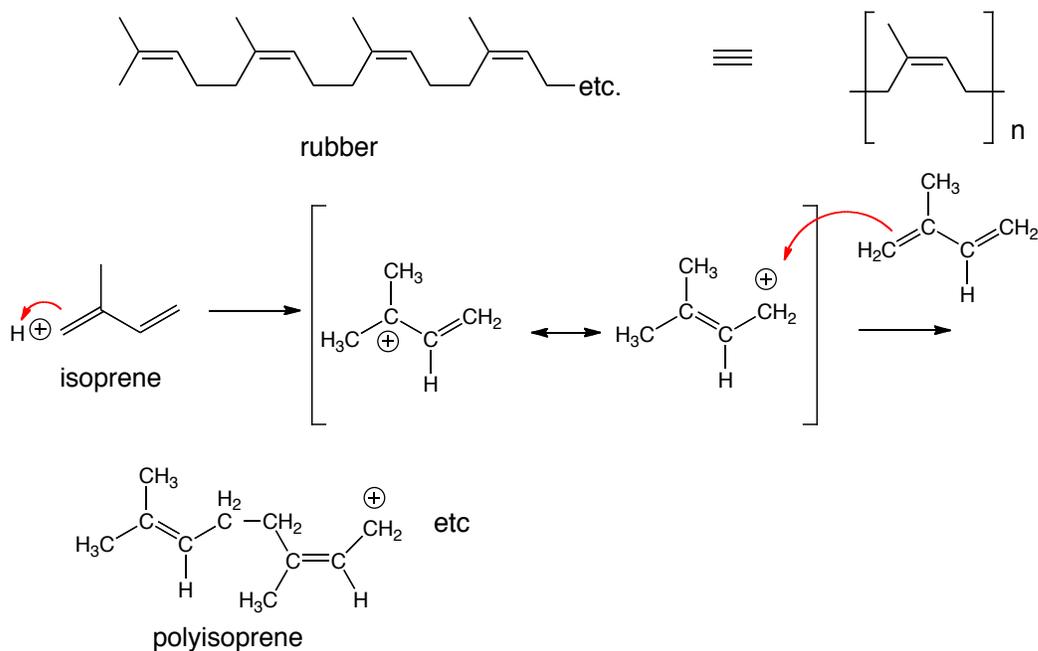


Practical Applications for Conjugated Addition Reaction:

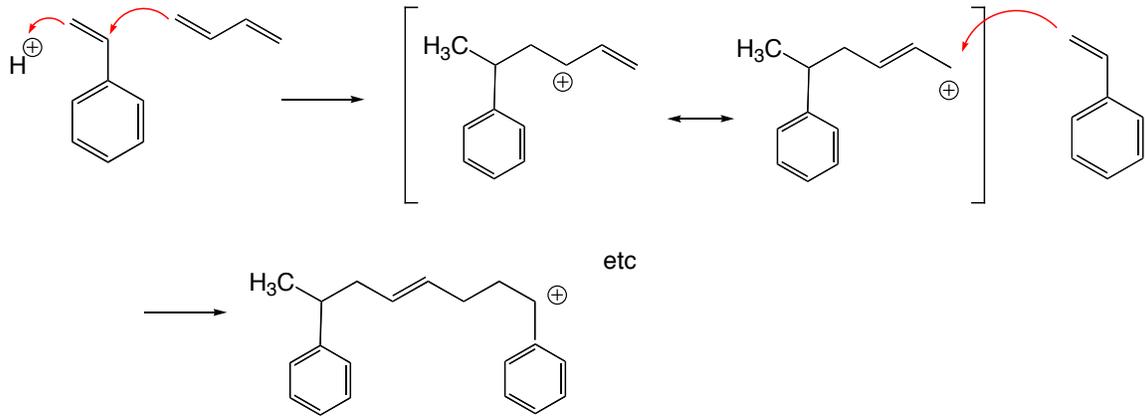
Example: Rubber formation – Formally by a conjugated addition reaction

Rubber is a natural product produced by rubber tree *Hivea brasiliensis*. The rubber is collected in the form of syrup (latex) and after concentration as raw rubber it is very sticky (like chewing gum). This is not very useful.

