DIENES

Dienes are alkenes with 2 double bonds.
IUPAC: Same as alkene, but change -ene to -adiene and use two numbers to locate the two double bonds (number from the end of the chain which makes the smaller of these numbers smaller).

Double bonds separated by more than one single bond are *isolated.* Compounds with isolated double bonds have the same chemical properties as alkenes.

Double bonds that alternate with single bonds,
eg C=C-C=C, are *conjugated*.

Double bond arrangements like C=C=C are *cumulated*. Compounds containing two carbon-carbon cumulated double bonds are called *allenes.*

Conjugated dienes differ from simple alkenes in that they

- ☞ are more stable,
- ☞ undergo 1,4-addition, and
- ☞ are more reactive.

Stability

Alkene Type	**~$\Delta H_{hydrogenation}$**
$RCH=CH_2$	30 kcal/mole,exotherm.
$R_2C=CH_2$, RCH=CHR	28
$R_2C=CHR$	27

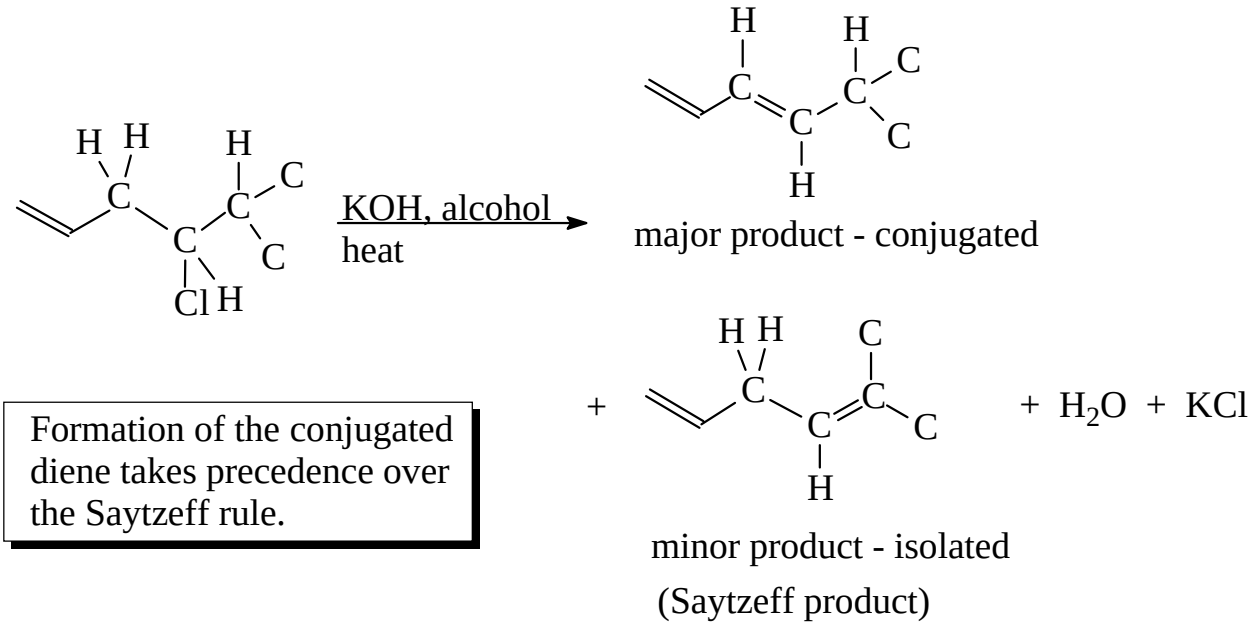
For dienes with *isolated* double bonds, the $\Delta H_{hydrogenation}$ calculated by adding the appropriate values from the table above together is very close to the experimental value.

For *conjugated* dienes, the experimental $\Delta H_{hydrogenation}$ is *smaller* than the calculated one, which is based on isolated double bonds.

Conjugated Diene	Calculated ΔH_h	Experimental ΔH_h
$CH_2=CH-CH=CH_2$	60 kcal/mole	57
$CH_2=C(CH_3)-C(CH_3)=CH_2$	56	54

Therefore, conjugated dienes are more stable than isolated dienes.

