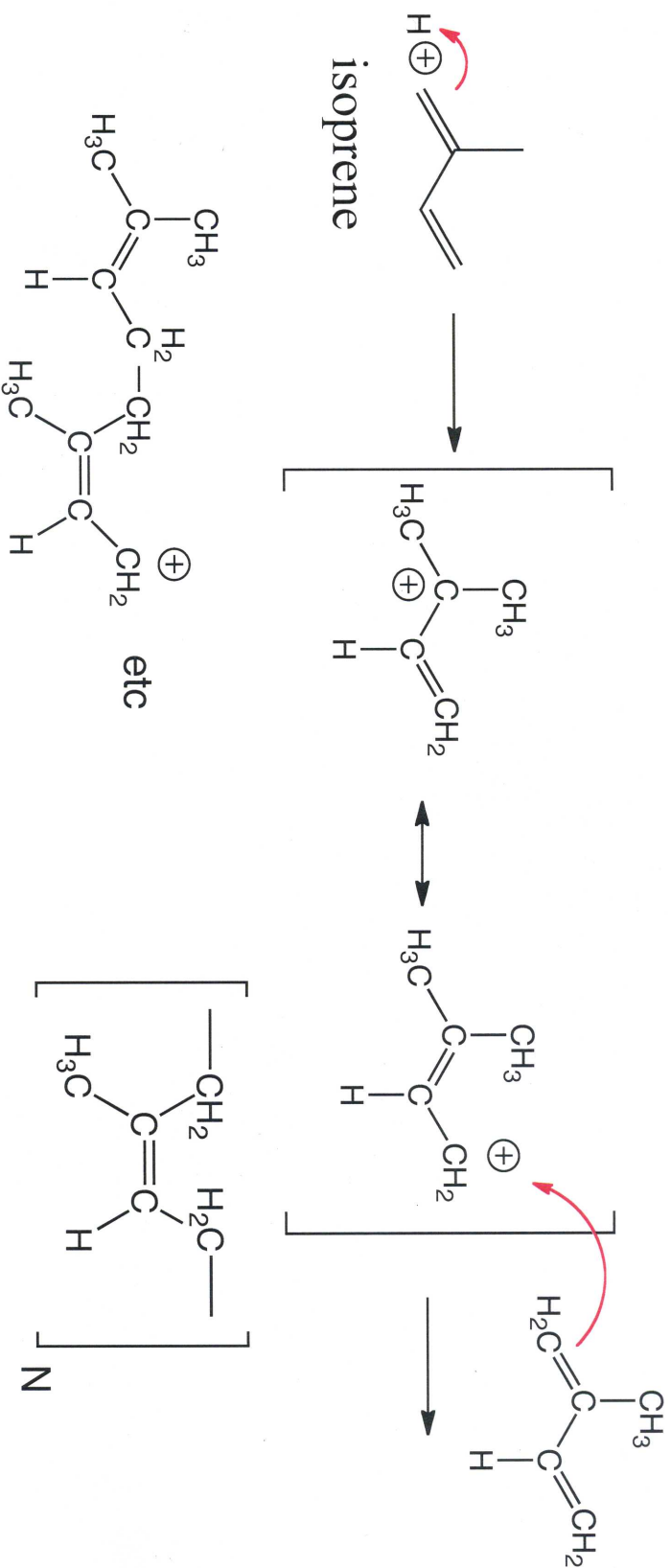


Rubber: Formally by a conjugated addition reaction



Rubber is a natural product produced by rubber tree *Hivea brasiliensis*

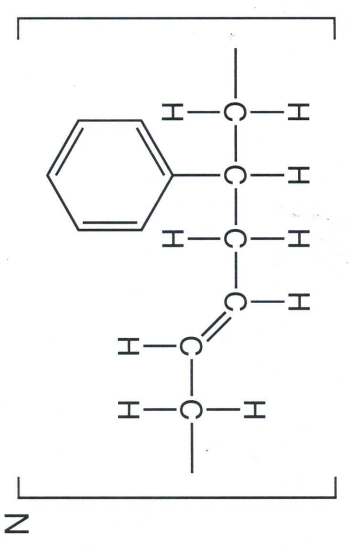
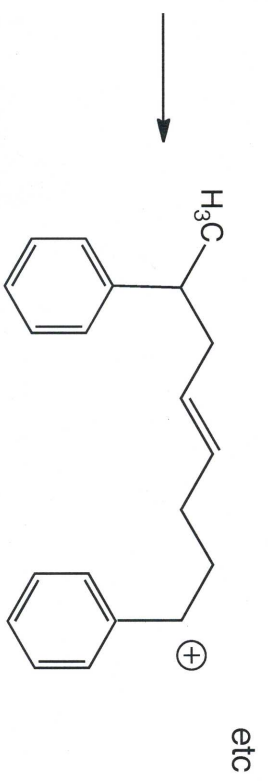
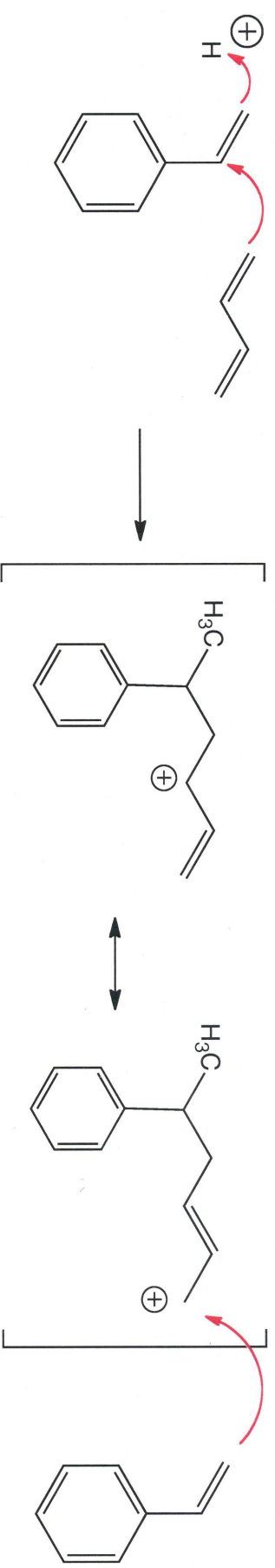
Vulcanized rubber has C and S added, then heated

Rubber cannot be synthesized using the same reaction as styrene polymer: Why?

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Copolymers by conjugated addition reaction

Example: SBR (Styrene Butadiene Rubber) Synthesis by **Conjugated Cation**



SBR (Styrene Butadiene Rubber)

Diels-Alder Reaction

46 A

Discovered by Otto Diels & Kurt Alder in 1928 - Nobel in 1950

conjugated diene in **cisoid** form reacts with alkene



transoid conformation

cisoid conformation

Diels-Alder rxn is example of a [4+2] **electrocyclic** reaction: **concerted**

in concerted reaction all bonds form and break at same time



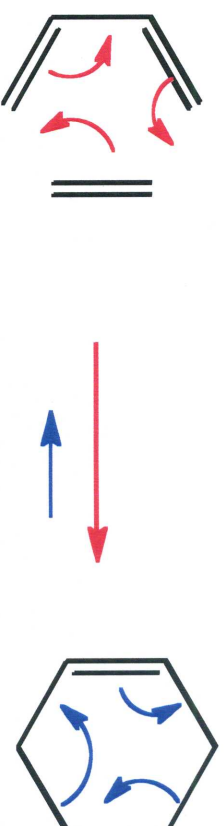
concerted reactions are always **stereospecific**

In stereospecific rxns:

