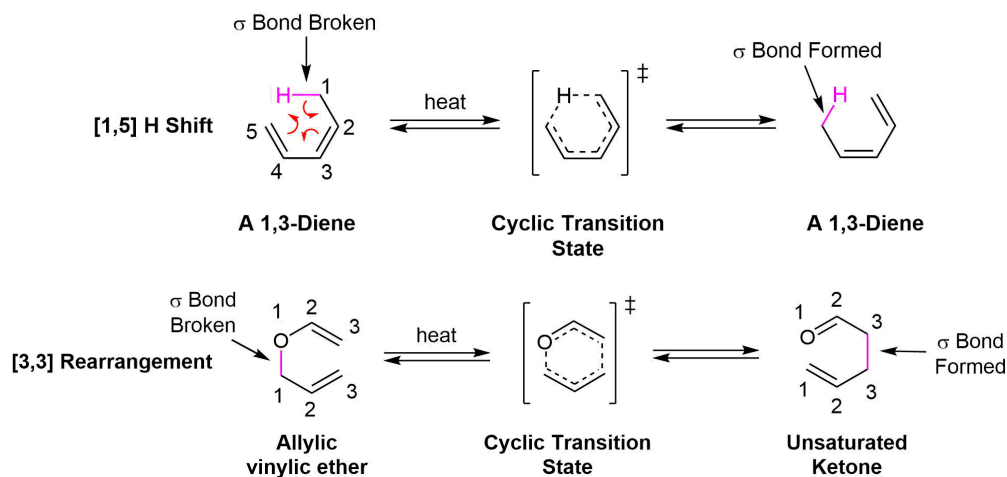


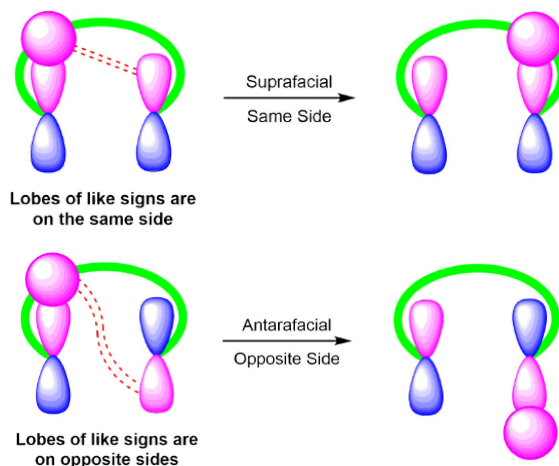
29.7: SIGMATROPIC REARRANGEMENTS

Molecular rearrangements in which a σ -bonded atom or group, flanked by one or more π -electron systems, shifts to a new location with a corresponding reorganization of the π -bonds are called **sigmatropic reactions**. The reactant and product have the same number and type of bonds, just different bond locations. These rearrangements are described by two numbers set in brackets, which refer to the position of the sigma bond in the reactant that is broken compared to the position of the sigma bond in the product that is formed. The most common examples include hydrogen shifts across a diene system (called a [1,5] H shift) and rearrangements of double allyl-type systems (called [3,3] rearrangements).

As shown in the examples below, the atoms on the sigma bond in the reactant that is broken (magenta bond) are both labeled "1", and the numbering of atoms on each side of that sigma bond continue until the atoms connected by the new sigma bond in the product (magenta) are reached. Thus, the H shift is [1,5] because the key sigma bond in both the reactant and product is to the H while the H moves from C-1 to C-5. For the [3,3] rearrangement, the broken sigma bond migrates across two allyl-type systems and forms between atoms "3" and "3" in the product. This particular example is a Claisen rearrangement since an allyl vinyl ether is transformed into a 1,4-carbonyl alkene.



The migration of a group during a sigmatropic rearrangement is controlled by the orbital symmetries of the alkenes involved. Sigmatropic rearrangements can occur on one face of the molecule (think top or bottom, like a syn addition to an alkene) which is called a **suprafacial** reaction or from one face to the other (think from top to bottom or vice versa, like an anti addition to an alkene) which is called **antarafacial**. We will explore this idea further in the next section.



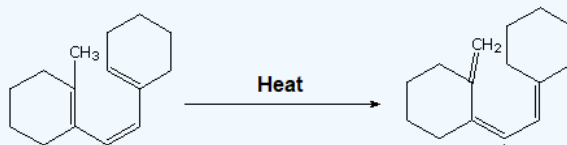
GENERALIZED STATEMENT OF WOODWARD-HOFFMANN RULES FOR SIGMATROPIC REARRANGEMENTS

Suprafacial and antarafacial sigmatropic rearrangements are considered symmetry-allowed by the Woodward-Hoffmann rules. However, suprafacial reactions are much more common. Note! These rules for sigmatropic rearrangements are the same as those given for cycloaddition reactions in **Section 30-3**.

| Number of Double Bonds | Thermal | Photochemical |
|------------------------|--------------|---------------|
| Odd | Suprafacial | Antarafacial |
| Even | Antarafacial | Suprafacial |

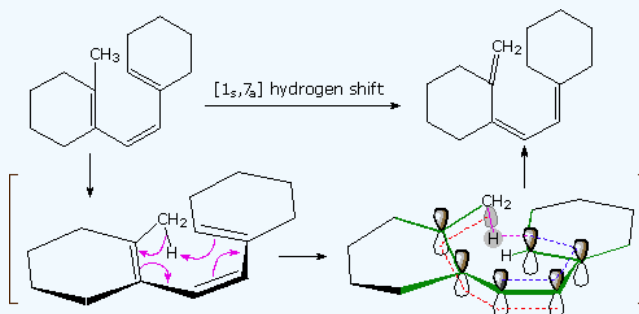
? EXERCISE 29.7.1

For the following sigmatropic hydrogen shift please use braided number to describe the reaction. Predict if the hydrogen shift will be suprafacial and antarafacial. Lastly, draw in arrows to describe the mechanism for this reaction.



Answer

An example of an $[1,7]$ hydrogen shift is shown in the following diagram. The conjugated alkene has three double bonds, which is an odd number, and the reaction is occurring under thermal conditions. This means the reaction is predicted to be suprafacial. The conjugated triene assumes a nearly planar coiled conformation in which a methyl hydrogen is oriented just above the end carbon atom of the last double bond. A $[1_s, 7_a]$ sigmatropic hydrogen shift may then take place, as described by the four curved arrows. With reference to the approximate plane of this π -electron system (defined by the green bonds), the hydrogen atom departs from the bottom face and bonds to the top face, so the transfer is antarafacial.



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