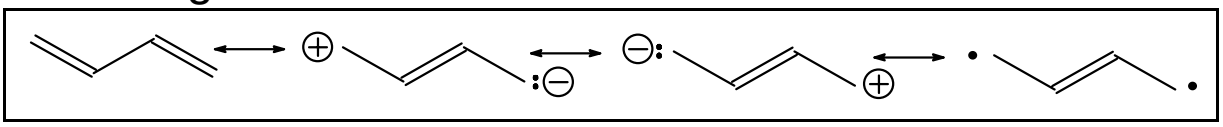
This stability is reflected in the fact that, where possible, conjugated dienes are the preferred diene products of elimination reactions ---



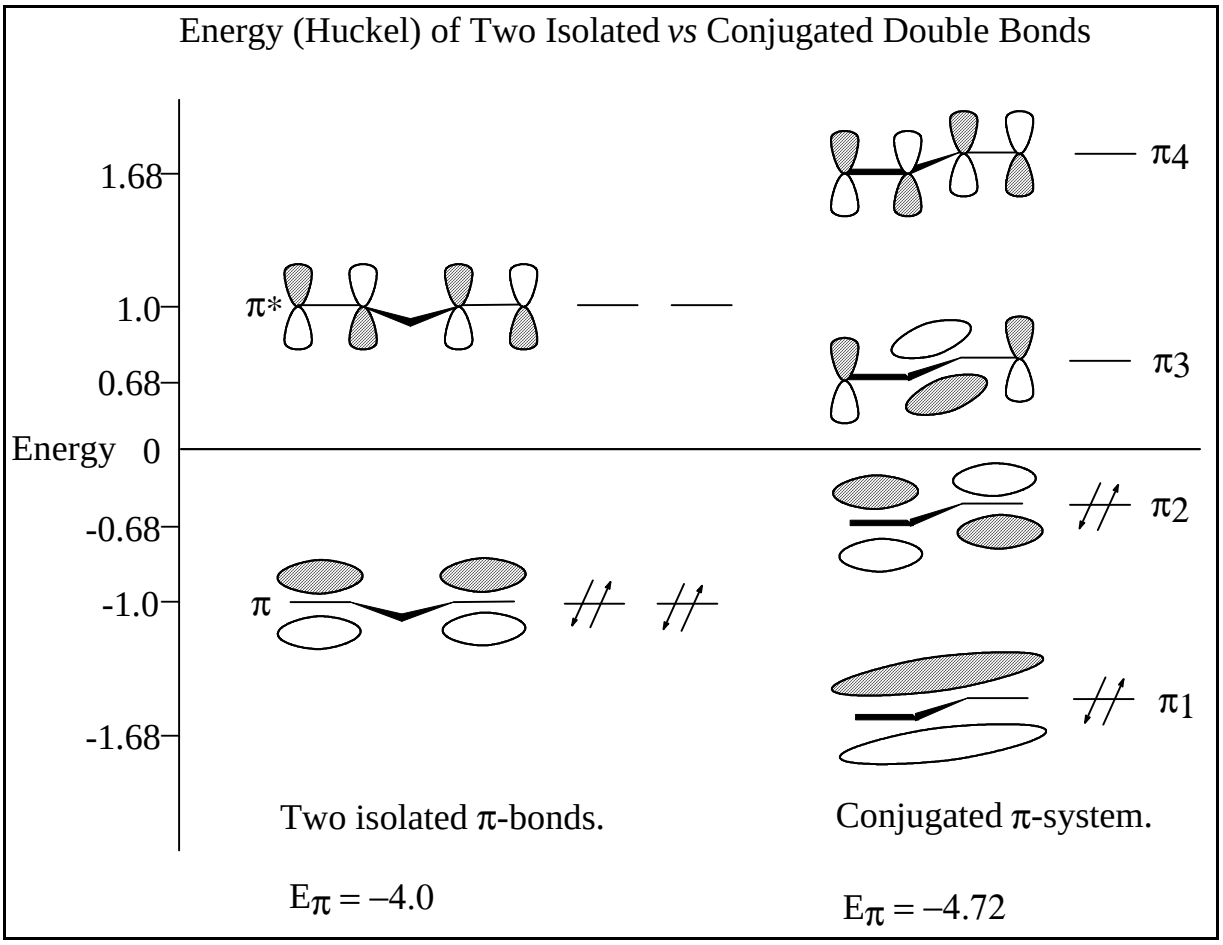
Formation of the conjugated diene takes precedence over the Saytzeff rule.