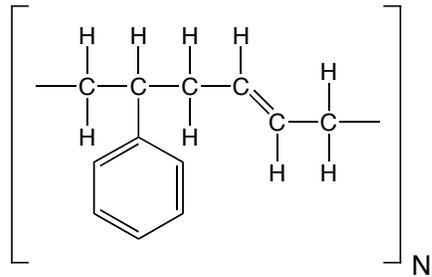


Rubber can be viewed as a polymer of 2-methyl-1,3-butadiene, which is also known as isoprene. Addition of acid will form a resonance-stabilized cation. Note that non-enzymatic polymerization (e.g. in lab synthesis) would give undesirable trans isomer instead of the cis naturally formed in plants by enzymatic processes.

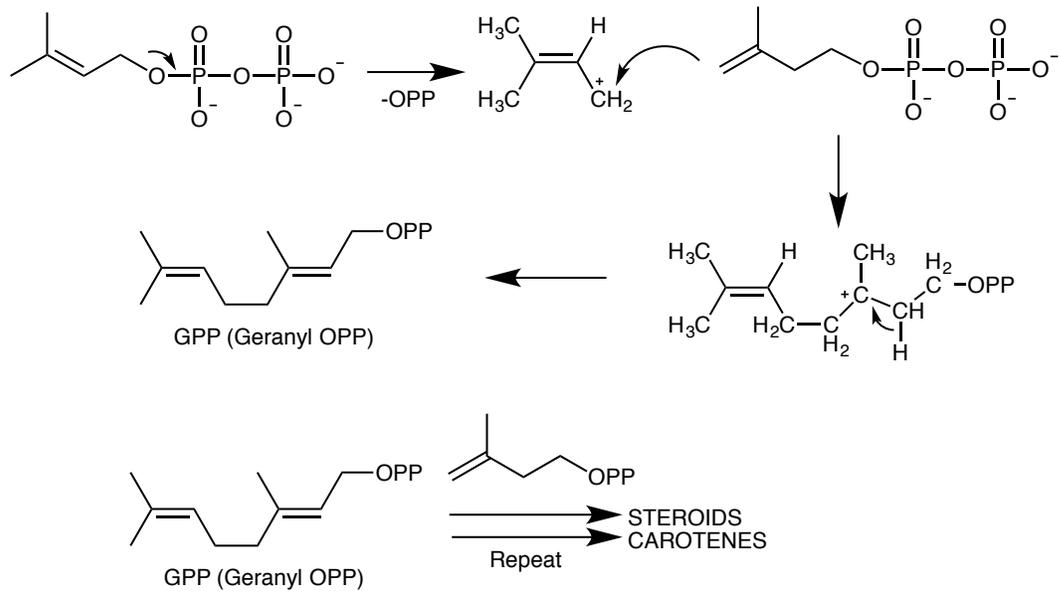
Example: Styrene Butadiene Rubber (SBR) synthesis (by conjugated cation)
 SBR is a **copolymer**.



Another representation:

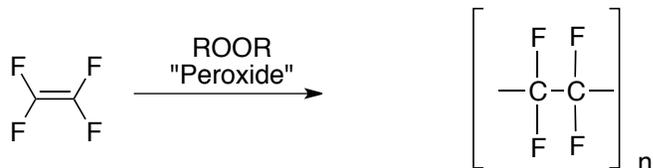


Example: Terpenes

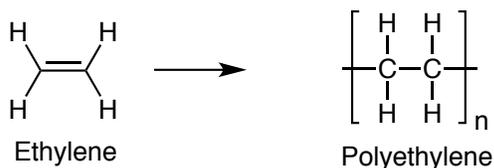


More examples

Teflon is a polymer of tetrafluoroethene and used in non-stick coatings



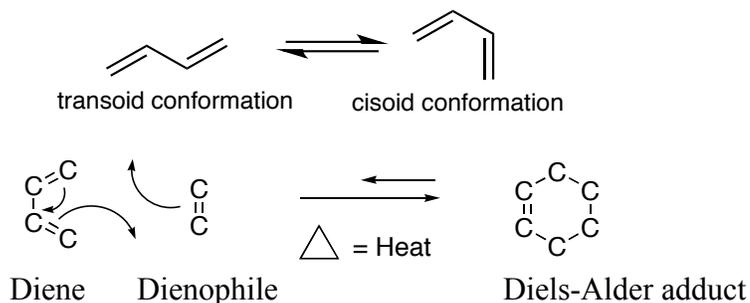
If you started with ethylene (ethene) instead, you would get polyethylene



