

Orbital-Symmetry-Disallowed Energetically Concerted Reactions

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When a properly constructed molecular orbital correlation diagram for a thermally activated chemical transformation links all bonding levels in starting material with bonding levels in product, the reaction is a symmetry-allowed process. Orbital symmetry relationships endow the reaction with a strong stereochemical bias: other things being equal, the symmetry-allowed stereochemical alternative will be favored over a symmetry-forbidden one. Reactions, then, tend to occur with conservation of orbital symmetry.²⁻⁴

The fundamental simplicity and physical significance of these hypotheses have been partially obscured through differing understandings of what a concerted reaction is: too often concerted and allowed have been used as interchangeable synonyms. This Account attempts to make clear a distinction between the terms, and thus refute the mistaken supposition that all allowed reactions are concerted, and all forbidden reactions nonconcerted.

Orbital Symmetry and State Conservation

Reactions such as the thermally activated valence isomerizations of even-electron closed-shell hydrocarbons usually occur with high stereoselectivity in the sense predicted by orbital symmetry theory.⁴ Cyclobutenes, for instance, rearrange thermally to butadienes in a conrotatory fashion, it being the stereochemical alternative giving correlation between bonding molecular orbitals in reactant and product.

More fundamentally, this stereochemical mode gives direct correlation between the most stable electronic states of starting material and product. The ground state of cyclobutene, with a molecular orbital configuration or level occupation given by $\dots \sigma^2 \pi^2$, correlates with the ground configuration of butadiene $\dots \chi_1^2 \chi_2^2$ in the conrotatory mode only.^{5,6}

The total activation energy for such processes may be small or large, depending on all contributing factors, but there is no orbital symmetry imposed barrier. The state correlation diagram for a reaction predicted to

be orbital-symmetry allowed is schematically a straight line (Figure 1).

For the disrotatory cyclobutene opening, the ground state starts toward a correlation with a doubly excited state of butadiene, $\dots \chi_1^2 \chi_3^2$, but since states of like symmetry never cross, this correlation is avoided: ground states of reactant and product are directly correlated, at a higher energetic cost (Figure 2).

For every orbital-symmetry forbidden reaction there is a theoretical opportunity for reaction to occur in a state-conservative manner as in Figure 2; but this possibility would be irrelevant if the state-conservative process had such a high activation energy that thermal activation led instead to a state-crossing event,⁷ giving a triplet open-shell diradical species as an intermediate which proceeded to one or a variety of products.

But some orbital-symmetry-forbidden reactions might have such low activation energies for state-conservative processes that singlet-triplet state crossings would be precluded and even orbital symmetry allowed alternatives would be unable to compete kinetically. Geometrical constraints can make some particular allowed reactions energetically prohibitive; the electronic features of certain molecules may enable them to convert to symmetry-forbidden products by one-step state-conservative reaction profiles when this is energetically advantageous relative to alternatives involving triplet diradical intermediates. Thus the normal correspondences between facility and allowedness, and between allowed and one-step processes, are not absolute.

(1) National Institute of General Medical Sciences Predoctoral Fellow, 1968-1971.

(2) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(3) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(4) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1971.

(5) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

(6) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

(7) (a) W. Kauzmann, "Quantum Chemistry," Academic Press, New York, N. Y., 1957, pp 536-545, 696-697, 700-702; (b) T. L. Cottrell, "Dynamic Aspects of Molecular Energy States," Oliver & Boyd, London, 1965, pp 58-61; (c) E. E. Nikitin, "Theory of Thermally Induced Gas Phase Reactions," Indiana University Press, Bloomington, Ind., 1966, pp 65-67; (d) E. E. Nikitin in S. Claesson, Ed., "Fast Reactions and Primary Processes in Chemical Kinetics," Interscience, New York, N. Y., 1967, pp 165-183; (e) D. Phillips, "Photochemistry," *Chem. Soc. Specialist Periodical Rept.*, **1**, 4 (1970); (f) G. S. Hammond, *Advan. Photochem.*, **7**, 373 (1969); (g) T. Förster, *Pure Appl. Chem.*, **24**, 443 (1970); (h) B. R. Henry and M. Kasha, *Annu. Rev. Phys. Chem.*, **19**, 161 (1968); (i) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966); (j) L. Landau, *Phys. Z. Sowjet.*, **1**, 89 (1932); **2**, 46 (1932); (k) C. Zener, *Proc. Roy. Soc., Ser. A*, **137**, 696 (1932); **140**, 660 (1933); (l) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964); (m) C. A. Coulson and K. Zalewski, *Proc. Roy. Soc., Ser. A*, **268**, 437 (1962); (n) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

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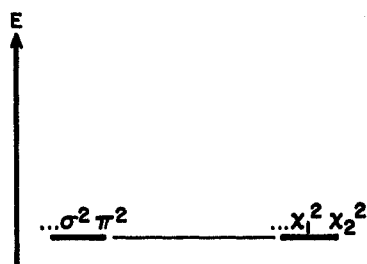


Figure 1. Electronic state correlation diagram for the orbital symmetry allowed conrotatory thermal isomerization of cyclobutene to butadiene.