This stability can be explained by electron delocalization in the conjugated diene

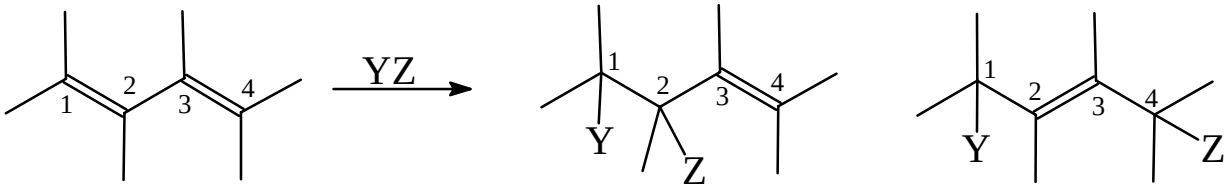
☞ using the resonance model ---



☞ or the molecular orbital model ---


Energy (Huckel) of Two Isolated vs Conjugated Double Bonds
1.68
1.0
0.68
Energy 0
-0.68
-1.0
-1.68
π*
π
π4
π3
π2
π1
Two isolated π-bonds.
Eπ = –4.0
Conjugated π-system.
Eπ = –4.72

Electrophilic Addition to Conjugated Dienes:
1,2- vs. 1,4- Addition ---



1,2-addition 1,4-addition

Note the "shift" of the π-bond.

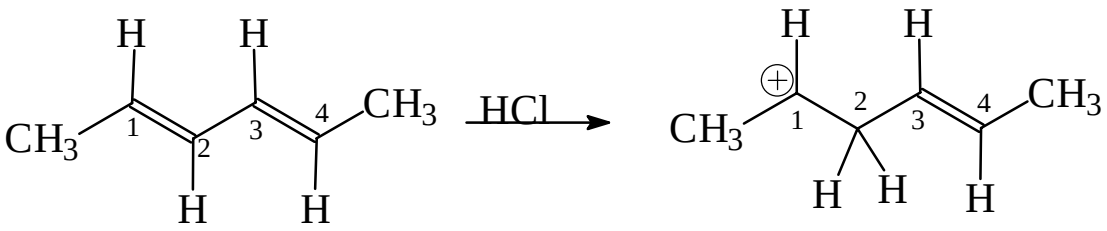
eg $CH_3CH=CH-CH=CHCH_3$ + HCl ——————>

CH_3-CH_2-CHCl-CH=$CHCH_3$ *via* 1,2-addition

+

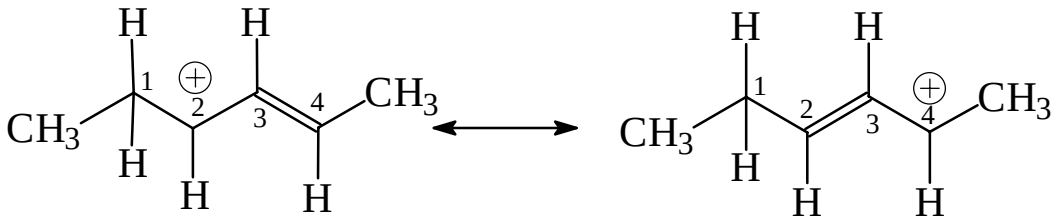
CH_3-CH_2CH=CH-CHCl-CH_3 *via* 1,4-addition

Mechanism ---



ordinary 2º carbocation -
VERY LITTLE FORMED

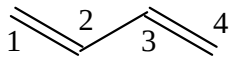
+



2º allylic type of carbocation; ~ stability of 3º carbocation.

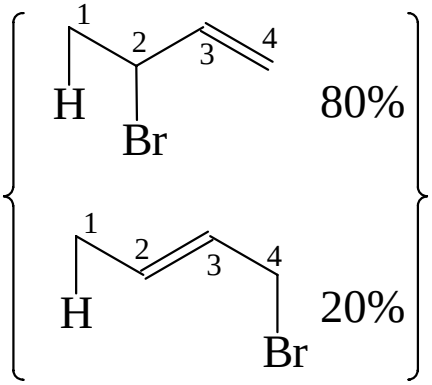
Since the positive charge is shared between the carbons labeled 2 & 4
Cl^- can attack either.

