

Continue



Electrocyclic reactions pdf

Electrocyclic reactions. Electrocyclic reactions pdf notes. Electrocyclic reactions examples. Types of electrocyclic reactions pdf.

Electrocyclic Reactions and 4-Membered Rings: Conrotatory and Disrotatory Ring Opening and Closure October 27th, 2022 In this article, we delve into electrocyclic ring-opening and ring-closing processes involving systems with four pi electrons ("4n" systems). The outcome of these reactions under "thermal" conditions (heating without UV light) differs from those obtained under "photochemical" conditions (irradiation with UV light), as the stereochemistry below demonstrates. This difference arises from a change in orbital symmetry, leading to distinct end-carbon rotations during ring-opening and closure. We will examine the rules for systems with six pi electrons ("6n") and higher in a future post. For now, let's focus on electrocyclic reactions in 4-membered rings. 1. Electrocyclic Ring-Opening of Cyclobutene to Give Butadiene In 1905, chemists Richard Willstätter and Wolfgang von Schmaedel accidentally discovered the electrocyclic ring-opening reaction while performing a routine elimination reaction at the University of Munich. The expected product was cyclobutene, but they also isolated considerable amounts of 1,3-butadiene. This unexpected result remained unexplained until today. Willstätter went on to synthesize cyclooctatetraene and later won the Nobel Prize in Chemistry for determining the structure of chlorophyll and other plant pigments. Over time, the reaction was studied further, verifying that heating cyclobutene indeed forms 1,3-butadiene. Interestingly, however, heating cyclobutane does not lead to any ring-opening reaction. 2. Electrocyclic Ring-Closure of 1,3-Butadiene to Give Cyclobutene In time, it was also found that 1,3-butadiene is capable of undergoing the converse reaction: a ring-closure to give cyclobutene. Due to ring strain, this closure is usually unfavorable, but certain substituted dienes can be coaxed into closing the ring. More details on ring strain and its calculation will follow in a future post. cyclobutene is more reactive than cyclobutane with a higher energy requirement of about 29.6 kcal/mol compared to 26.3 kcal/mol for cyclobutane. This implies that both cyclobutene and 1,3-butadiene can interconvert through a common transition state, leading to an equilibrium at high temperatures. Understanding the bonds formed and broken during these reactions is crucial. In the forward direction, a C-C pi bond and a C-C sigma bond break, while two new C-C pi bonds form. In the reverse direction, two C-C pi bonds break, and a new C-C pi bond and a C-C sigma bond are formed. Both directions share the same transition state. Electrocyclic ring-opening reactions are stereospecific, meaning that starting materials with different configurations always yield stereoisomeric products. For example, heating cis-3,4-dimethylcyclobutene produces a trans, cis diene, while heating trans-3,4-dimethylcyclobutene produces a trans, trans diene. These reactions are predictable due to the Woodward-Hoffmann rules and the conservation of orbital symmetry. Analyzing the frontier orbitals, specifically the highest-occupied molecular orbital (HOMO), helps predict the product's configuration. In thermal electrocyclic reactions, such as the reaction involving 1,3-butadiene, understanding the HOMO is crucial. The HOMO of butadiene has a single node between C-2 and C-3, which affects the outcome of the reaction. Cyclobutene undergoes electrocyclic ring opening where a sigma bond is formed between C-1 and C-4 termini. The p orbitals on these carbons, which were previously involved in pi bonds with C2 and C3 respectively, contribute to the formation of this new sigma bond through constructive overlap when they rotate in the same direction, either both clockwise or counter-clockwise. This rotation is known as conrotatory motion. When both terminal carbons rotate in the same way during electrocyclic ring opening, it results in a specific stereochemistry for any substituents attached to them. This concept is crucial for predicting the products of 4pi electrocyclic reactions. For example, considering the reaction pathway from cis-3,4-dimethylcyclobutene or trans-3,4-dimethylcyclobutene leads to the formation of a diene with either cis-, trans- or trans, trans stereochemistry, respectively. The process can also be reversed, where a diene undergoes conrotatory ring closure to form cyclobutene, which is typically unfavorable due to ring strain unless it relieves strain as in the case of a cyclic diene containing a trans double bond. Electrocyclic reactions can also occur under photochemical conditions using light (hv), particularly UV light for dienes. However, unlike thermal conditions, photochemical pathways do not follow the same conrotatory motion rules and thus yield different stereochemistry products. Under "thermal" conditions, cis-3,4-dimethylcyclobutene undergoes ring-opening to form trans,trans-diene. However, under "photochemical" conditions, such as those induced by UV light, the product formed is cis-trans-. This phenomenon can be attributed to the promotion of an electron from the highest-occupied molecular orbital (HOMO) to the lowest-energy unoccupied molecular orbital (LUMO) upon exposure to UV radiation. In electrocyclic reactions, terminal carbons with substituents exhibit conrotatory behavior when rotating in both clockwise or counterclockwise directions under certain conditions. Conversely, photochemical conditions like UV light prompt a disrotatory fashion where one carbon rotates clockwise and the other counterclockwise. This principle is essential for understanding larger pi systems, which will be discussed further in subsequent posts. The concept of electrocyclic reactions was initially understood through experimental observations, as evidenced by Woodward and Hoffmann's work on orbital symmetry conservation in the 1960s. Key definitions include stereospecific reactions, where starting materials differing only in configuration yield stereoisomeric products, and conrotatory and disrotatory motions, which are fundamental to electrocyclic reactions. The presence of a trans double bond in the ring makes ring closure more favorable, leading to strained structures. Theoretical studies have investigated alternate electrocyclic pathways and substituent effects on rates and stereoselectivities. A classic study by Brauman and Archie Jr. explored the stereochemistry of electrocyclic ring opening. More recent research has focused on torqueselectivity, where one rotation mode is favored over the other. Woodward and Hoffmann's paper defined key terms in electrocyclic reactions, including conrotatory and disrotatory modes. The strain energy of cyclobutene is notable for its relatively high value compared to other small ring hydrocarbons. Research has also explored the photochemistry of cyclobutene, including examples of photochemical ring-opening of several cyclobutenes.