

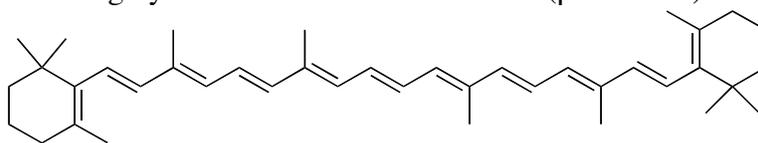
Absorption and Reflection of Visual Light

Molecules absorb different wavelengths of visible light and reflect other wavelengths giving them certain colours. If a molecule absorbs all wavelengths of visible light, it appears black in colour. If it reflects all wavelengths of visible light, it appears white in colour. Below is an abbreviated list of wavelengths absorbed and the visual colour it represents.

Absorbed Wavelength (Å)	Colour Absorbed	Visual Colour
4000-4350	violet – blue	yellow – green
4900-5000	blue – green	red
5800-5950	yellow	blue
5950-6050	orange – red	green
6050-7500	red	blue – green

Conjugated Dienes and Colour

Beta-carotene (depicted below) is the orange colour in carrots. Ordinary “white” light from the sun, consisting of all wavelengths in the visible spectrum, strikes beta-carotene and the 400 to 500 nm (blue) wavelengths of light are absorbed. The other wavelengths are reflected to our eyes. We therefore see the white light with the blue subtracted out, and we perceive a orange-yellow colour of beta-carotene (β -carotene).

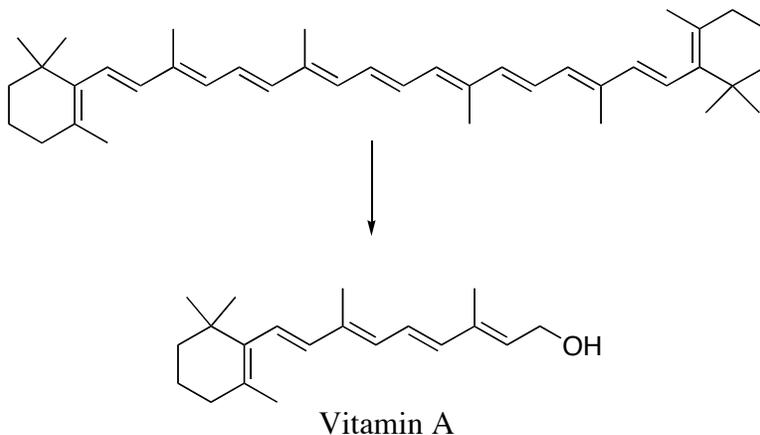


β -carotene

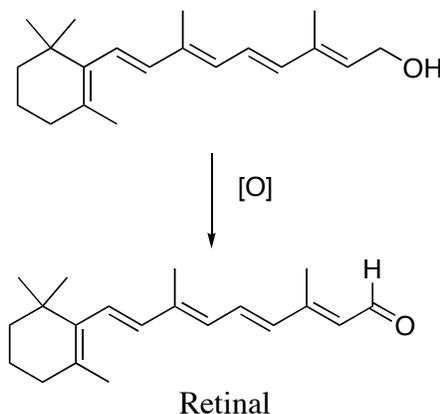
Beta-carotene is found in every single photosynthetic plant and is biosynthesized in nature to about 10^9 metric tones per year. Animals are not able to biosynthesize carotenes and must take them up in the diet.

The Chemistry of Vision

Not all conjugated molecules are coloured (> 7 conjugated double bonds necessary). They also make up the light sensitive substances responsible for the visual systems of organisms. A key component of our vision arises from the body's ability to synthesize Vitamin A from beta-carotene (shown below) in which the C_{40} beta-carotene is broken down into the C_{20} vitamin A.