stereochemistry of the starting material determines stereochemistry of product

Diels-Alder Reaction

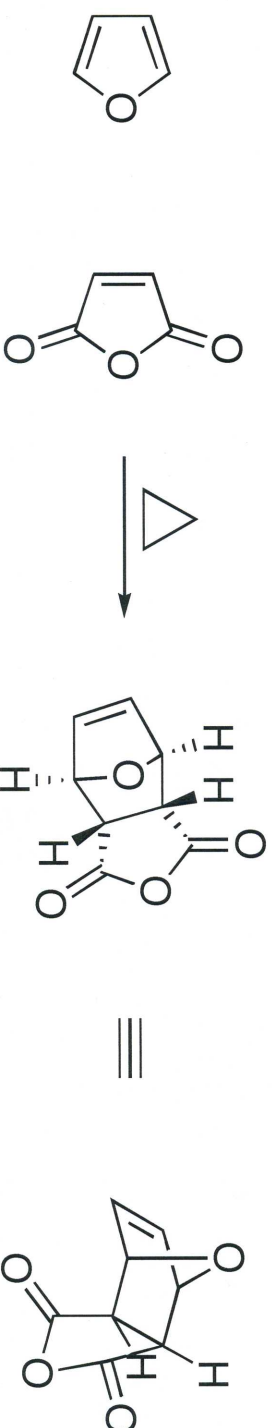
46B



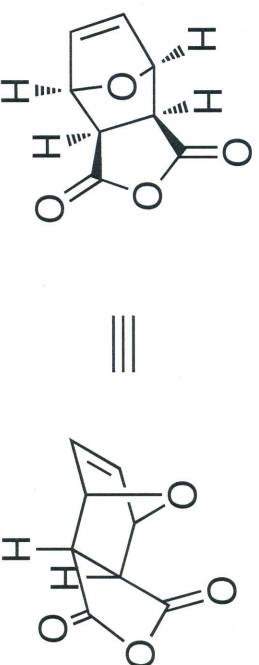
reversible in principle - usual cyclohexene favoured

note 6 pi (π) electrons: aromatic transition state

an example to help predict stereochemistry:

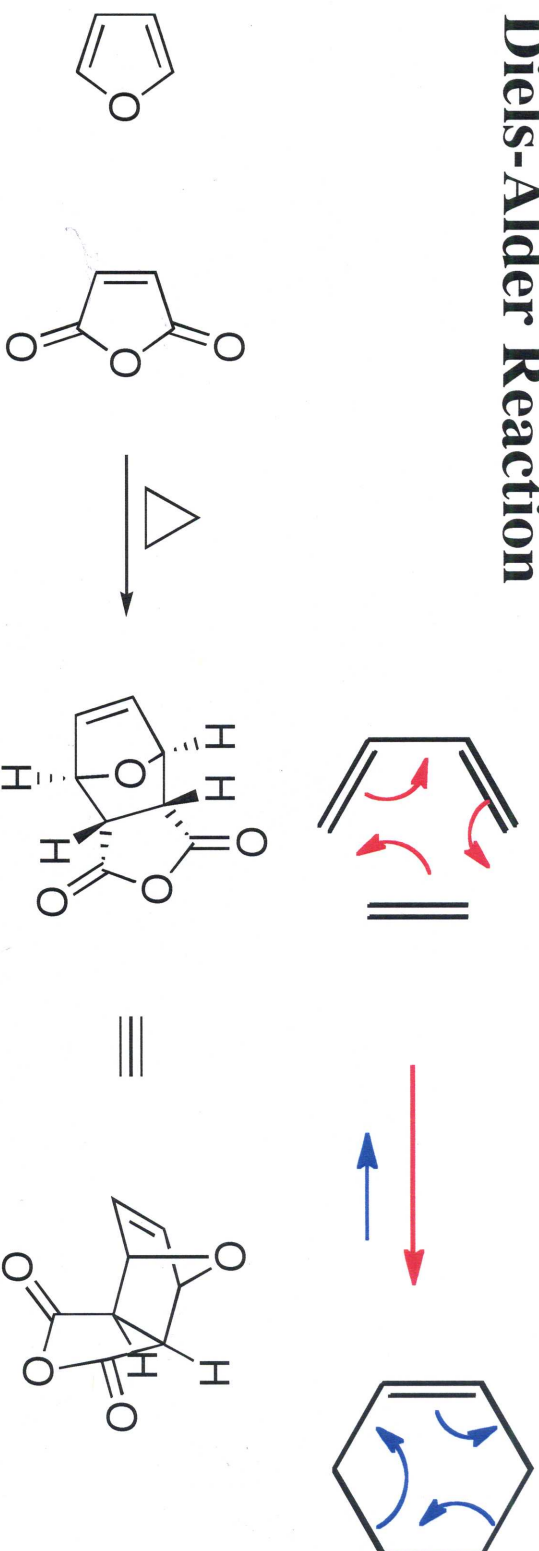


endo product favoured

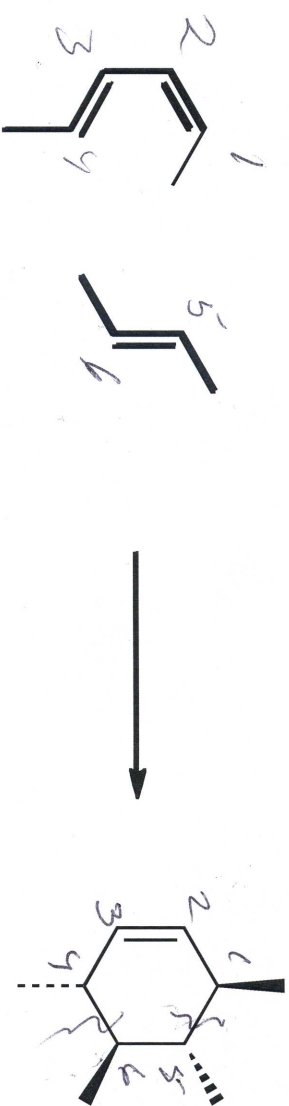


exo product not favoured

Diels-Alder Reaction



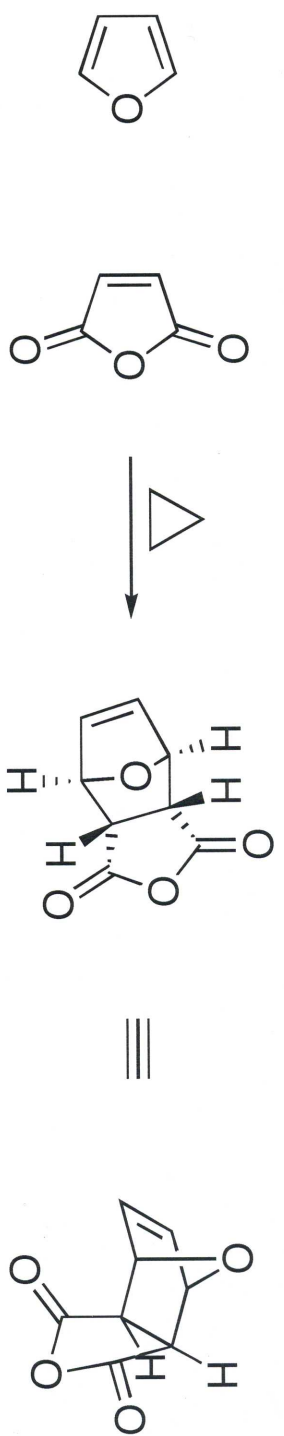
