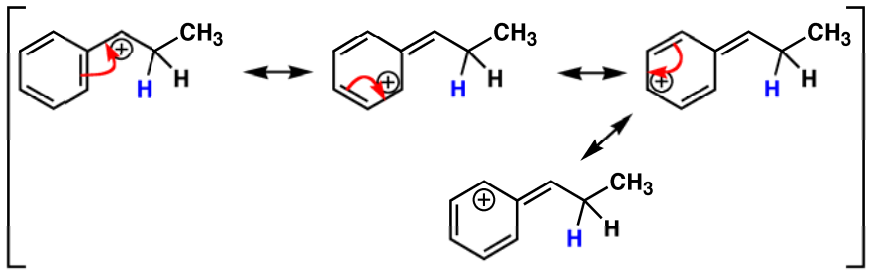


To answer a question like this, draw the structure of all possible intermediates and compare

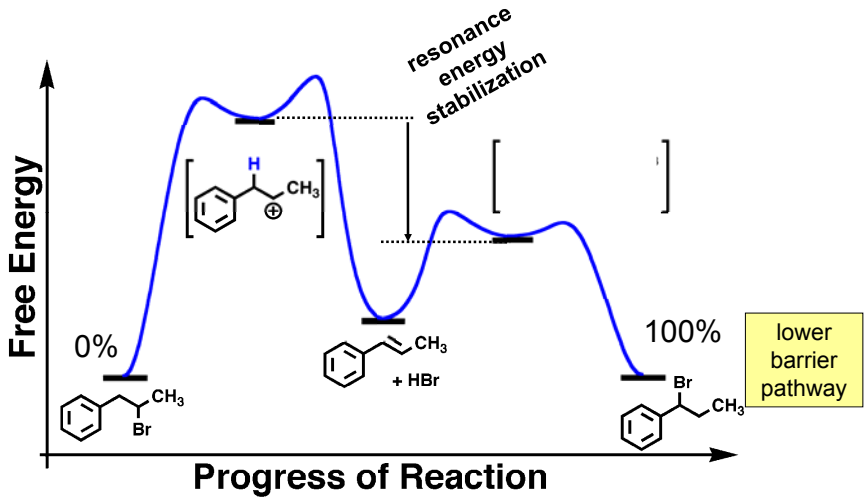
Consider the Possible Intermediates



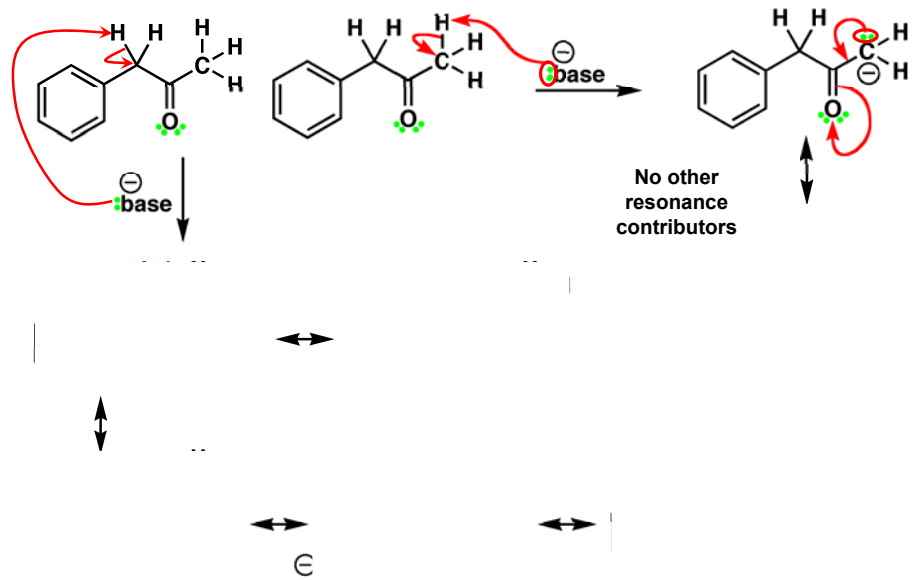
One is more stable than the other because it has a number of significant resonance contributors - draw them