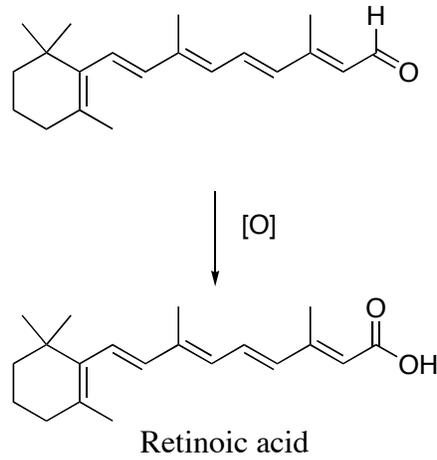


In the liver, vitamin A is further oxidized to retinal, a process in which the primary alcohol functionality is oxidized to the aldehyde.

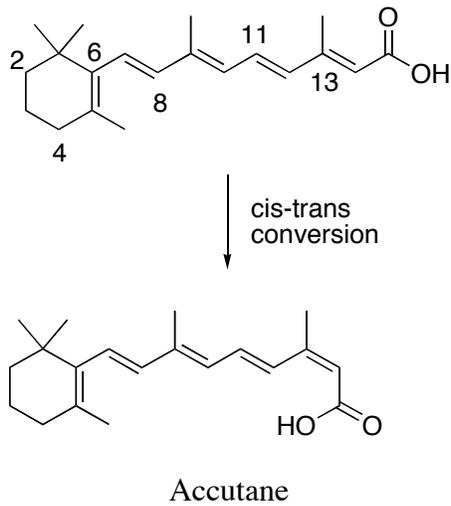


In the eye, retinal reacts with a protein called opsin to give rhodopsin, the visual pigment that is the actual light sensitive substance. Isomerization of the C11-C12 bond causes conformational change in the 3D structure of the protein that results in nerve impulses being sent to the brain which are perceived as vision.

Further oxidation of the aldehyde to a carboxylic acid in retinal yields retinoic acid, a chemical messenger in the body which provides signals for fetal development.

