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PRIMARY AND SECONDARY ORBITAL EFFECTS IN DYOTROPIC REARRANGEMENTS

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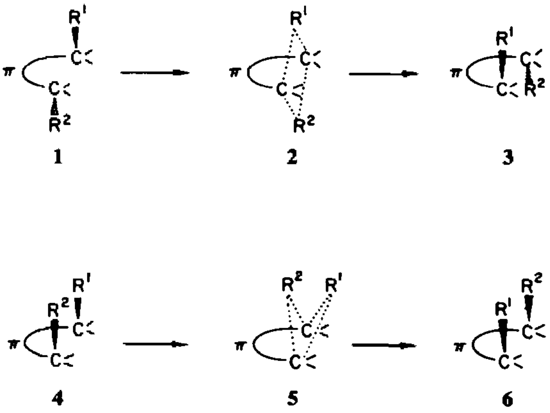
Abstract – A new class of orbital symmetry controlled reactions which involve the simultaneous migration of two σ-bonds is discussed. Analysis of the stereochemical fate of the migrating groups in thermal and photochemical shifts, based on the Woodward-Hoffmann rules and supported by MINDO/2 calculations, is presented.

Recently we defined a dyotropic reaction as an uncatalyzed process in which two σ-bonds simultaneously migrate, intramolecularly.[1] Reactions in which the two σ-bonds interchange their positions were designated as Type I, while those of Type II do not lead to positional interchange. In this paper we outline a general theory covering these rearrangements.

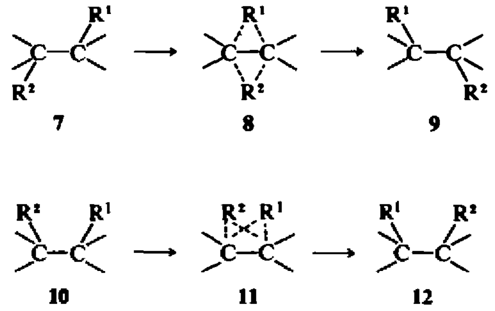
Type I Reactions

Transformations belonging to this class involve two migrating groups and two stationary atoms. Scheme 1 depicts a rearrangement in which stationary atoms bearing the migrating groups are connected by a π-system.



SCHEME 1

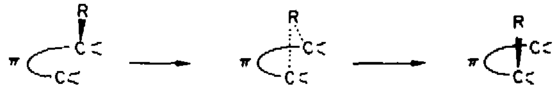
If both groups (R) migrate suprafacially, the *anti* conformation 1 leads to inversion of configuration at both stationary terminal atoms 3. The *syn* conformation 4 results in double retention 6. The fate of the configuration of the migrating groups can be illustrated best by considering molecules which lack π-systems, i.e. those in which the two stationary atoms are directly bonded to each other (Scheme 2).



SCHEME 2

Such concerted shifts involve four-membered transition states, 8 and 11, and are clearly pericyclic reactions subject to orbital symmetry restrictions.[2] Assuming retention of configuration of the migrating groups, both the *anti* and the sterically unfavorable *syn* reaction path can be analyzed within the Woodward-Hoffmann formalism as a thermally forbidden, photochemically allowed $[\sigma_s2+\sigma_s2]$ process.[1] Interestingly, the use of a correlation diagram employing a plane of symmetry bisecting the bond between the two stationary atoms leads to an erroneous conclusion, since the symmetry element does not bisect a bond which is being broken or made, a requirement for the derivation of correlation diagrams.[2]

In Scheme 1, cyclic four-membered arrays (2 and 5) predominate, and the additional π-system is not directly involved in the reaction in the usual sense. Thus, as a first approximation, these shifts should behave much like those in Scheme 2. In striking contrast to sigmatropic rearrangements,[2] in which the stereochemistry of the migrating group is determined by the number of π-electrons (Scheme 3), the course of dyotropic reactions should be nearly independent of the nature of the π-system.



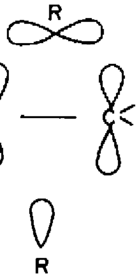
Scheme 3

Factors involved in Type 1 reactions

The thermally forbidden $[\sigma_s2+\sigma_s2]$ mode can be changed to a thermally allowed process by appropriate variation of the migrating groups (*primary orbital effects*); and the transition state 2 can be stabilized by interaction with suitably chosen π-systems (*secondary orbital effects*).

Primary orbital effects

A simple way to alter the $[\sigma_s2+\sigma_s2]$ process is to let one of the groups R migrate as an antarafacial component with inversion of configuration, thereby setting up a thermally allowed $[\sigma_s2+\sigma_a2]$ reaction. This is possible only if the migrating group has a p-orbital available as in **13**.