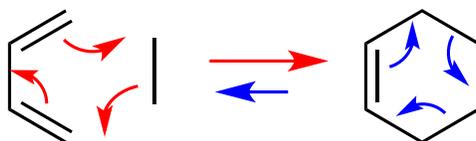
Diels-Alder Reaction

The Diels-Alder reaction was discovered in 1928 by Kurt Alder and Otto Diels. Both later won the Noble Prize in 1950 for their discovery.

The Diels-Alder reaction consists of a conjugated diene in cisoid form reacting an alkene (also called an olefin, or for these reactions a dienophile because it is 'diene loving'). When heated, it forms two new carbon-carbon bonds in a single step and forms a cyclic molecule (a cyclohexene). The reaction is theoretically reversible but the stability of the product drives the reaction to completion. The Diels-Alder reaction is an example of a [4+2] **electrocyclic reaction**. The [4+2] refers to the 4 π -electrons from the diene and the 2 π -electrons from the dienophile. The mechanism of the Diels-Alder reaction occurs through a pericyclic process in which the π -electrons move in a cycle or ring.

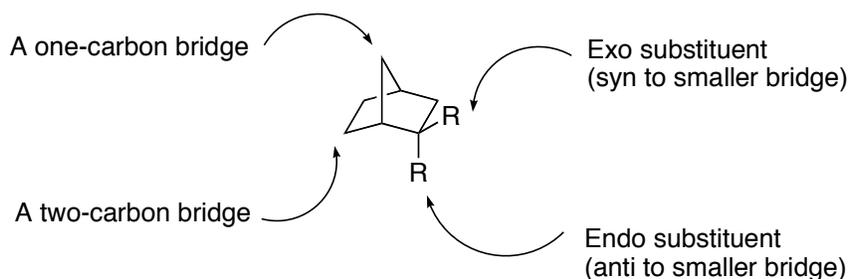


Although the transoid conformation of dienes is more favoured, the cisoid and transoid conformations are in equilibrium, so as the cisoid reacts with the alkene, more is formed.

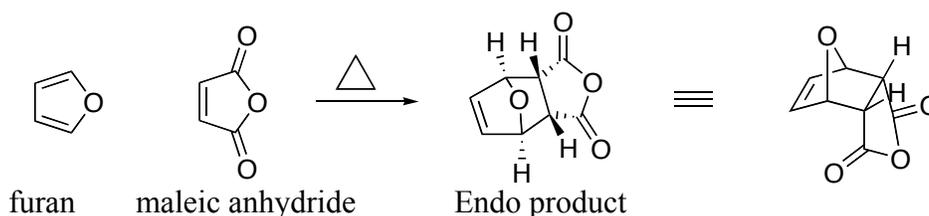


The mechanism is **concerted**, which means that all the bonds form and break at the same time (an S_N2 reaction is also concerted). As a result, the reaction is also **stereospecific**, which means that the stereochemistry of the starting materials determines the stereochemistry of the products.

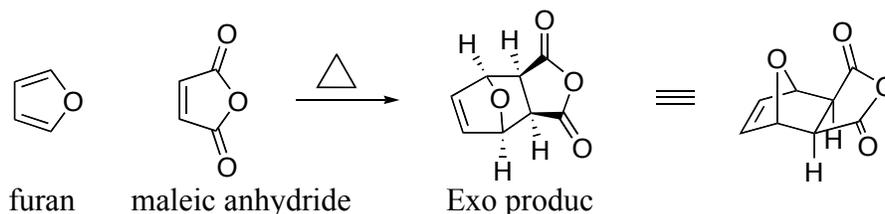
Starting from achiral substrates, a racemic mixture of stereoisomers can be formed. The diene and dienophile line up in such a way that the endo product rather than the exo product is formed. Endo and Exo are used to indicate the relative stereochemistry of a bicyclic structure. A substituent on one bridge is said to be endo if it is anti (trans) to the smaller of the two bridges and exo if it is syn (cis).



