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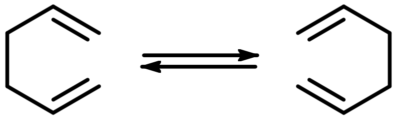
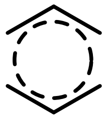
sigmatropic rearrangement

A molecular rearrangement that involves both the creation of a new σ-bond between atoms previously not directly linked and the breaking of an existing σ-bond. There is normally a concurrent relocation of π-bonds in the molecule concerned, but the total number of π- and σ- bonds does not change. The term was originally restricted to intramolecular pericyclic reactions, and many authors use it with this connotation. It is, however, also applied in a more general, purely structural, sense. If such reactions are intramolecular, their transition state may be visualized as an association of two fragments connected at their termini by two partial σ-bonds, one being broken and the other being formed as, for example, the two allyl fragments in (a'). Considering only atoms within the (real or hypothetical) cyclic array undergoing reorganization, if the numbers of these in the two fragments are designated i and j, then the rearrangement is said to be a sigmatropic change of order $[i, j]$ (conventionally $[i] \le [j]$). Thus the rearrangement (a) is of order [3,3], whilst reaction (b) is a [1,5]sigmatropic shift of hydrogen. (N.B. By convention square brackets [...] here refer to numbers of atoms, in contrast with current usage in the context of cycloaddition.)

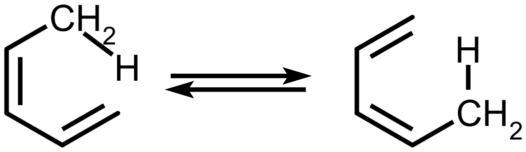
(a)



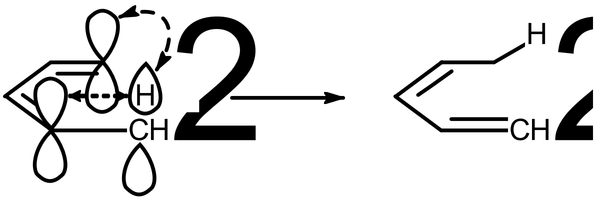
(a')



(b)



The descriptors a and s (antarafacial and suprafacial) may also be annexed to the numbers i and j; (b) is then described as a [1s,5s] sigmatropic rearrangement, since it is suprafacial with respect both to the hydrogen atom and to the pentadienyl system:



The prefix 'homo' (meaning one extra atom, interrupting conjugation — *cf.* 'homoaromaticity') has frequently been applied to sigmatropic rearrangements, but is misleading.

See also: cycloaddition, tautomerism

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Source:
PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1163