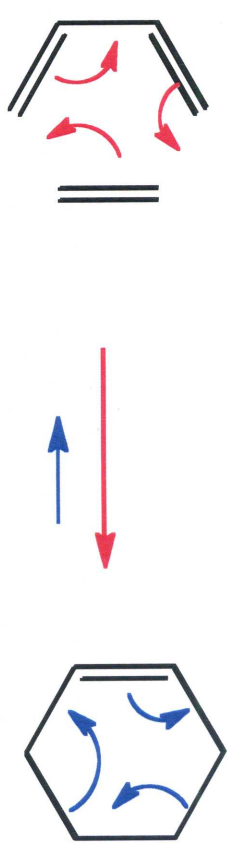
How to apply to other cases:



endo product favoured

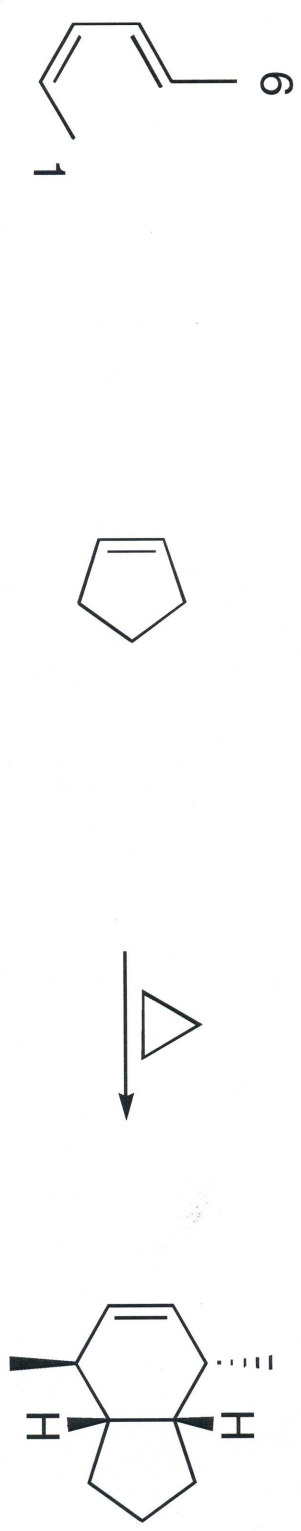
46C2

Diels-Alder Reaction



How to apply to other cases:

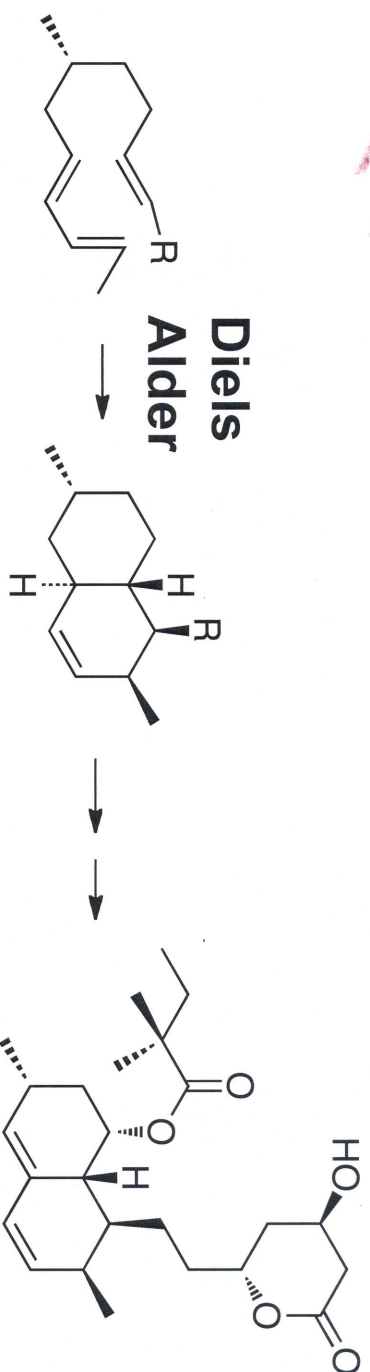
endo product favoured



2Z, 4E-hexadiene (diene) and cyclopentene (dienophile) to produce an endo product methyl at C6 is in position of the H in furan and therefore will be pointing down methyl at C1 is in position of the O in furan and therefore will be pointing up

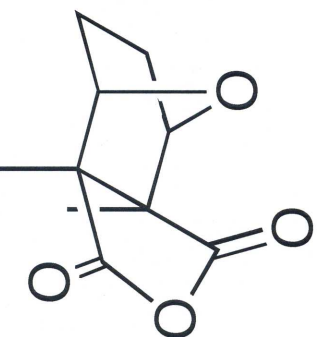
Example of Diels-Alder adduct in Nature

460



simvastatin = Zocor

cholesterol-lowering agent

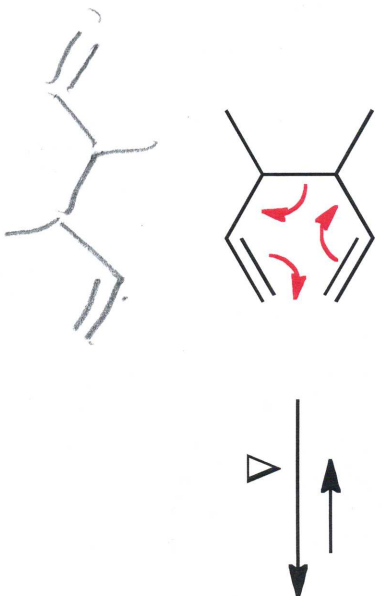


cantharidin from *Cantharis vesicatoria* (Spanish fly)

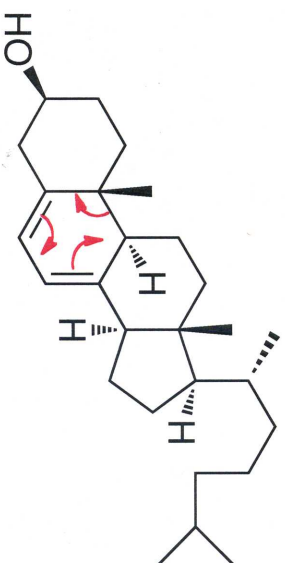
this one not made in Nature by Diels Alder reaction

Other Electrocyclic Reactions

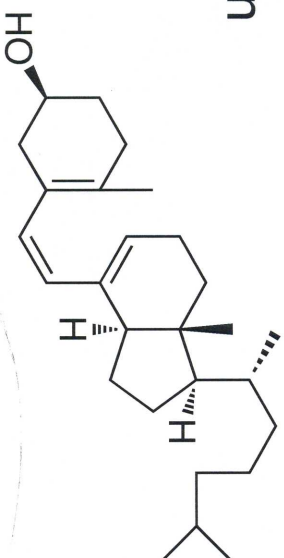
Cope reaction: 6 electrons participate



favours less sterically crowded isomer
same as (different conformation)

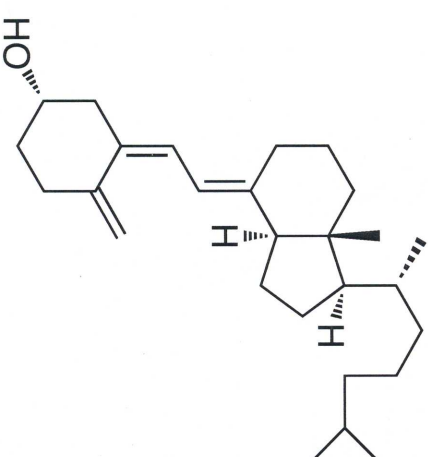


in skin



previtamin D3

dehydrocholesterol
= provitamin D3

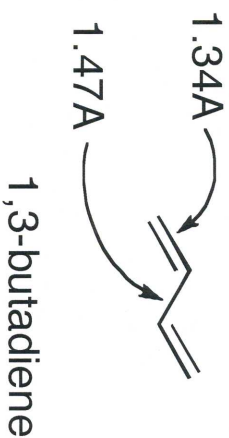
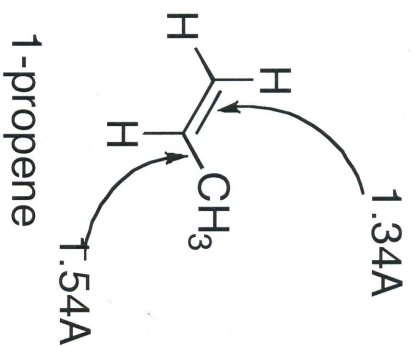


vitamin D3

deficiency disease is rickets - identified in 1650

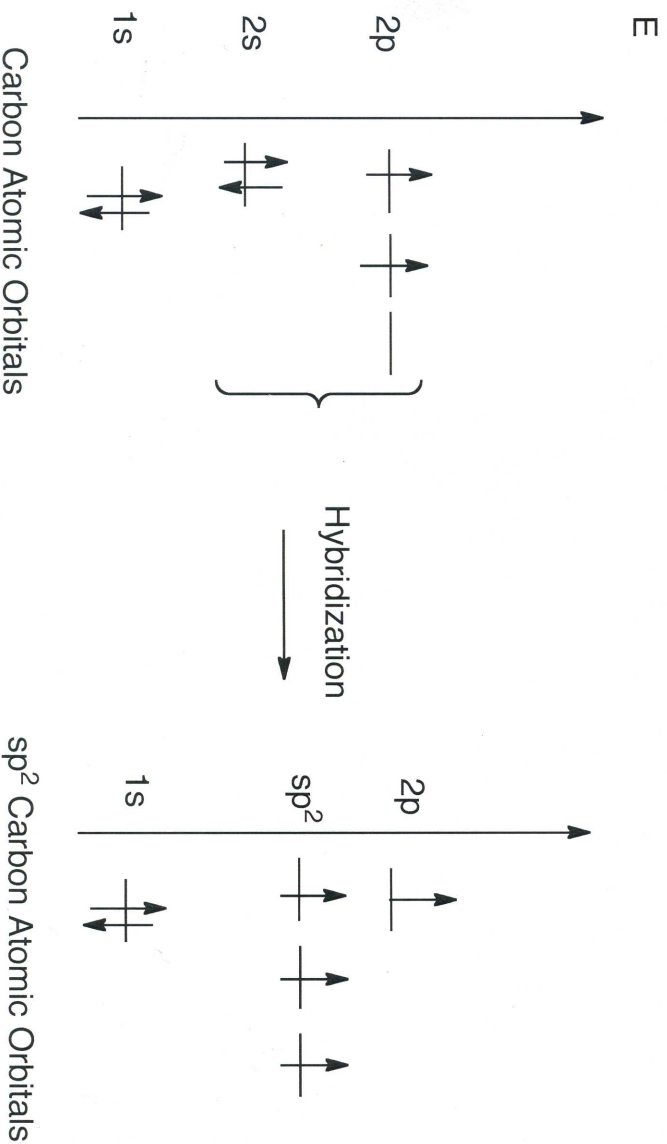
Bond & Energy Characteristics of Conjugated Systems