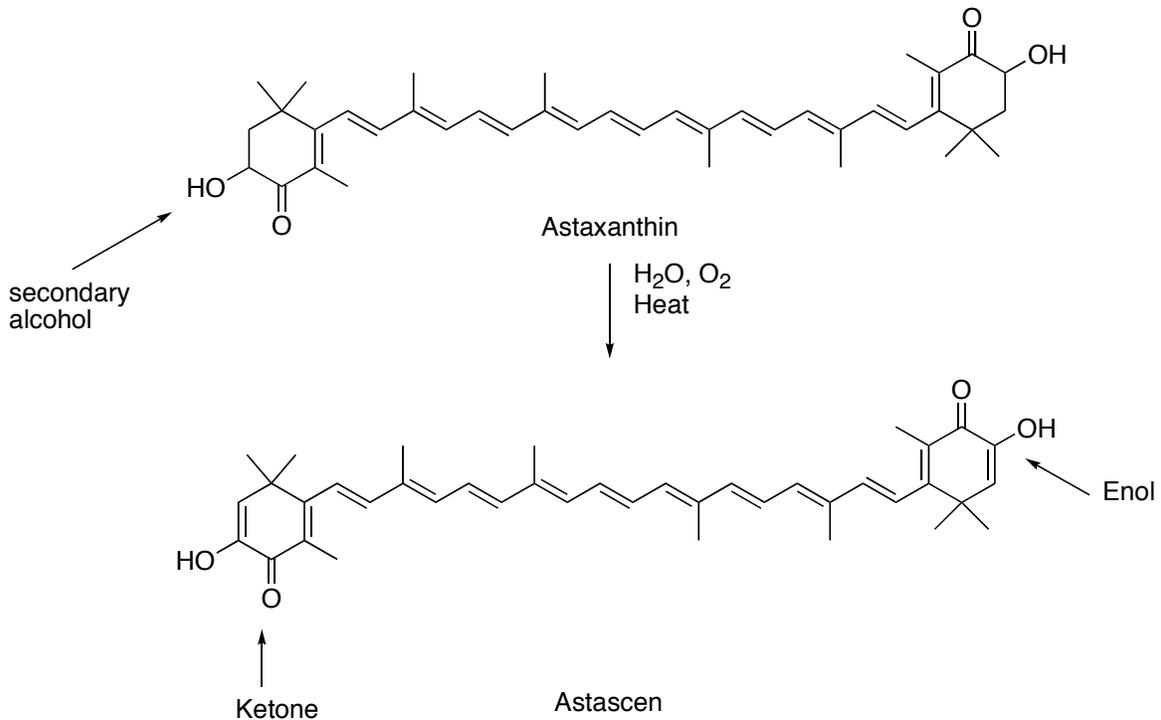


Conversion of the C13 double bond in retinoic acid to the cis conformation gives the drug Accutane, which is an anti-acne drug. It has teratogenic properties (i.e. can cause malformations and other birth defects)



Xanthophylls

Xanthophylls are oxygenated carotene molecules. In the below example, astaxanthin, a blue-green pigment in algae, is converted to astascene with the addition of heat, water and oxygen. Astascene is red in colour and contains an enol functional group. Crustaceans (lobsters) eat algae in their natural habitat and therefore ingest astaxanthin. When a lobster is cooked, it turns a bright red colour, which is mainly due to the formation of astascene.

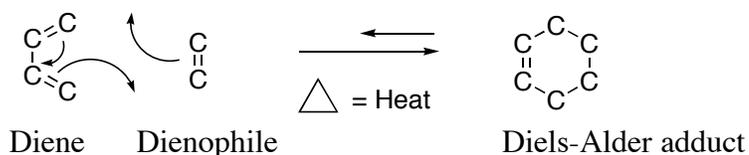


Hemoglobin (red colour in blood) and chlorophyll A (green colour in plants) are two more examples of conjugated molecules that absorb light and serve critical functions.

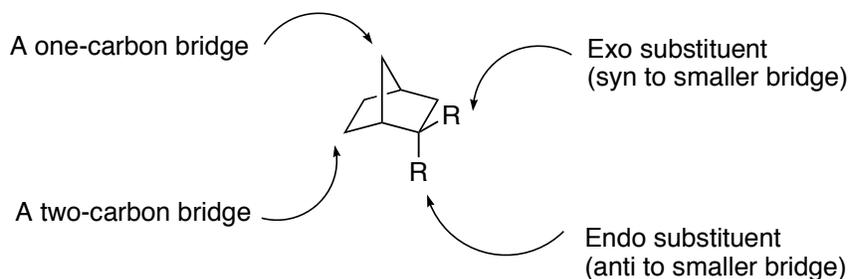
Diels-Alder Reaction

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.

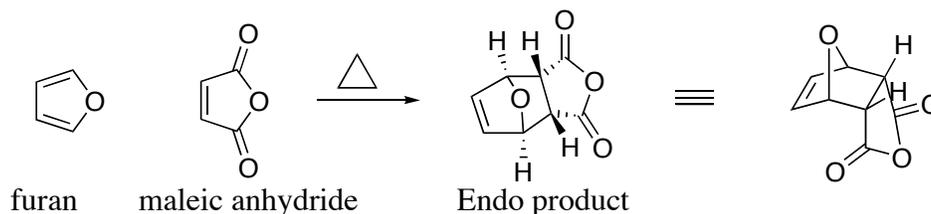
The Diels-Alder reaction consists of a conjugated diene in cisoid form reacting an alkene (dienophile). When heated, it forms two new carbon-carbon bonds in a single step and forms a cyclic molecule (a cyclohexene). The reaction is theoretically reversible but the stability of the product drives the 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.