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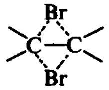

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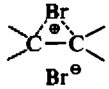

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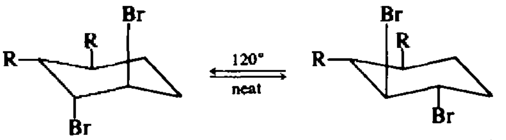
Although a number of double σ-shifts have been invoked, no unambiguous mechanistic evidence has been presented to date.[3] For the intramolecular isomerization of 5α,6β-dibromo steroids to the 5β,6α-dibromo isomers Grob and Winstein[3a] and Barton[3b] suggested a two-step mechanism involving ion-pairs. In non-ionizing solvents such as heptane, this two-step mechanism was postulated to merge with a fully concerted process[3b] shown in **14**. The reaction was recently re-investigated in the cyclohexane series by Berti:[3c]



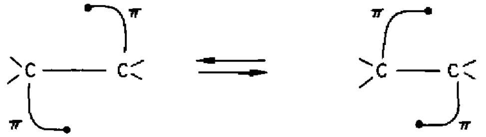
R = H, alkyl ester

This rearrangement could proceed by a shift in which one of the bromine atoms utilizes a p-orbital according to **13**. It is also conceivable that a lone electron pair directly participates. Whether such a $[\sigma_s2+\sigma_s2+\omega_s2]$ process is energetically favored over the $[\sigma_s2+\sigma_a2]$ shift is difficult to assess. In any case a non-polar concerted mechanism seems unlikely in view of the mild conditions under which the reaction proceeds. A tight, high-energy and short-lived ionpair **15**, representing a trough along the potential energy surface, is more likely. At this point of the reaction partial orbital overlap may be maintained, but is no longer the dominant factor, since charge separation has become important. Reactions of this type belong to those cases in which electrostatic factors override orbital symmetry restrictions. Similar factors may prevail in a number of coenzyme B_{12} mediated isomerizations involving cobalt as one of the migrating groups.[4] Mechanisms adhering to Scheme 1 or 2 remain to be established.

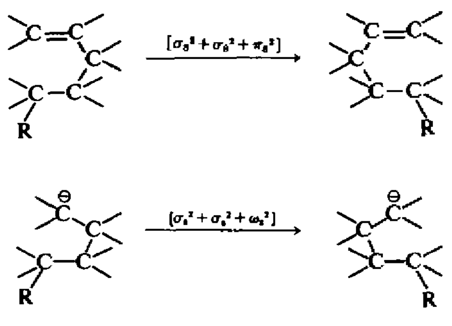
A second, more fundamental way to alter the $[\sigma_s2+\sigma_s2]$ process is to incorporate a suitable π-system as a migrating group. Scheme 4 shows the general form in which two such π-systems migrate.

Two of the large number of thermally allowed possibilities are shown below (Scheme 5)

To our knowledge no such reactions have been reported. Similar systems in which one of the migrating groups is forced into a rigid geometry by incorporation into a ring are also conceivable. Performing this operation on the first of the two examples depicted above, we arrive at the closely related cyclopentene system. In this case one of the σ-bonds (in group R) migrates in the previously described manner. The motion of the second σ-

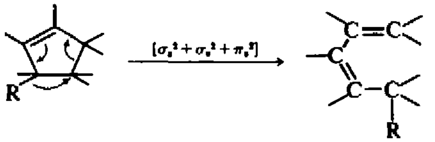


Scheme 4

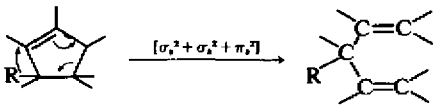


Scheme 5

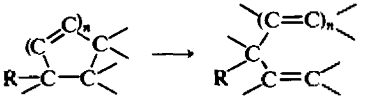
bond, however, results in ring opening and formation of an additional double bond:



Interestingly, this system can also undergo a different mode of transformation which combines features of dyotropic, sigmatropic and electrocyclic reactions:

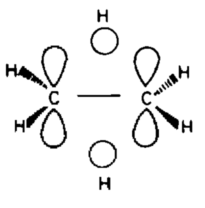


Obviously, this novel reaction is not restricted to the cyclopentene system. Assuming retention of configuration in R, disrotatory ring opening for n = odd, and conrotatory ring opening for n = even is predicted for in the following general reaction:



Secondary orbital effects

The four-membered transition state **8** ($R^1 = R^2 = H$) can be viewed as the interaction of ethylene with two hydrogen atoms above and below the plane of the π-system **16**. The six hydrogen and two carbon atoms give rise to seven doubly occupied and seven empty MOs. The form and energy of these MOs were established by applying the Hartree-Fock procedure at the MINDO/2 level.[5] The highest occupied molecular orbital (HOMO) has the form **17**. The striking feature of this occupied MO is the nodal plane bisecting the ethylenic segment and passing through the two bridging hydrogen atoms. Indeed, it is this π*-type orbital which is responsible for the transition state **8** being thermally forbidden. The information gained from the calculations is consistent with the Dewar-Zimmerman rules,[6] which state that thermally forbidden reactions have anti-aromatic transition states. Our MINDO/2 calculation gives an energy difference between staggered ethane and the bridged form **16** of ΔE = 5·9 eV.[†] In his study on the stabilization of diborane-like structures of ethane, Hoffmann[7] found ΔE values of 6·7 eV, 7·9 eV and 8·6 eV using extended Hückel, CNDO and *ab initio* methods, respectively. The point to be made here is not the comparative values of ΔE, but rather that all four methods give rise to the same qualitative conclusion regarding the rather high energy content of **16**. Clearly, thermal reactions of the present type involving two hydrogen atoms are not feasible.



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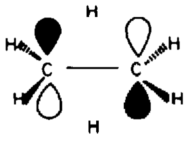

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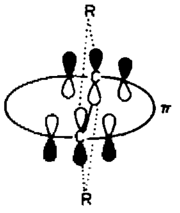
Using the frontier orbital method,[8] three simple qualitative models can be developed which lead to a stabilization of the anti-aromatic transition state.[1,7] By tying a π-system having a low-lying, anti-symmetric lowest unoccupied molecular orbital (LUMO) to the stationary end-atoms of **8**, the HOMO **17** can be stabilized. **18** shows the favorable symmetry-allowed HOMO-LUMO interaction of two such π-systems. Candidates for the interacting π-systems are polyenes with (4n+2) electrons, or single atom components having empty *d*-orbitals such as the $>SO_2$ moiety.



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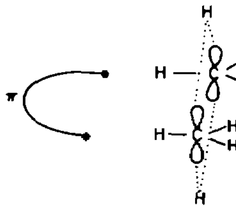

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This same approach can be applied to the closely related system **2** (Scheme 1), in which the two stationary end-atoms are not directly bonded to each other as in **18**. Union of two methyl "radicals" and the two hydrogen atoms with the additional π-system, as depicted in **19**, gives rise to **2**. The precise geometry will vary from system to system. In our MINDO/2 calculations we therefore did not optimize the geometry, but rather probed the effect of various geometric changes. The orbital properties of the four-membered pericycle were determined in the absence of the π-system, i.e. calculations were performed on the interaction of two methyl radicals with two hydrogen atoms. The results show that the form and energy of the

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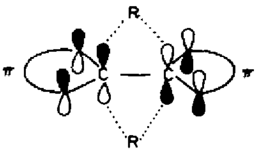
[†] In the ethylenic segment a C—C bond length of 1·65 Å and a C—H bond length of 1·09 Å were used. The other two hydrogen atoms were placed 0·93 Å above and below the C—C midpoint. This corresponds to the optimized geometry used by Hoffmann.[7]

HOMO depends upon the value of the through-space distance between the carbon atoms. This is not surprising, since the energy of a π^*-type orbital is expected to fall off as the distance between the stationary atoms is increased. In all calculations the HOMO and the next lower lying MO were rather close in energy. For example, at a distance of 1·8 Å, the HOMO was precisely the same form as was found for the previous system **16**, i.e. it is again a π^*-type orbital of the form **17** and lies 0·26 eV above the next lower MO. The important point again is not the numbers, but the qualitative information. The anti-bonding component can be stabilized in the same way as was previously discussed. π-systems having $(4n+2)$ electrons interact favorably.

A second method by which **8** is stabilized is to attach the ends of a π-system to one or both of the stationary end-atoms. Unlike the case above, favorable interaction comes about for π-systems having 4n electrons. **20** shows the HOMO-LUMO interaction of two appropriately attached π-systems.



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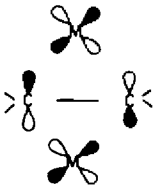

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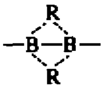
A third stabilizing orbital interaction results if the migrating groups themselves have low-lying empty orbitals of proper symmetry. Group IV elements having empty *d*-orbitals, **21**, group III elements having empty *p*-orbitals or transition metals are candidates. Such "internal" stabilization of antiaromatic transition states is reminiscent of intermolecular metal-catalyzed forbidden-to-allowed pericyclic reactions.[9]

Turning from these three methods of stabilizing the unfavorable $[\sigma_s2+\sigma_s2]$ transition state, we consider the effect of changing the nature of the stationary end-atoms. Some examples are shown (**22** to **25**).