47

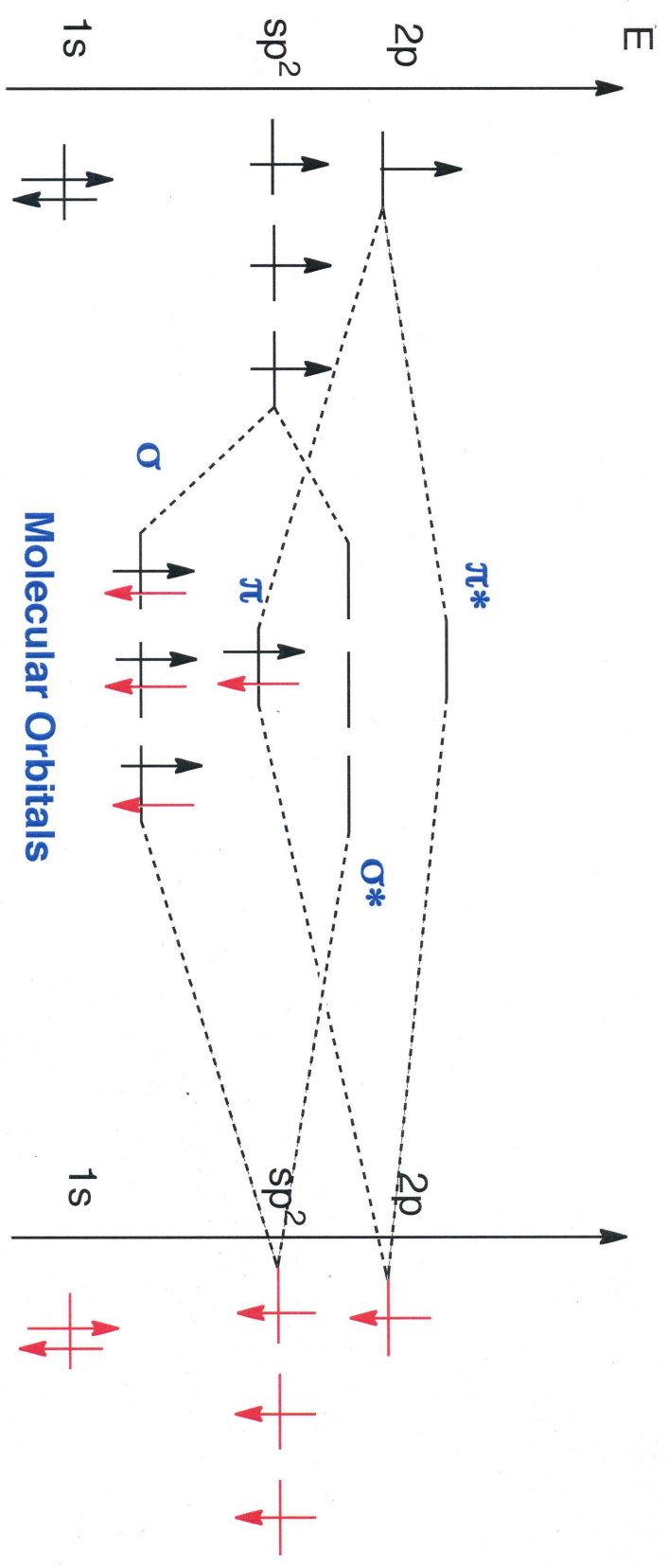


1,3-butadiene likes to be planar because of π molecular orbitals that align to overlap

Review formation of π (π) molecular orbitals from p atomic orbitals



Review formation of pi (π) molecular orbitals from p atomic orbitals



sp^2 Carbon Atomic Orbitals

sp^2 Carbon Atomic Orbitals