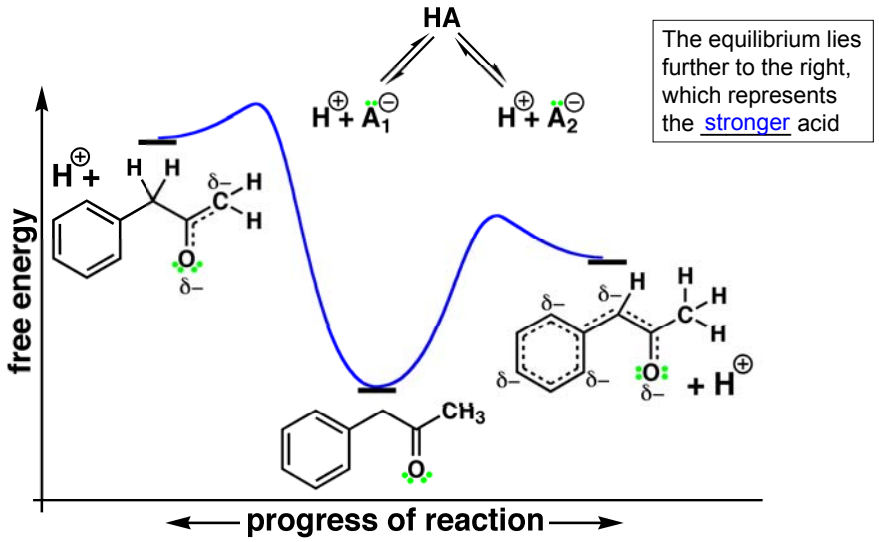
Comparison Using Reaction Coordinate Diagram



Resonance Contributors and Acidity



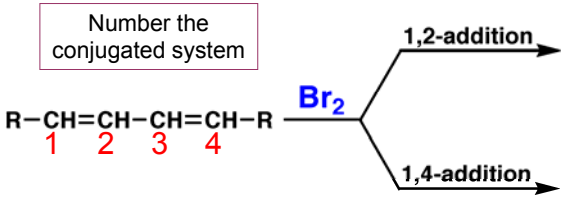
Comparison of Deprotonation Reactions



The equilibrium lies further to the right, which represents the stronger acid

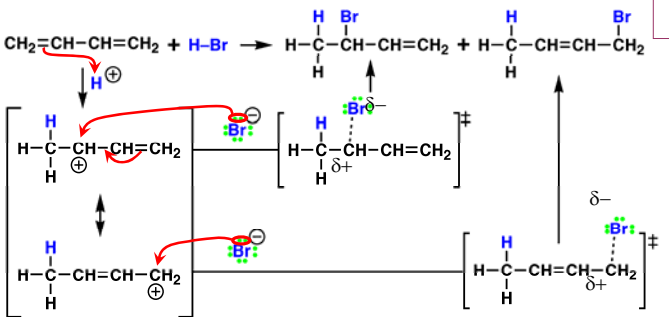
Electrophilic Addition to Conjugated Dienes

Number the conjugated system

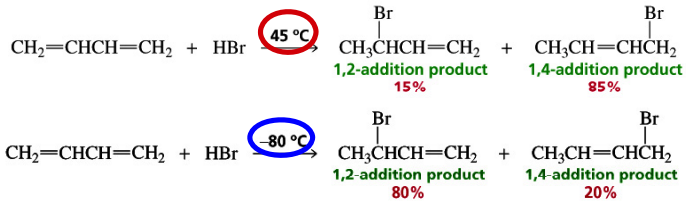


1,2-addition is also called: direct addition
1,4-addition is also called: conjugate addition