Clearly, each of these systems has its own orbital peculiarity which is expected to have a profound influence on the energy of the transition state. Indeed, the distinction between primary and secondary orbital effects may no longer be meaningful. For example, in **22** we expect symmetry-allowed participation of the empty *p*-orbitals of boron, similar to the three-center bonding in bridged boron compounds.[10] In **23**, **24** and **25** lone electron pair and/or *d*-orbital participation will be dominant factors in the energetics of the transition state. Of course, the strength of the bonds which are being broken varies from system to system and should also play an important role.



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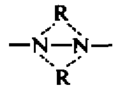

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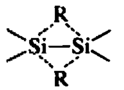

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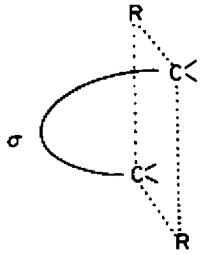
Besides the possibility of π-systems as in **2**, the end-atoms can also be connected to each other by σ-sequences, e.g., **26**. For the case in which the end-atoms are boron, the structure corresponding to **26** is symmetry-allowed and represents the *ground state* of the molecule **27**.[11] These observations suggest that a range of molecular systems is conceivable, from such stable systems as **27** to the high energy, symmetry-forbidden transition state **2**.



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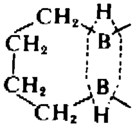

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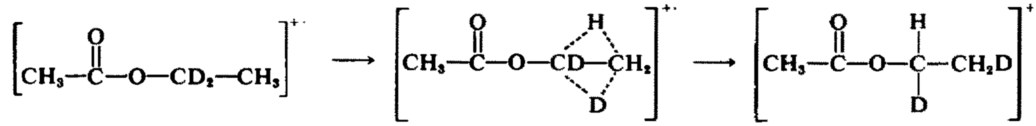
Other factors. Simultaneous rupture of two σ-bonds in organic reactions is by no means rare. Olefin-forming eliminations, cycloreversions and group transfer reactions are common examples. In all of these cases, as in dyotropic reactions, bond rupture is accompanied by bond formation. Nevertheless, the simultaneous breakage of two bonds is usually considered to be a high energy process. According to the Rice-Ramsperger-Kassel-Marcus (RRKM) theory of unimolecular reactions,[12] intramolecular transfer of energy between vibrational degrees of freedom in a thermally activated molecule is assumed to be fast compared to the rate of reaction. However, the probability that two bonds are stretched to the same extent at the saddle point of the reaction coordinate is low. Thus, dyotropic reaction modes are not expected to be fully symmetrical. It is likely that in the transition one bond has stretched considerably, the other less so. We anticipate the degree of lagging to be inversely proportional to the degree of vibrational coupling. This statistical mechanical restriction should have an important influence on the geometry of the transition state.

Photochemical Reactions. It is normally assumed that the selection rules for photochemical pericyclic reactions are precisely opposite to those of thermally induced processes.[2] Thus, as already mentioned, the $[\sigma_s2+\sigma_s2]$ process (Scheme 2) should be photochemically allowed. No such photochemical reactions have been postulated to date. However, electron impact induced rearrangements have been studied. The intramolecular hydrogen scrambling observed in ethyl propionates[13] and acetates[14] has been postulated to occur via four-membered cyclic transition states:

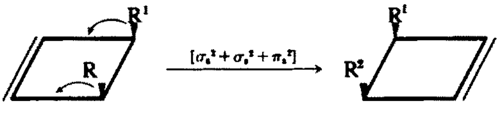


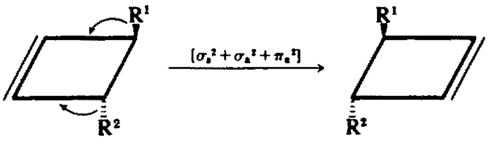
$$\left[CH_3-\overset{O}{\overset{\|}{C}}-O-CD_2-CH_3\right]^{+\cdot} \longrightarrow \left[CH_3-\overset{O}{\overset{\|}{C}}-O-\underset{D}{\overset{H}{CD-CH_2}}\right]^{+\cdot} \longrightarrow \left[CH_3-\overset{O}{\overset{\|}{C}}-O-\underset{D}{\overset{H}{C}}-CH_2D\right]^{+\cdot}$$