1,2- vs. 1,4-Addition: Rate vs. Equilibrium Control



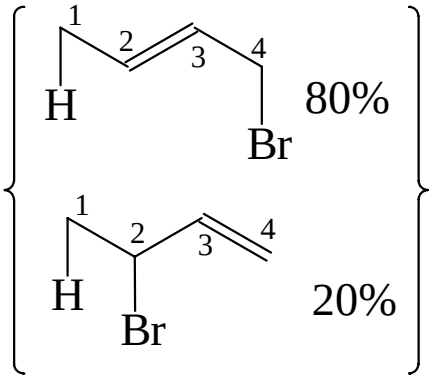
HBr →

Low temp (-80º C)



40ºC →

High temp (40º C)



At -80º the 1,2-isomer converts to 1,4-isomer very slowly. Since 1,2- predominates here, it is formed faster.

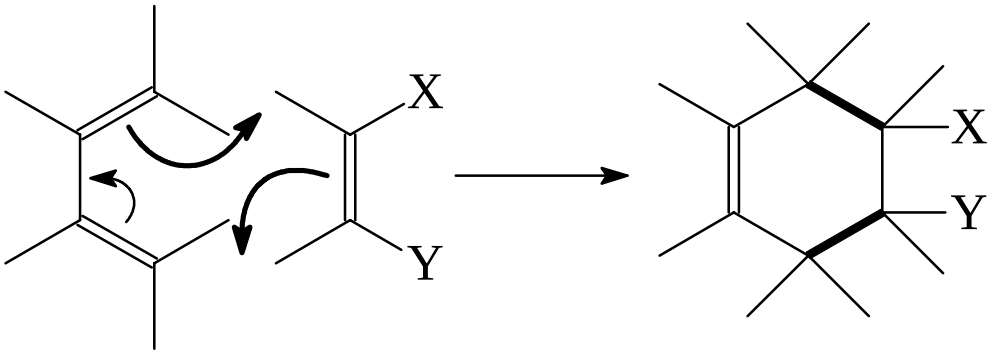
Reaction rates determine product here:
Kinetic Control

At 40º the 1,2- and 1,4- isomers interconvert, giving an equilibrium mixture. The 1,4-isomer is more stable and predominates.

Equilibrium constant determines product here:
Thermodynamic Control

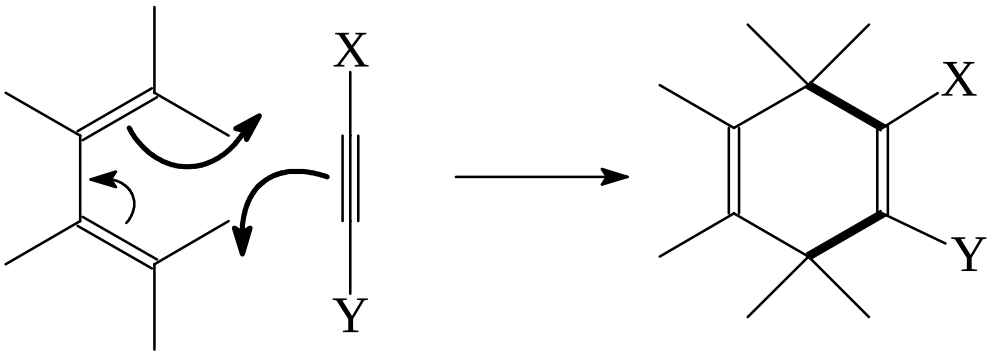
In this case, the less stable product is formed faster. How does this happen?

Diels-Alder Reaction



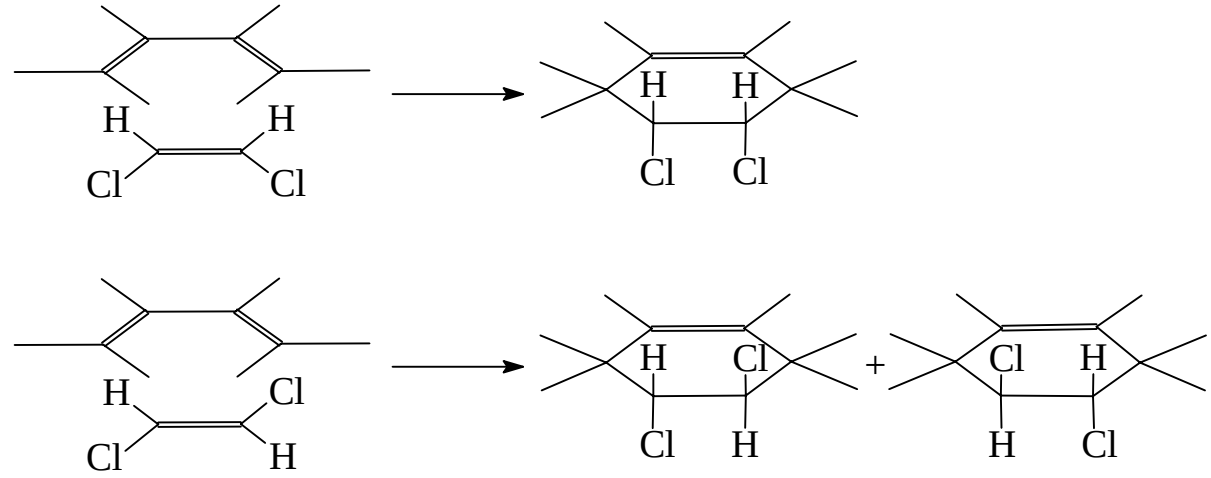
diene dieneophile (X, Y: typically one or both are electron withdrawing) a substituted cyclohexene