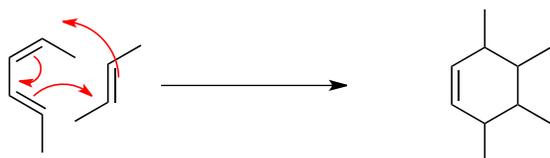
An example to apply to other systems is the Diels-Alder reaction of furan (diene) and maleic anhydride (dienophile). In this reaction, the dienophile approaches the 5-membered ring furan from the bottom side, producing an endo Diels-Alder adduct.



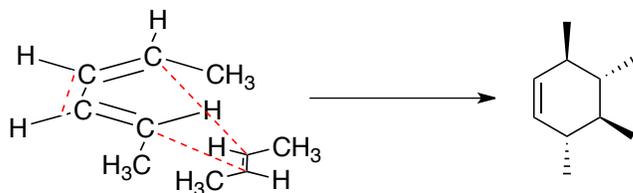
The exo product, which is not favored and not formed, would arise in the following manner.



Stereospecific Diels-Alder

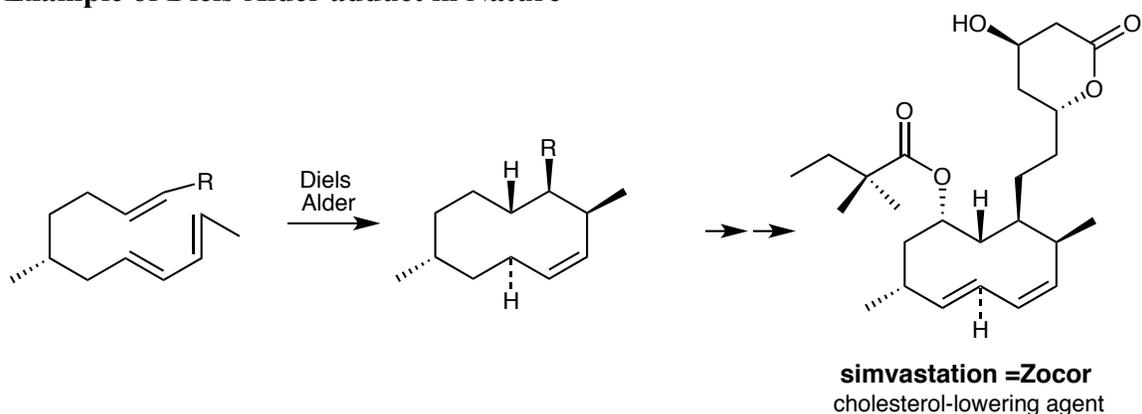


But how do we determine if the methyl groups are up or down?



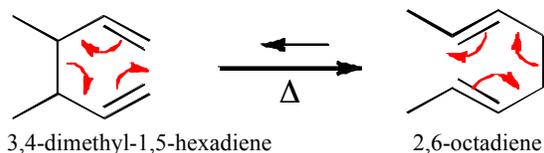
This can be done with models, but a simple way is to remember the stereochemical outcome of one Diels-Alder reaction (e.g. furan + maleic anhydride) and apply the substituent location (up or down) to the current example.

