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Molecular rearrangements in which a σ -bonded atom or group, flanked by one or more n -electron systems, shifts to a new location with a corresponding reorganization of the n -bonds are called sigmatropic reactions. The total number of σ -bonds and n -bonds remain unchanged. These rearrangements are described by two numbers set in brackets, which refer to the relative distance (in atoms) each end of the σ -bond has moved, as illustrated by the first equation in the diagram below. The most common atom to undergo sigmatropic shifts is hydrogen or one of its isotopes. The second equation in the diagram shows a facile [1,5] hydrogen shift which converts a relatively unstable allene system into a conjugated triene. Note that this rearrangement, which involves the relocation of three pairs of bonding electrons, may be described by three curved arrows. These reactions are particularly informative in that [1,3] hydrogen shifts are not observed. The reactant in the first equation is a deuterium labeled 1,3,5-cyclooctatriene. On heating, this compound equilibrates with its 1,3,6-triene isomer, and the two deuterium atoms are scrambled among the four locations noted. If [1,3] or [1,7] hydrogen shifts were taking place, the deuterium atoms would be distributed equally among all eight carbon atoms. On prolonged heating, or at higher temperatures these cyclooctatrienes undergo electrocyclic ring opening to 1,3,5,7-octatetraene and reclosure to vinyl-1,3-cyclohexadienes. The second example shows another [1,5] hydrogen shift, from the proximal methyl group to the carbonyl oxygen atom. The resulting dienol rapidly exchanges OH for OD before the [1,5] shift reverses. In this manner the reactive methyl is soon converted to CD₃. Since hydrogens alpha to a carbonyl group are known to undergo acid or base catalyzed exchange by way of enol intermediates, we might expect the α -CH₂ group to exchange as well. However, if care is taken to remove potential acid or base catalysts, the thermal [1,3] shift necessary for the exchange is found to be very slow. The [3,3] sigmatropic rearrangement of 1,5-dienes or allyl vinyl ethers, known respectively as the Cope and Claisen rearrangements, are among the most commonly used sigmatropic reactions. Three examples of the Cope rearrangement are shown in the following diagram. Reactions 1 and 2 (top row) demonstrate the stereospecificity of this reaction. The light blue σ -bond joins two allyl groups, oriented so their ends are near each other. Since each allyl segment is the locus of a [1,3] shift, the overall reaction is classified as a [3,3] rearrangement. The three pink colored curved arrows describe the redistribution of three bonding electron pairs in the course of this reversible rearrangement. The diene reactant in the third reaction is drawn in an extended conformation. This molecule must assume a coiled conformation (as above) before the [3,3] rearrangement can take place. The product of this rearrangement is an enol which immediately tautomerizes to its keto form. Such variants are termed the oxy-Cope rearrangement, and are useful because the reverse rearrangement is blocked by rapid ketonization. If the hydroxyl substituent is converted to an alkoxide salt, the activation energy of the rearrangement is lowered significantly. The degenerate or self-replicating Cope rearrangement has been a fascinating subject of research. For examples . Two examples of the Claisen Rearrangement may be seen by clicking on the above diagram. Reaction 4 is the classic rearrangement of an allyl phenyl ether to an ortho-allyl phenol. The methyl substituent on the allyl moiety serves to demonstrate the bonding shift at that site. The initial cyclohexadienone product immediately tautomerizes to a phenol, regaining the stability of the aromatic ring. Reaction 5 is an aliphatic analog in which a vinyl group replaces the aromatic ring. In both cases three pairs of bonding electrons undergo a reorganization. By clicking on the above diagram a second time two examples of [2,3] sigmatropic rearrangements will be displayed. The allylic sulfoxide in reaction 6 rearranges reversibly to a less stable sulfenate ester. The weak S-O bond may be reductively cleaved by trimethyl phosphite to an allylic alcohol and a thiol (not shown). Reaction 7 shows a similar rearrangement of a sulfur ylide to a cyclic sulfide. The [2,3]-Wittig rearrangement is yet another example. Contributors A 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 n -bonds in the molecule concerned, but the total number of n - and σ -bonds does not change. The term was originally restricted to 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 , their may be visualized as an 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 $\backslash(i)$ and $\backslash(j)$, then the is said to be a sigmatropic change of order $\backslash(i)$, $\backslash(j)$ (conventionally $\backslash(\text{}i)\text{}j$ or $\backslash(\text{}i)\text{}j$). Thus the (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 ) S05660-1.png S05660-2.png The descriptors a and s and may also be annexed to the numbers $\backslash(i)$ and $\backslash(j)$. (b) is then described as a [1s,5s] sigmatropic , since it is with respect both to the hydrogen atom and to the pentadienyl system: S05660-3.png The prefix '' (meaning one extra atom, interrupting — cf. ) has frequently been applied to sigmatropic rearrangements, but is misleading. See also: cycloaddition, tautomerismSource: PAC, 1994, 66, 1077. (Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)) on page 1163 [Terms] [Paper] In [1, n] sigmatropic rearrangements, a residue (mostly a hydrogen atom) migrates from one end of a n system to the other. The nomenclature of [1, n] sigmatropic rearrangements derives from the position of the residue R before and after the reaction. For example, a [1,3] sigmatropic rearrangement describes a reaction in which the residue migrates from position 1 to position 3. During the migration of the residue in [1, n] sigmatropic reactions shown above, one end of the σ bond remains attached to the rest of the molecule. However, there are cases in [n , m] sigmatropic rearrangements where both termini of the σ bond move: Page 2 In principle, there are two stereochemical pathways by which the hydrogen atom can migrate. In suprafacial rearrangements the hydrogen atom moves along the top or bottom of the n -plane while in antarafacial mode the hydrogen moves across the n -system. 