**Pericyclic reactions in organic chemistry pdf**
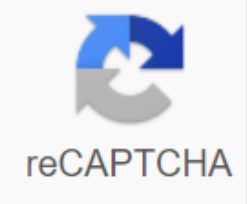
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There are many reactions in organic chemistry that go through cyclical transient states. They can be classified as a whole as pericyclic reactions. An important and familiar example is the reaction of Dils-Alder, in which the conjugated dien cycloadd to alken or alkin: This reaction was described earlier (section 13-3A) and is an example of cycloaddition. Such reactions occur thermally (just by heating reactionary means) and appear to be fully aligned. By this we mean that the reactionary are converted into products in one step, without involving the formation of intermediate reactions. The main evidence of coherence of cycloaddiums is the fact that they are very stereospecific and are associated with suprafacial addition of both components. The configuration of substitutions in diena and dinophila persists in the aduc: unlike cycloaddition, thermal cycloadditions are rarely observed, and when they are observed, they are not stereospecific and are obviously a step-by-step reaction (see section 21-11): Why do cycloadditions differ from each other? A simple molecular orbital theory provides an elegant explanation for this difference, based on the 4n and 2 rule described in section 21-9. To understand this, we need to take a closer look at what how dual-bond orbits interact in agreed-upon mechanisms of addition by suprafacial overlap, as in No(36) and No (37): Mixing six overlapping atomic orbits (36) provides a set of six benzo-like molecular orbits (figure 21-5) and, for (37), a set of four-cyclic orbits (No.9). Rule 4n 2 applies to such systems, and a transitional state such as (36), which has six electrons, can therefore be much more favorable than one, for example, (37), which has four electrons. From this we can conclude that the agreed reactions of cycloaddition involving electrons, in which electrons (4n) (4n) (4n) tend to be more favorable than electrons. Indeed, transitional states such as No (37) tend to be less favourable than transitional states for the formation of biradica or ions (section 21-11). There is a way around the rule 4n 2 , which is not very important for substances similar to benzene, but is very important for cycloaddia reactions. Let's see how this works for cyclical conjugated polyenes. From the molecular-orbital diagrams of the drawings 21-5, 21-7, 21-9 and 21-14, you will see that the molecular orbit with the least energy has no nodes (phase changes). The model of such an orbit, commonly called the Hyukel orbital station, can be built by attaching to the ends of the tape or a strip of parallel orbits represented on the left side of Figure 21-15. However, one could join orbits by making one turn in the strip which will give the orbit with the least energy with one knot, as on the right side of the picture 21-15. The band with one such turn is called the Miabius strip and has a topological property to have only one side. Figure 21-15: Normal (Heokel) and Miabius orbit rings. To clarify the difference between the two rings, visualize a strip of black-red writing tape, black, representing phase q (I) and red orbital phase. Now join the ends together without, or with, one twist in the lane. There will be a node (left) or one node (right). If we now calculate the orbital energies for the Mebius orbital stations, as we did in the normal orbits of Hukel in figure 21-13, we will get the results shown in figure 21-16. From this, we see that the situation is being favored and (4n ) is unfavorable. While the energies of molecular orbital stations in the Jukel location can be obtained by inserting the landfill into a circle with angular downwards (section 21-9A), in the location of TheUbius orbital energies are derived from the landfill, inscribed sideways downwards. Figure 21-16: Calculated (pi)-molecular orbital energies for overlapping orbits in The Mebius cyclical systems. If you compare the orbital energies of the cycle systems Hjukel and Meubius (figures 21-13 and 21-16), you can see that the Hukel systems have only one low-energy MO, while the Moebius systems have two. The Jukel systems have an odd amount of gluing orbital (which, when full, place 2, 6, 10, 14, or (4n) electrons) and Mobius systems have an even amount of gluing orbital (which, when full, hold 4, 8, 12, or (4n) electrons). Molecular orbits of The Woman have zero or even zero (see, for example, benzene, figure 21-5); Mebius' molecular orbits are not shown, but they have one or the odd number of nodes. The relevance of all this may seem weak, especially because there is no known example of a simple cyclical polyene with the Mobius system. However, the location of Mobius has to do with cycloaddition, because we can imagine alkens, alcanions, alcanions and so on, approaching each other to produce the transient states of Mobius when electrons are involved. For example, consider two ethine molecules that we showed earlier, breaking the rule 4n 2, passing the cycloaddition through the transitional state presented (37 euros). There is an alternative transitional state, No (38), in which four orbits (p) come together