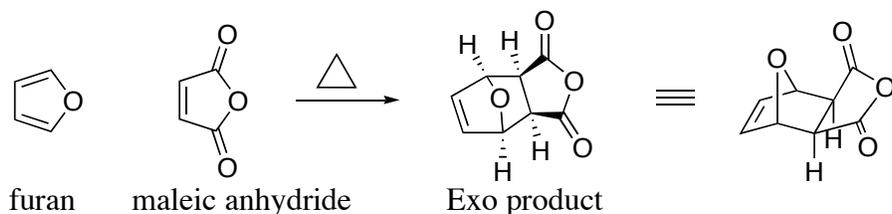
The mechanism is **concerted**, which means that all the bonds form and break at the same time (an S_N2 reaction is also concerted). As a result, the reaction is also **stereospecific**, which means that the stereochemistry of the starting materials determines the stereochemistry of the products. Starting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

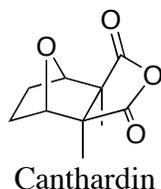


The exo product, which is not favored and not formed, would arise in the following manner.



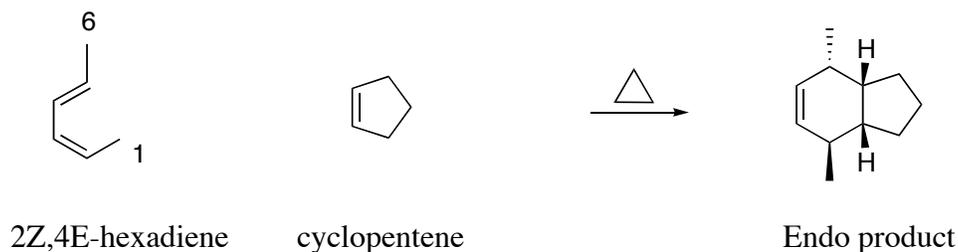
Example of possible Diels-Alder adducts in Nature

The Spanish fly (*Cantharis vesicatoria*) produces the molecule cantharidin, which contains an exo Diels-Alder product with an anhydride functional group.



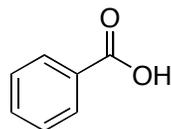
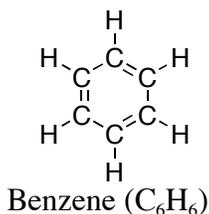
Example of Predicting Stereochemistry

The following example uses 2Z, 4E-hexadiene (diene) and cyclopentene (dienophile) to produce an endo product. As shown before with the furan and maleic anhydride reaction, the stereochemistry of the endo product can be predicted. The methyl group at C6 is similar to that of the H in furan and therefore will be pointing down. The position of the C1 methyl group is similar to that of the oxygen in furan and therefore will point up in the endo product (by convention drawn away from (outside of) the cyclohexene ring).



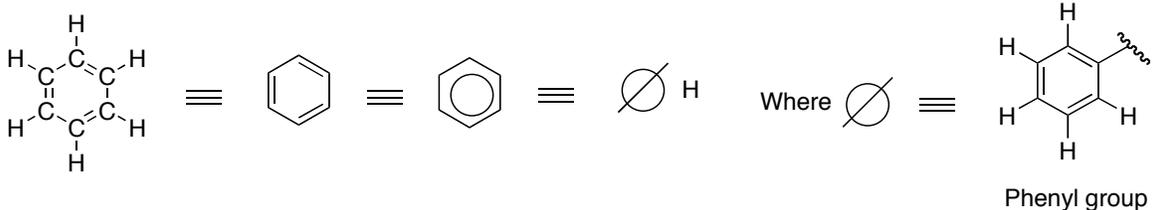
Aromatic Compounds

Benzene was first isolated in 1825 by Michael Faraday. Its structure was later determined by Joseph Loschmidt and F. August Kekule to contain a cyclic, 6-membered ring containing alternating single and double bonds with 6 π -electrons. The name benzene come from benzoic acid.

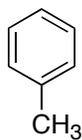


Benzoic acid

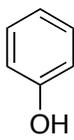
There are a few ways of drawing benzene. It is seen as alternating double and single bonds, a central circle or as the Greek symbol ϕ (phi).



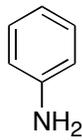
Structures to Know



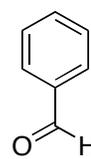
Toluene



Phenol



Aniline



Benzaldehyde