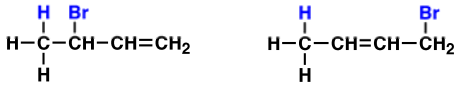
Note: the double bond shifts over



Kinetic vs. Thermodynamic Control

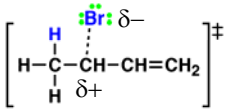


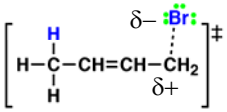
1,2-addition



1,4-addition

Which product is more stable? 1,2-product or 1,4-product **(recall that the greater number of alkyl groups bound to sp^2 carbons, the more stable the alkene)**

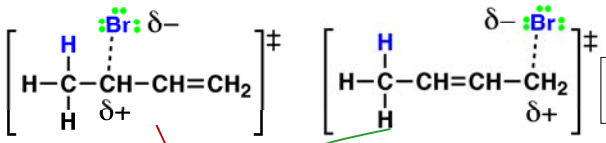




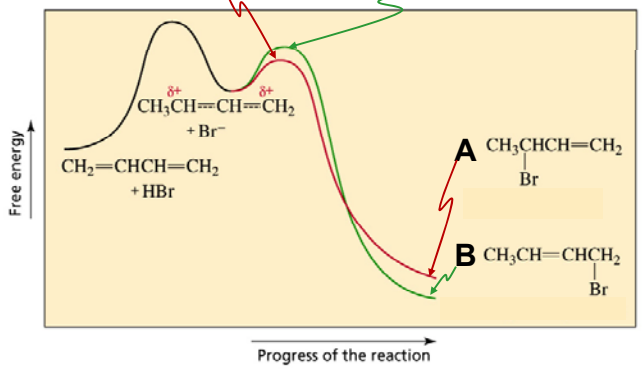
Which TS≠ is more stable? TS≠ 1,2-product or TS≠ 1,4-product

The TS≠ for 1,2-product resembles _____
The TS≠ for 1,4-product resembles _____

Comparison Using a Reaction Coordinate Diagram



The product formed faster? **A** or **B**

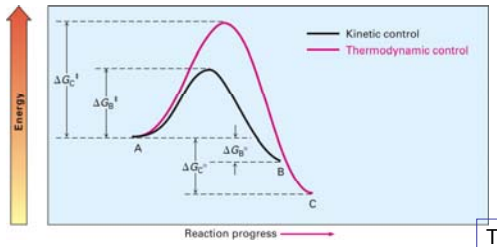


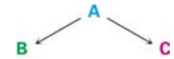
The more abundant product at equilibrium? **A** or **B**

A is called the _____ product

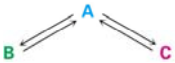
B is called the _____ product

Kinetic vs. Thermodynamic Control



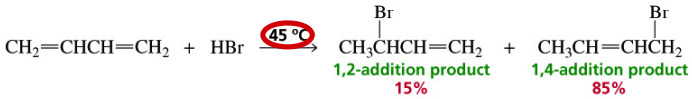


The product of an irreversible reaction *depends on relative rates*; such reactions under **kinetic control**.

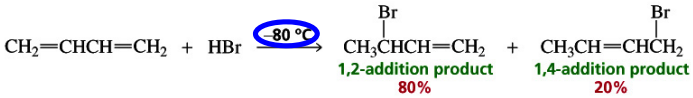


The product of a reversible reaction *depends on product stability*; such reactions are said to be under **thermodynamic control**.