Example of Diels-Alder adduct in Nature

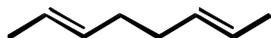


Cope Rearrangement

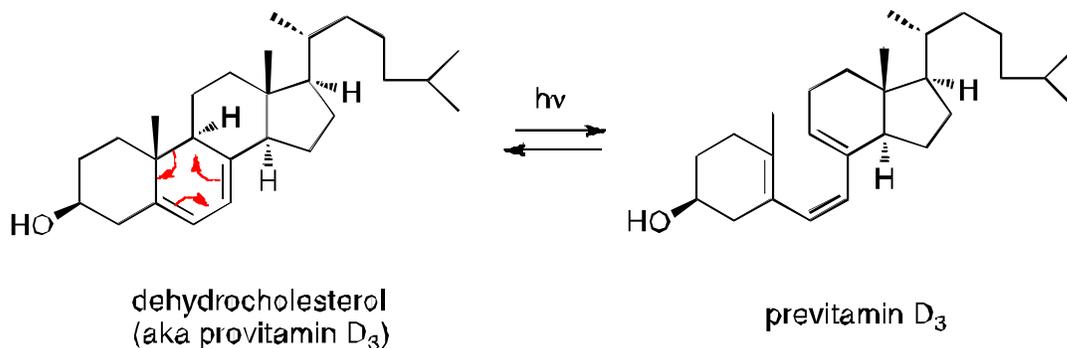
This is another pericyclic reaction that, like the Diels-Alder reaction, involves 6 electrons.



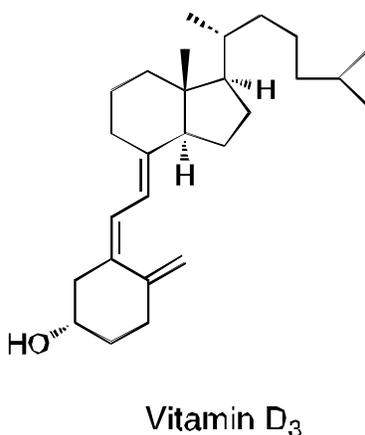
Note the steric interference between the two methyl groups in the first isomer. This example favours the sterically less crowded isomer, which can be redrawn as:



This reaction occurs in nature, as shown below:

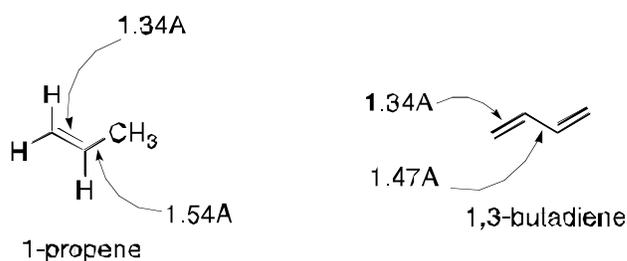


This goes on to form Vitamin D₃, whose structure you should be able to recognize.



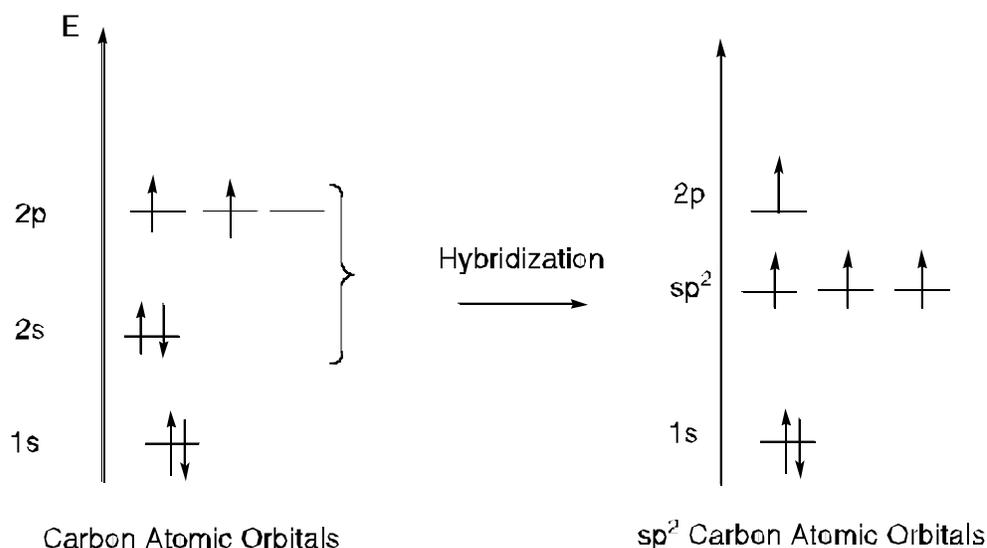
Vitamin D deficiency is known to cause rickets. Rickets was first identified around the year 1650. Prevention by a dietary factor was determined in 1914, and vitamin D structure was elucidated in the 1930s