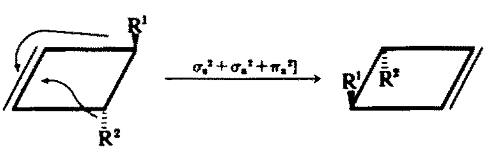
The existence of excited electronic states in mass spectrometry is well-documented.[15] The participation of an electronically excited state in the above cyclic rearrangement is in accord with the theory of dyotropic reactions. However, detailed application of orbital symmetry to mass spectrometry is difficult, since the nature of the excited states is usually not known with certainty.[16]

Type II Reactions

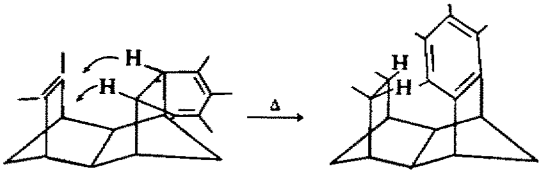
A systematic treatment of this class of reactions is impracticable, since a wide variety of structural reorganizations are conceivable.[1] Several examples will be analyzed, the first belonging to the cyclobutene system.







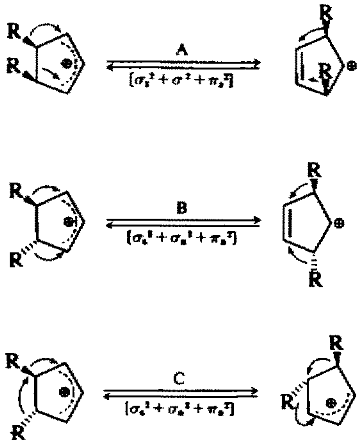
Assuming retention of configuration of the groups R, all three reactions are thermally allowed. They are unlikely to be observed, however, since the competing electrocyclic ring opening to butadienes is known to be facile.[17] Nevertheless, a process corresponding to the first of the above depicted examples has been shown to occur in a different system:[18]



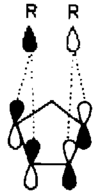
No doubt, the driving force in this rearrangement is provided by the formation of the aromatic ring. Furthermore, models show that the two migrating hydrogen atoms are fixed in a rigid position which facilitates smooth dyotropic motion.

Analysis of the next higher homolog, the cyclohexadiene system, has shown the dyotropic rearrangements to be photochemically allowed.[1] In accord with this prediction is the photochemically-induced racemization of dihydropyrazine derivatives,[19] a system isoelectronic with 1,4-cyclohexadiene.

As in the case of Type I dyotropic reactions, those of Type II are not restricted to neutral molecules. Indeed, it is the study of ionic reactions which may be most fruitful. The potential energy surface of carbonium ion rearrangements are likely to involve dyotropic reaction modes. Such processes could serve to circumvent high energy carbonium ions which would otherwise have to be postulated. The cyclopentenyl cation serves as an example.[20] Three of several conceivable dyotropic shifts are shown below.



According to the Woodward-Hoffmann formalism, all three reactions are thermally allowed. In accord with this prediction are the orbital correlation diagrams which can be derived for reaction A using a plane of symmetry and for B using a twofold axis of symmetry.[21] Which one of these two allowed processes is preferred? This question can be answered by viewing the transition state as the interaction of a cyclopentadienyl cation interacting with the antisymmetric combination of the R-groups. Neglecting interaction between the two R-groups (which should indeed be small), this model predicts the "boat" transformation I to be energetically more favorable than the "chair" transformation II.



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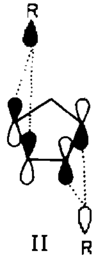
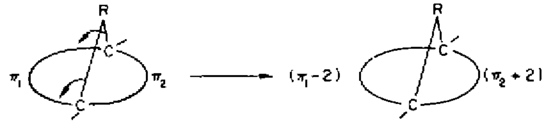


II

In reaction C one of the R-groups follows the other R-group in its "tracks", a process which is normally referred to as neighboring group participation. Some "lagging behind" may be anticipated. In this system the leaving group does not depart from the substrate as in solvolyses, but is accepted by one end of the host allyl cation. The motion of this group without anchimeric assistance from the second group would result in the transformation of a resonance-stabilized allyl cation to a higher energy ion localized on one atom. We suggest that related processes may be a general phenomenon in deep-seated carbonium ion rearrangements.[22]

A different variation of Type II reactions involves the migration of two σ-bonds which are connected to the *same* substituent. Such processes have the advantage that the vibrational modes of the two σ-bonds are expected to be strongly coupled. One possible system is shown below. Since the two σ-bonds contain four electrons, the reaction is predicted to be thermally allowed if the sum of the electrons in the two π-systems results in $(\pi_1 + \pi_2) = 4n + 2$.



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