There are other variations on this theme, *eg*---

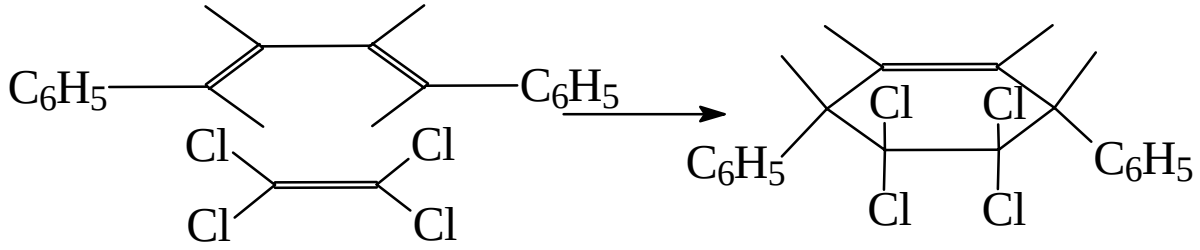


Stereochemistry ---

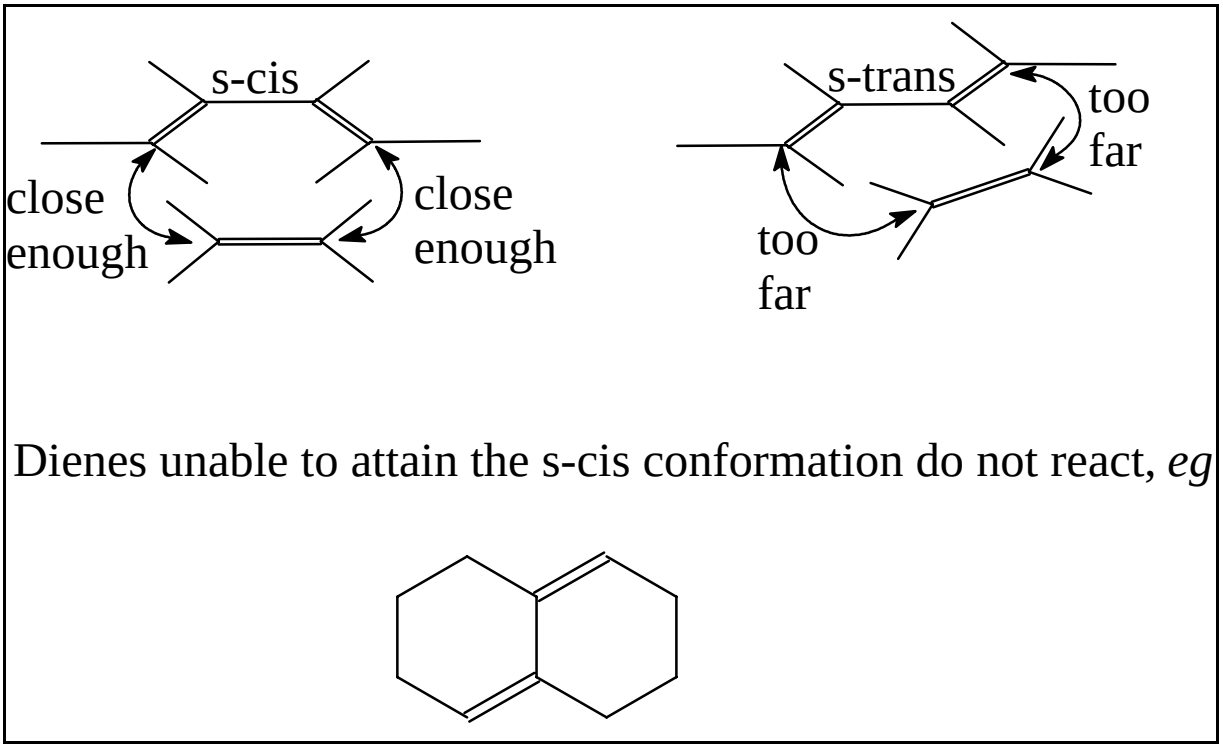
1) With respect to the dieneophile, the addition is stereospecifically syn, *eg*



