

Some Stereochemical Nomenclature

Auxiliary

A chiral group that is temporarily incorporated in a molecule to achieve control of stereochemistry. Must be easily added and removed.

Chiral Pool

This is the collective name given to all the chiral molecules that are available cheaply as a single enantiomer. Most are produced as a single enantiomer by Nature, e.g. amino acids, sugars.

D/L stereochemistry

Absolute configurations assigned to a molecule through experimental chemical correlation with the configuration of D/L glyceraldehyde. Often applied to amino acids and sugars, although (R) and (S) are preferred.

Diastereomer/diastereoisomer

Stereoisomers with two or more chiral elements (stereogenic centres, chiral axes etc.) and where the molecules are not mirror images of one another, for example, d-erythrose and d-threose; often contracted to diastereomer.

Enantiomer

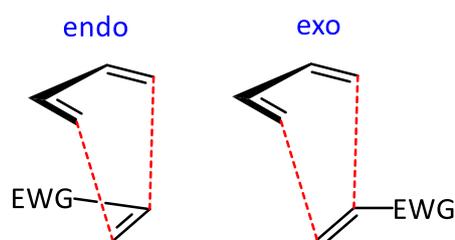
A stereoisomer that is non-superimposable on its mirror image.

Enantiomeric excess (ee)

Percentage by which one enantiomer is in excess relative to the other. Frequently used as a measure of enantiopurity. $ee = (E_1 - E_2) / (E_1 + E_2)$ where E_1 is the amount of the major enantiomer.

endo and exo

[In relation to Diels-Alder reactions] The geometry of approach where the electron-withdrawing substituent on the dienophile is oriented underneath the diene (*endo*) or out into space (*exo*). The resulting products are often referred to as the *endo* and *exo* products

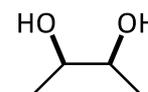


Epimer/epimerization

An epimer is the stereoisomer obtained when a single stereogenic centre is inverted in a molecule. Where this is the sole stereoisomer this process leads to the opposite enantiomer, where there are multiple stereogenic centres in the molecule this leads to another diastereoisomer of the molecule.

meso

The name given to an achiral member of a set of diastereoisomers which includes one or more chiral members. The presence of a symmetry element renders it achiral, e.g.



Optical activity/isomer/purity

Optical activity (or **optical rotation**) is the experimentally-observed rotation of the plane of plane-polarized light passing through a sample. Frequently given as $[\alpha]_D^{20}$. An **optical isomer** is a synonym for an enantiomer. **Optical purity** is the ratio of the optical rotation given by a particular sample as a

percentage of the optical rotation of a pure enantiomer of the sample, expressed as a percentage. It gives the same value as *ee*.

Prochiral

A prochiral molecule is an achiral molecule where one chemical step (e.g. nucleophilic addition to an aldehyde) will yield a chiral molecule.

Racemic

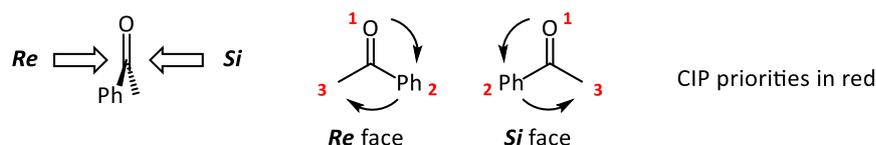
A chiral molecule present as a 1:1 mixture of both enantiomers. Often denoted (\pm). A racemic mixture exhibits an optical rotation of zero.

Racemization

This is the process of converting one enantiomer of a compound into a 50:50 mixture of both enantiomers.

Re and *Si*

These labels are closely linked to the (*R*) and (*S*) stereochemical descriptors used to denote stereogenic centres. They relate to the faces of a prochiral (flat) molecule. If the atom has three groups attached, approaching from the *Re* face will orient the groups in a clockwise order according to the Cahn-Ingold-Prelog (CIP) rules, and anticlockwise from the *Si* face.



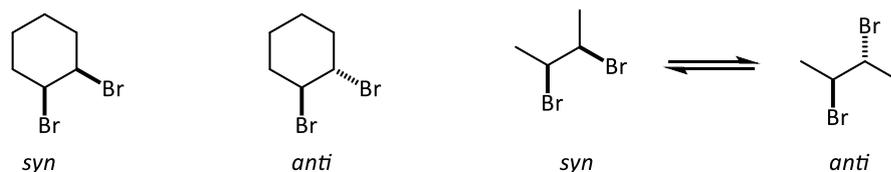
The result is that attack from the *Re* face leads to the (*R*) product, as long as the nucleophile doesn't have a higher CIP priority than the groups already present.

Scalemic

A scalemic mixture of enantiomers is a non-racemic mixture, where one enantiomer is in excess but both are present to some extent. Quite an old-fashioned and rarely used term.

Syn/anti

These prefixes indicate whether substituents are on the same (*syn*) or opposite (*anti*) sides of a molecule. Often used in cyclic molecules, where their meaning is unambiguous. When used for acyclic molecules, these must be accompanied by a drawing of the molecule (since *syn* and *anti* could be exchanged by simple bond rotation).



Torquoselectivity

Defined as the preference for the inward or outward rotation of substituents during an electrocyclic ring opening. I will use more generally to refer to the absolute direction of rotation of groups in electrocyclic ring-closure reactions, e.g. torquoselectivity would be a preference for one of the below reactions over the other, both of which are thermally Woodward-Hoffmann allowed:

