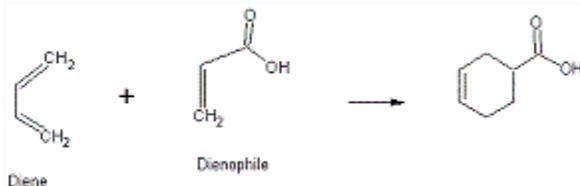


Conjugation of Double Bonds

A diene is said to be conjugated when its double bonds are not directly next to each other, but rather separated by a single bond in between them ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$).

Conjugated dienes are particularly stable due to the delocalization of the pi electrons along sp^2 hybridized orbitals, and they also tend to undergo reactions atypical of double bond chemistry. For instance, chlorine can add to 1,3-butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) to yield a mixture of 3,4-dichloro-1-butene ($\text{ClCH}_2-\text{CHCl}-\text{CH}=\text{CH}_2$) and 1,4-dichloro-2-butene ($\text{ClCH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$). These are known as 1,2 addition and 1,4 addition, respectively. 1,2-addition is favored in mild reaction (irreversible) conditions (the kinetically preferred product) and 1,4-addition is favored in harsher reaction (reversible) conditions (which results in the thermodynamically preferred product).

Another interesting conjugated diene reaction is the Diels-Alder reaction, in which a conjugated diene reacts with an alkene (called a "dienophile" in this case) in order to yield a cyclic product. In Diels-Alder type reactions, the substituent on the dienophile will go into either an exo or endo position in the final product. ("*Endo*" in this case meaning *trans to the substituents on the ends of the diene*, and "*exo*" meaning the same thing, only *cis*.)



Common Reactions of Conjugated Dienes

Conjugated dienes have enhanced stability as compared to molecules without conjugated double bonds due to resonance. In general, this makes them slightly less reactive than other types of alkenes in general and dienes specifically. However, many reactions proceed through high-energy cation or radical intermediates; in these cases the resonance stabilization of the intermediate allyl species makes conjugated dienes more reactive than non-conjugated dienes or simple alkenes.

Hydrobromination:

Adds a Bromine and a Hydrogen to a conjugated Diene.

Example:

Butadiene + HBr \rightarrow 3-bromobutene (Low Temperature) + 1-bromobut-2-ene (High Temperature) + 1-bromobutene (Not Observed)

Thermodynamic and Kinetic Control of Reaction:

At low temperature the reaction is under KINETIC CONTROL: the 3-bromobutene is formed faster because it has a lower transition state free energy, as the intermediate cation is more stable at the secondary carbon.

At high temperature the reaction is under THERMODYNAMIC CONTROL: the 3-bromobutene still forms more quickly, but the reaction has enough energy to reverse, and the more stable product (1-bromobut-2-ene) is formed.

Diels-Alder Reaction

One of the most important of all diene reactions is the Diels-Alder Reaction, in which a conjugated diene reacts with a dienophile to form a cyclohexene.

Requirements: The diene must be able to access the s-cis conformation for the reaction to take place.

DIENEOPHILES - A species which likes to attack Dienes

- A Dienophile must contain a double or triple bond. Typically, an electron withdrawing group is conjugated to the dienophile to make it electron-poor (nitriles, ketones, and esters are common electron withdrawing groups). Because the reaction is highly stereospecific, the configuration of the dieneophile will determine the relative stereochemistry of the cyclohexene product.

The Diels-Alder reaction occurs most effectively with an electron-poor dieneophile and an electron-rich diene ('normal demand'). 'Inverse demand' Diels-Alder reactions can also be carried out, in which the dienophile is electron-rich and the diene electron-poor.