2) With respect to the diene, the addition is stereospecific and syn, *eg*

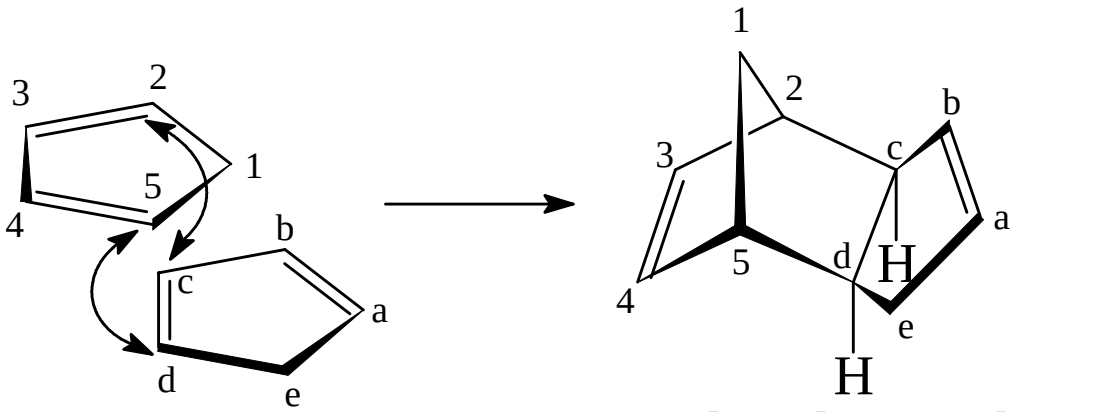


3) The diene must be in the *s-cis* conformation for reaction to occur. [The mechanism is concerted --- no intermediates.]

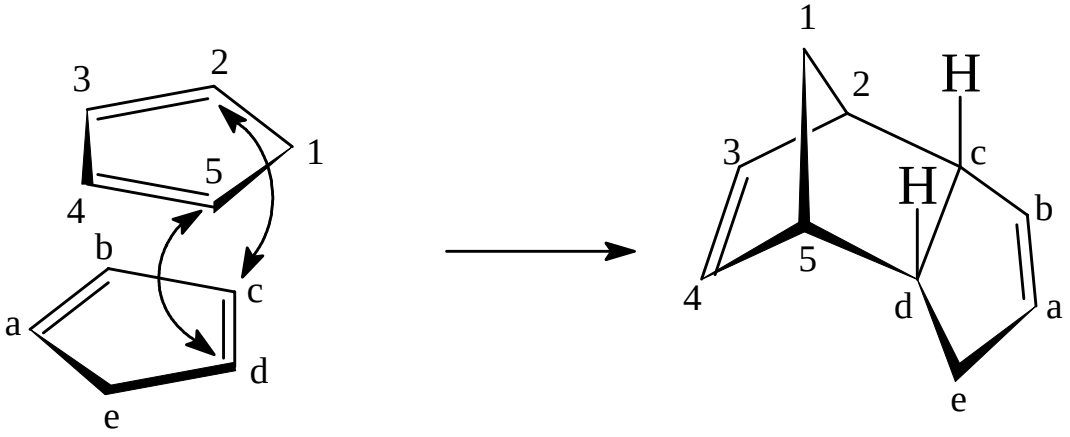


Dienes unable to attain the s-cis conformation do not react, *eg*

4) If the diene is cyclic and the dieneophile has an unsaturated substituent, the *endo* product is usually favored over the *exo* product [the reaction is *stereoselective*; one diasteromer (*endo*) is favored over another (*exo*)].



cyclopentadiene *exo*-dicyclopentadiene



cyclopentadiene *endo*-dicyclopentadiene