3D Animation of a suprafacial [1,5] sigmatropic H-migration 3D Animation of an antarafacial [1,7] sigmatropic H-migration Suprafacial sigmatropic rearrangements proceed through Hückel aromatic transition states and antarafacial rearrangements via Möbius transition states. Because of the strong deformation required of the conjugated system Möbius topology can only be realized in large molecules. During the migration of organic residues inversion at the migrating carbon atom can take place. In this case the transition state also displays Möbius topology but it is easier to realize geometrically in smaller systems than it is during antarafacial migration. 3D Animation of alkyl migration with retention 3D Animation of alkyl migration with inversion General rules. Stereochemical rules for [1, n] sigmatropic reactions 4n+2 Electrons: supra and retention, respectively 4n Electrons: antara and inversion, respectivelyThe opposite behavior is observed in photochemical reactions. Page 3 Basically, [n , m] sigmatropic rearrangements can proceed through a chair or boat transition state. Only the chair transition state has been observed experimentally though both are suprafacial and are allowed in 4n+2 electron systems. 2D Animation of the Cope rearrangement 3D Animation of the Cope rearrangement Large substituents similar to their behavior in chair conformations of cyclohexane rings prefer an equatorial configuration in the transition state of [3,3] sigmatropic reactions. Heating 5,5,3,4-dimethyl-1,5-hexadiene to approximately 200°C yields in 90% a product derived from a chair transition state with equatorial methyl groups. The product arising from a diaxial conformation is formed in only 10% yield. Obviously, the reaction does not proceed through the boat transition state. Page 4 2D Animation of [1,3] sigmatropic rearrangement with inversion Photochemical [1,3] hydrogen migrations are allowed suprafacially. Anionic 1,2 rearrangements such as the Wittig or Stevens rearrangement formally can also be considered 4 electron [1,2] sigmatropic processes: Because of the small size of the system, the rearrangement can neither proceed through an antarafacial allowed process nor with inversion. However, since a geometrically possible suprafacial rearrangement is forbidden, these reactions are two step processes. Page 5 2D Animation of the sigmatropic hydrogen shift in cyclopentadiene. The situation becomes more complicated when different conformers of the same compound react. In order to test the Woodward-Hoffmann rules, Roth synthesized a chiral 1,3-pentadiene system containing different substituents: Only compounds with (E) configuration at the terminal double bond and (S) stereochemistry at the terminal sp³ stereocenter together with the corresponding (Z),(R)-isomer were found. Antarafacial hydrogen shift was not observed. [1,5] sigmatropic migrations of alkyl residues (suprafacial, retention) are relatively rare. 2D Animation of [1,5] sigmatropic alkyl migration with retention It is known that 7,7-substituted cycloheptatrienes isomerize via a cascade of electrocyclic and [1,5] sigmatropic rearrangements. Page 6 In 1,5-cyclohexadiene, the parent system for [3,3] sigmatropic rearrangements, reaction takes place at 300°C with an activation energy barrier of approximately 34 kcal/mol. These rearrangements of 1,5-diene systems, discovered first by Hurd and later by Cope, are generally called Cope rearrangements. The oxy-Cope rearrangement takes place at lower temperatures. Formation of a resonance stabilized enolate anion is the driving force in the reaction. The synthetically more important Ireland-Claisen rearrangement takes place at even milder temperatures to yield the highly stable carboxylate anion.[3,3] Sigmatropic rearrangement in which one C-atom in the 1,5-diene is substituted by an O-atom are called Claisen rearrangements.Loss of aromaticity initially leads to a ketone (quinone) which spontaneously tautomerizes to the corresponding aromatic phenol. The key step in the Fischer indole synthesis is a "nitrogen variation" of the Claisen rearrangement[2,3] Sigmatropic rearrangements can be observed in sulfur and nitrogen ylids.Deprotonation of allylic ethers with strong bases leads to [2,3] Wittig rearrangements.The driving force behind most [2,3] sigmatropic rearrangements is the transformation of an unstable carbanion into a stable product. Utilizing the reduction of ring strain helps to increase the thermodynamic driving force in [3,3] sigmatropic rearrangements and to lower the activation energy. The activation energy barrier is reduced from 34 kcal/mol to 19 kcal/mol if the single bond to be broken in the 1,5-cyclohexadiene system is part of a three-membered ring. The resulting product of the rearrangement is a 7-membered ring.When bridging the two terminal double bonds with a CH₂ -group (homotropylidene) the reaction becomes tautomeric, i.e., product and educt are indistinguishable as in the parent system 1,5-hexadiene. Bridging the two CH₂ groups with an additional double bond affords the especially interesting bullvalene. This molecule contains a three-fold axis of symmetry and three symmetrical and equivalent Cope systems.Each of these 1,5-diene units can undergo a Cope rearrangement again yielding bullvalene. In all, there are more than 1.2 million tautomeric forms possible. At 100°C the reaction is so fast that only one peak is being observed for all H atoms in 1H-NMR. Structures of this type are called fluxional. Page 7



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