The thermodynamic product predominates when the reaction is reversible (higher temperature, or longer reaction time)



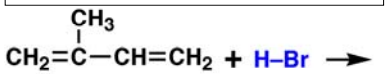
The kinetic product predominates when the reaction is irreversible (lower temperature and shorter reaction time)



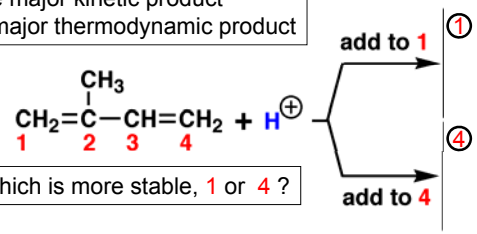
Predicting Products From Unsymmetrical Dienes

The major products of the reaction are those obtained by adding the electrophile to the terminal sp^2 carbon that generates the most stable carbocation

Possible Products	
1,2-addition	1,4-addition



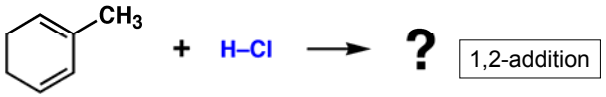
•Circle the major kinetic product
•Box the major thermodynamic product



Which is more stable, 1 or 4 ?

Unsymmetrical Dienes

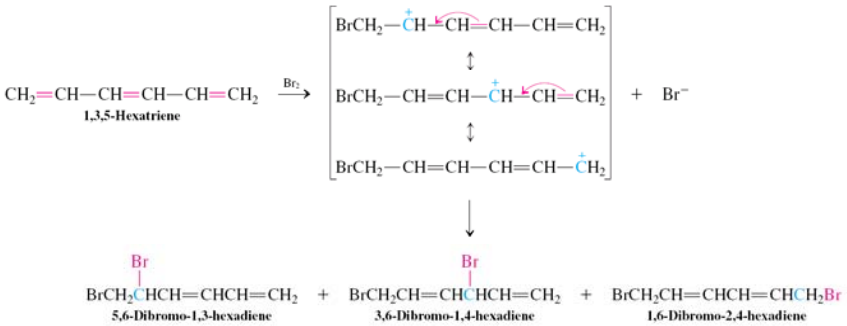
Possible Products



1,2-addition

Larger Conjugation Systems

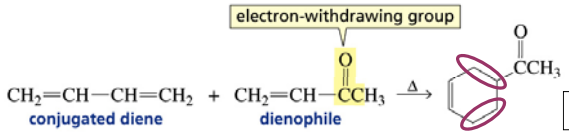
1,4-addition



Diels-Alder Cycloaddition

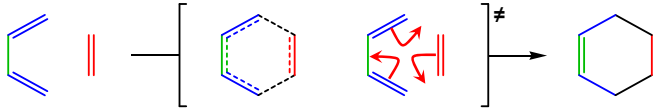
Conjugated dienes undergo a special reaction with (electron deficient) alkenes and alkynes

A pericyclic reaction; bonds made and broken simultaneously (also known as a concerted reaction)



Indicate new C–C bonds

Two Pictures of the TS≠

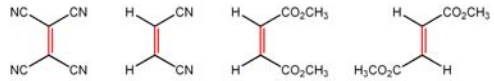


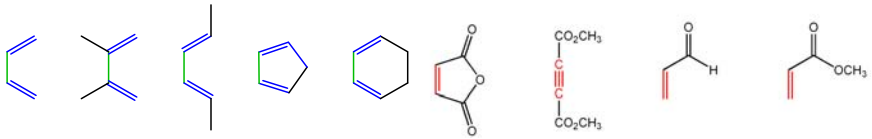
typical dienophiles:

electron deficient

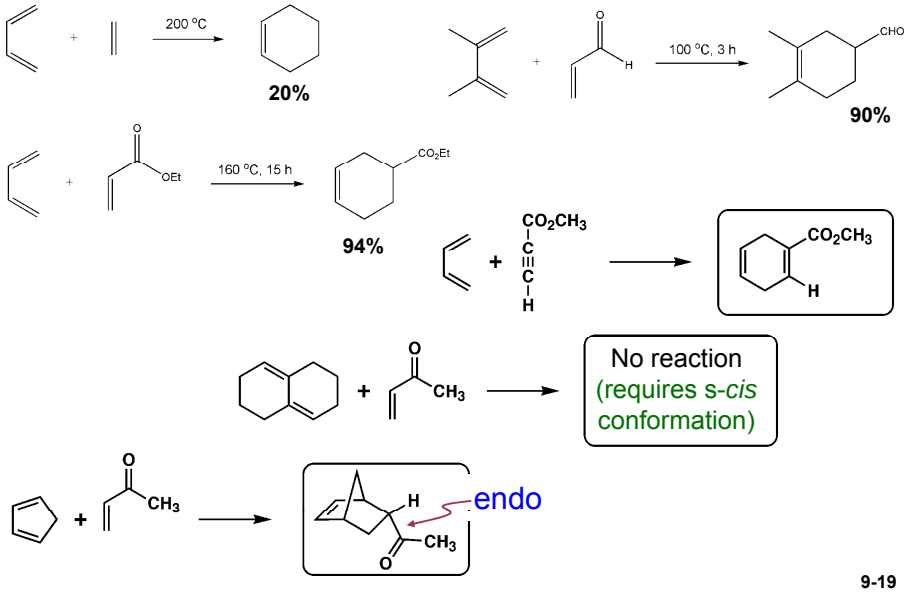
typical dienes:

electron rich

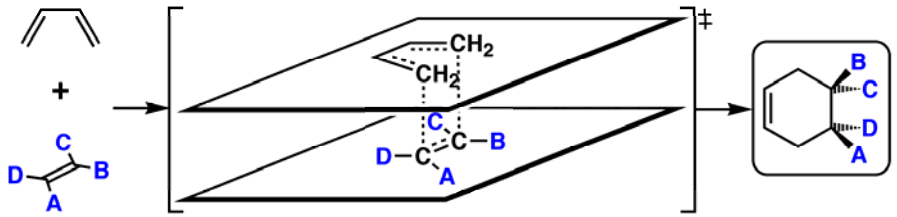


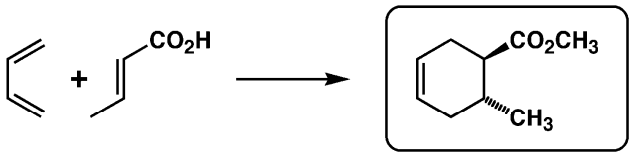


Representative Diels-Alder Reactions



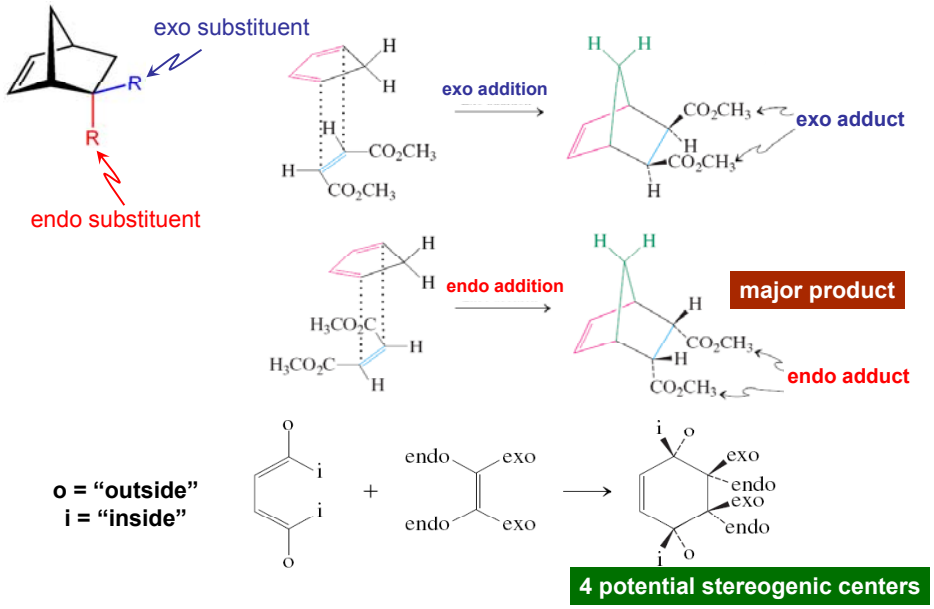
Diels-Alder Stereochemistry



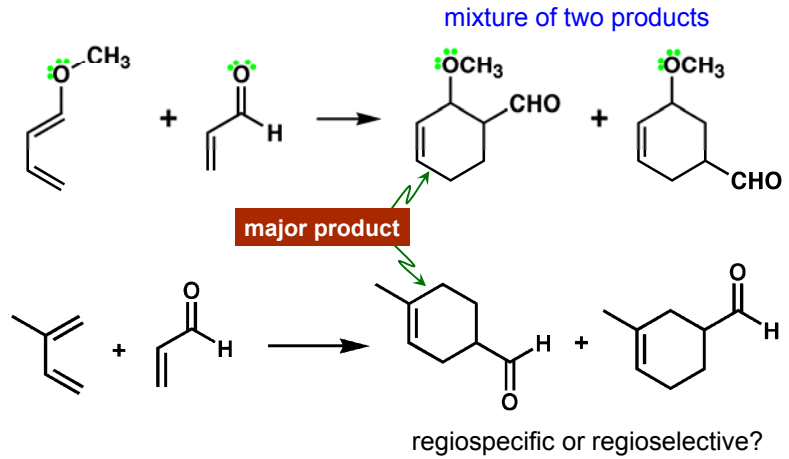


Stereoselective or stereospecific?

Endo Rule

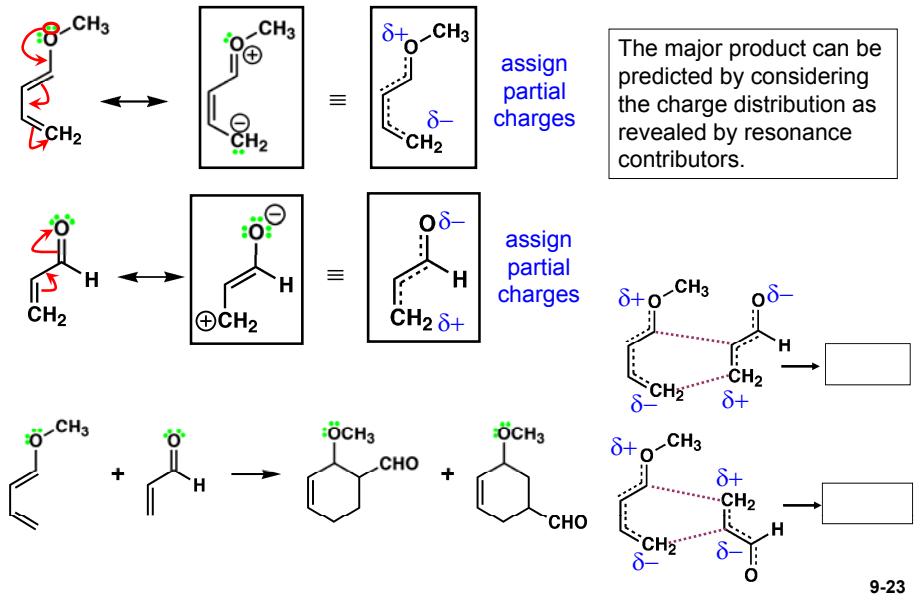


Regiochemistry of the Diels-Alder Reaction



Isomers having donor group (from diene) and acceptor group (from dienophile) oriented at 1,2- and 1,4- positions are usually the major product.

Resonance Contributors of Diels-Alder Substrates



The major product can be predicted by considering the charge distribution as revealed by resonance contributors.