in the Mebius mechanism (with one node for minimal energy). To reach this arrangement, the molecules of the ethylene approach each other roughly in perpendicular planes, so that the orbits (PP) overlap suprafacially in one etine and antarafatracially in another, as shown in (38): This pathway is electronic however, the sterile intervention between groups tied to a double bond is likely to be serious. Such repulsion can be relieved if there are no groups sticking side by side at one end of the double bond, as with the central carbon of 1.2-CH_2 CH_2 CH_2..... These substances often undergo cycloaddition quite easily (section 13-3D), and it is likely that these are consistent additions that occur along the Moebius route. The much less intense transitional state of Moebius can be formed from two molecules s-cis 1.3-butadien. When the 1.3-butadien heats itself, a few percent of the 1.5-cyclooctadien is formed, but it is not known for sure whether the mechanism is that shown: The basic reaction of Diels-Alder 4 and 2 cycloaddition, with butadiene acts as a diene and as a dienophile: Much of what we said about electronic factors controlling whether the cycloaddition reaction could be coordinated or not was originally formulated by American chemists R. B. Woodward and R. Hoffmann a few years ago in terms of what has come to be called the principles of orbital symmetry, or the rules of Woodward-Hoffman. The arguments for orbital symmetry are too complex for this book, and instead we will use the electronic rule 4n for normal arrangements of The Roundel systems and the rule of electrons for the mechanisms of Mobius. This is a particularly simple approach among the few phenomena available to account, to which Woodward and Hoffman have paid particular attention and explained what they call the preservation of orbital symmetry. So when cis-3.4-dimethylcyclobuten heats up, it gives only one of three possible cis-trans isomers 2.4-hexadien, namely, cis,trans-2,4-hexadiene: We can see how this can happen if, as the ring opens, the ends of the diene twist in the same direction (curvearrowright) or curvearrowleft curvearrowleft (curvearrowleft) as indicated in the equation. You will notice that in this particular case, if the conrotation occurs to the left, rather than the right, the same end results of the product: The conrotator movement of the groups is typical for the thermal openings of the cyclobuten ring and other rings involving electrons. When cyclobuten is so stusten that conrotacation cannot occur for sterile reasons, a concerted reaction cannot happen easily. Substances that might otherwise be predicted to be highly volatile often turn out to be relatively stable. An example is bicyclo-2.1.0-2-penten, which at first glance may seem incapable of isolation due to the possibility of immediate location up to 1.3-cyclocentadien. This permutation takes place, but not so quickly as to eliminate the isolation of the substance: How can we explain the fact that this substance can be isolated? The explanation is that if the reaction is to be conrotator, the product will not be the usual 1.3-cyclocentadyen - certainly very heavily stretched substance. (Try to make a ball and stick model it!) This means that the agreed mechanism is not favorable: It is of great interest and importance that, with electron systems (4n and 2), groups move in opposite directions (curvearrowleft)or (curvearrowright) or (curvearrowright)curvearrowleft, disrotatory). For example, in this case, disorotation of groups to each other will result in cis,cis,cis product. Since this product is not formed, it seems likely that the rotation of methyl groups to each other should be sterileally unfavorable: How can we explain the stereo-lectability of thermal electrocyclic reactions? Our problem is to understand why the agreed (4n) electrocyclic permutations are conrotator, while the relevant processes are disorotative. From what has been said before, we can expect that the conrotator processes are associated with the molecular orbits of Mebius, and the dystrotic processes are associated with the molecular orbit of Hyukel. Let's see why that's the case. Consider electrocyclic 1.3-dien and cyclobuten. In this case, the transitional state of Hubel (now with 40 knots) is formed as a result of disreahi isroyvation, but unfavorably with four (i.e. (4n)) electrons: In contrast, the transitional state of Mobius (one of which has an odd number of nodes) is formed as a result of the conrotation and favorably with four electrons (left (4n)) : You will notice that the closing of the 1.3-diene ring through a favorable state of The Mebius transition may be able to form only an anti-bond location of overlapping orbits that would correspond to the high energy of the cyclacon price. In fact, a normal cyclobuten will be formed because on the way down from the transitional state, the phases of orbits that will change the connection to give a gluing of the orbital location expected for the state of the Earth. The reverse occurs in the opening of the ring, so this reaction can also go through the favorable state of the Mebius transition. The same reasoning can be extended to electrocyclic reactions of 1.3.5-trien