Bond and Energy Characteristics of Conjugated System

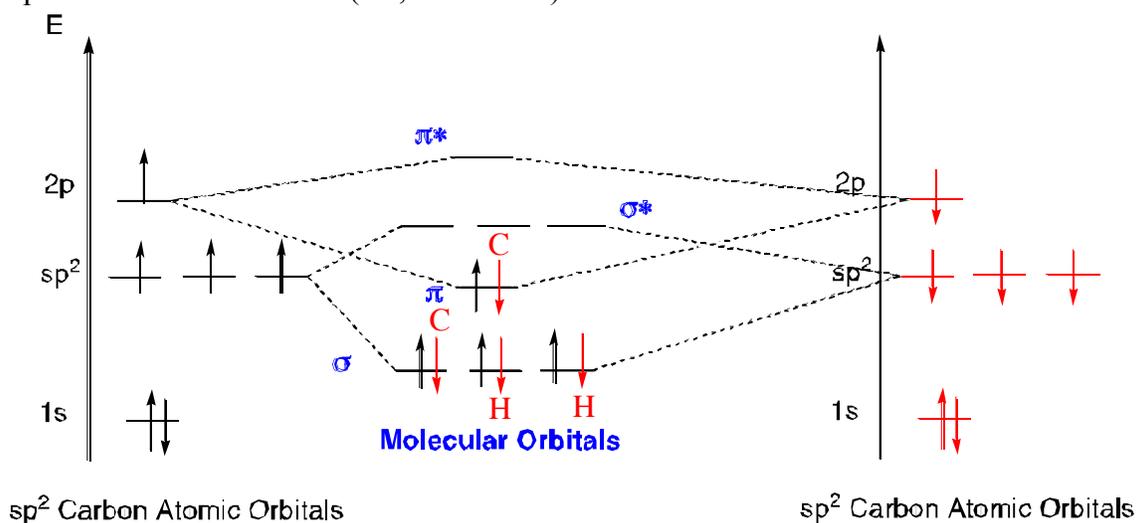


The C=C bond length in both propene and 1,3-butadiene is ca. 1.34 Å
In propene the C-C bond length is 1.54 Å, whereas the central C-C bond in 1,3-butadiene is shorter at 1.47 Å (has some small amount of double bond character) and is therefore stronger than a normal single bond.

Recall how we can show the energy levels of the atomic orbitals of C. If the C is sp^2 hybridized, two of the 2p orbitals “combine” with the 2s orbital to form two sp^2 hybrid orbitals.



The following molecular orbital (MO) diagram shows the construction of molecular orbitals from the hybrid orbitals of two sp^2 hybridized carbons doubly bonded together (i.e., ethane). One electron pair in the σ MO represents the single bond between the two carbons (and the other two represent C-H bonds), while the electron pair in the π MO represents the double bond (i.e., the π bond) between the two carbons.



In butadiene all four carbon atoms have a 2p orbital. These **atomic** 2p orbitals combine to produce four **π molecular** orbitals (the number of AOs combined equals the number of MOs formed). Since there are two double bonds, there are two bonding and two

antibonding π molecular orbitals (recall each π bond system is made by combining two $2p$ atomic orbitals). A bonding and an anti-bonding molecular orbital result.

In the diagram above, a sigma bond **molecular orbital** also forms by combination of sp^2 from the carbon on the right and sp^2 from the carbon on the left (one antibonding sigma star is also formed by this combination). Two other two sigma molecular orbitals with electrons and two more vacant antibonding sigma star orbitals that are shown come from combination of two hydrogen $1s$ atomic orbitals and the remaining two sp^2 carbon orbitals from the carbon on the left.