and 1.3-cyclogexadions, which include electrons and therefore favor the transitional states of Hukel, achieved by dystrocy. The three main types of pericyclic reactions are cycloaddition, electrocyclical permutation and sigmatropic permutation: the factors that control if and how these cyclizations and permutations occur can be understood consistently from the aroma or lack of aroma achieved in their cyclical transient states. In order for the agreed pericyclical reaction to be thermally favorable, the transient state must include electrons participating in the program if it is the Orbital Hurtel system, or electrons (4n), if it is the myubius orbital system. The Transition State of Hubel is a state in which the cyclical array of participating orbits has no nodes (or even number), and the transition state of Moebius has an odd number of nodes. Here we summarize the procedure for predicting feasibility and stereochemistion of thermally agreed reactions, including cyclical transitional states. 1.2 permutations of carbocations will be used to illustrate the approach. This is a very important reaction of carbocey, which we discussed in other chapters. We use it here as an example to illustrate how a quality MO theory can give an idea of how and why reactions occur: The first step of the procedure is to draw orbits as they are expected to be involved in a transitional state. Several agreements are possible. There are two such mechanisms, No. (41) and No. (42), for rearranging carbocations; the second step is to determine whether the transition states of Hubel or from the number of nodes. This is easy to do by assigning marks to shares orbits corresponding to their phases and counting the number of nodes that develop in a circle of overlapping orbits. The odd number indicates the transitional state of Mobius, while the even number, including zero, indicates the transitional state of Hyukel. There are alternative ways to account for transition states (41) and (42). Charts (43abc) and (44abc) represent the molecular orbits of different energies - those with more nodes with higher energies (c. Section 21-3C). There is no need to draw more than one such diagram to determine whether the transitional state is Mebius or Hyukel. Finally, we evaluate transition states according to rule (4n) or 4n 2. In the example given here, since only two electrons occupy molecular orbits, the transitional state of Hyukel (No43a) is favorable. The bonus based on these two formulations is that the stereochemization of the reaction can be predicted when we predicted which transitional state is a favored one. Thus, migrating groups in 1.2-carbokation permutations must move with the retention of the configuration in the transitional state of Yukel - and this has been tested experimentally. The alternative transitional state of Mebius predicts an inversion of the migration group configuration: You can use the procedures that have just been outlined to determine whether any heat reaction with a cyclical transient state can be favorable. A good place to start is the cycloaddition of Diels-Alder 1.3-butadien and etine, and after that, to show the electrocyclical ring opening of the cyclamic ring to be thermally favorable only conrotator opening of communication . Many pericyclical reactions occur photochemically, i.e. by exposure to ultraviolet light. One example is the transformation of norbornadien into a quadricyclone, described in section 13-3D. This reaction would be an unfavorable mechanism if it were undertaken by simple heating. In addition, thermodynamics favors opening the ring, not closing the ring. However, the quadricyclone can be isolated even if it is intensely strained, because to re-open the ring thermally involves the reverse of adverse 2 and 2 cycloaddition mechanism. Photochemical activation can be used to advance or reverse cycloaddiums and electrocyclic reactions that are thermodynamically unfavorable or have adversely agreed thermal mechanisms. Thus, the thermodynamically unstable dystrotic product can be obtained from 1.3-cyclocentadien by exposure to ultraviolet light: stereochemical results and the cyclical reactions of the are often the opposite of what is observed for the corresponding heat reactions. However, exceptions are known and the degree of stereospecific is not always as high as in thermal reactions. Other examples of photochemical pericyclic reactions are available in section 28-2D. Named after the mathematician A. F. Mabius. The purpose of orbital phases should take into account molecular symmetry, and while it is easy for open chain systems, it is much less simple for cyclical ones. Normally, you can avoid this problem by always trying to adjust your orbits so that there are no nodes or only one node in transition at the point where the connection is occurring or disrupted. John D. Robert and Marjorie K. Case and (1977) Basic Principles of Organic Chemistry, Second Edition. VA Benjamin, Inc. Menlo Park, CA ISBN 0-8053-8329-8. This content is copyrighted under the following terms: You get permission for individual, educational, research and non-commercial reproduction, distribution, display and execution of this work in any format.