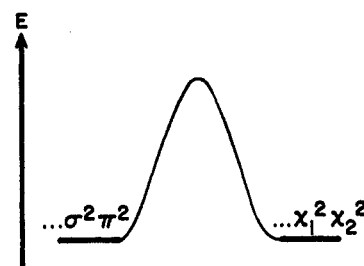


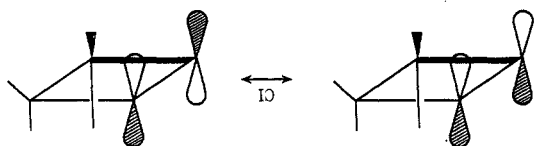
Figure 2. Electronic state correlation diagram for the orbital symmetry forbidden disrotatory thermal isomerization of cyclobutene to butadiene.

Configuration Interaction and Chemical Reactivity

The wave function for a closed-shell reacting system corresponding to the state correlation diagram of Figure 2 cannot be described at all adequately by a single Slater determinant. Such a single configuration treatment would lead to the correlation of ground state of reactant with doubly excited state of product, which can never happen. A linear combination of two or more Slater determinants and the mathematics of configuration interaction provide a more accurate description, and avoid the crossing of two states of like symmetry, as the real molecules must.

In some respects the situation is similar to the more familiar case where resonance involving two or more canonical forms must be taken into consideration. Approaching the transition state region of the thermal disrotatory and symmetry forbidden cyclobutene opening, the molecular wave function $\Psi = C_1|\dots\sigma^2\pi^2| + C_2|\dots\sigma^2\pi^*2|$ is a fair approximation. (If the two determinants were built from self-consistent field orbitals, this simple two-term linear combination would be a very good approximation, since, according to Brillouin's theorem, all matrix elements connecting ground configuration and singly excited configurations would be zero.)

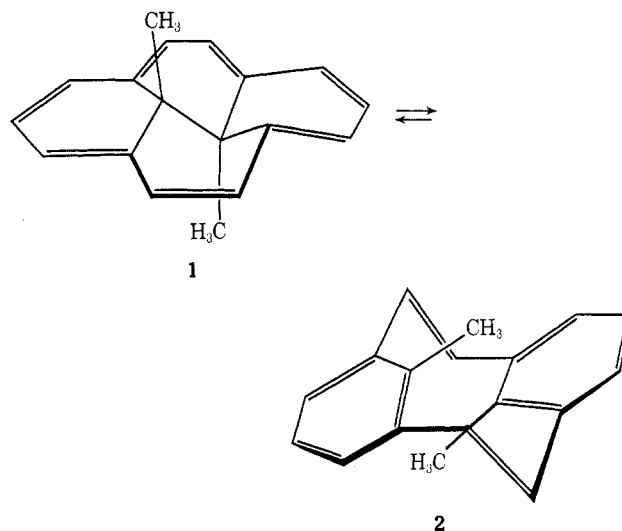
Symbolizing such a wave function through structures has many advantages, as well as some pitfalls. We are currently utilizing the device shown below, giving the phase character of the doubly occupied molecular orbital highest in energy in the two closed-shell configurations, together with a configuration interaction (CI) modified resonance arrow.



A more trouble-free and less informal notational method will doubtless evolve.

Calculations comparing the conrotatory and disrotatory modes in the thermal conversion of cyclobutene to butadiene give a striking indication of how significant configuration interaction may be: the energy difference between the two stereochemical modes is 100 kcal/mol according to valence-bond estimates,⁸ 49 kcal/mol from self-consistent field calculations,⁹ and only 13.6 kcal/mol when configuration

interaction calculations are done on the SCF functions.⁹



Configuration interaction has been recognized by Schmidt¹⁰ as necessary to account for the facile thermal interconversion of 15,6-dimethyldihydropyrene (1) and 15,6-dimethyl[2.2]metacyclophane-4,9-diene (2). This reaction, formally a 6- or a 14-electron conrotatory electrocyclic conversion, is thermally forbidden. It contains a symmetry-imposed barrier, for the highest occupied orbital of the reactant rises along the reaction coordinate toward an antibonding level of the product and crosses an antibonding orbital of opposite symmetry which correlates with the HOMO of the product. The ground and doubly excited configurations based on these orbitals, however, cannot cross; the transition-state energy for the isomerization is estimated to be some 5 kcal/mol below the crossing point given by the molecular orbital calculations.¹⁰

Molecules such as dihydropyrene and tetrahydropyrene^{10,11} derivatives have extended π systems and therefore low-lying electronically excited states, facilitating configuration interaction and accounting for the low activation energy orbital symmetry disallowed

(8) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

(9) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *ibid.*, **93**, 2117 (1971).

(10) W. Schmidt, *Helv. Chim. Acta*, **54**, 862 (1971), and references cited therein.

(11) V. Boekelheide and W. Pepperdine, *J. Amer. Chem. Soc.*, **92**, 3684 (1970); C. E. Ramey and V. Boekelheide, *ibid.*, **92**, 3681 (1970).

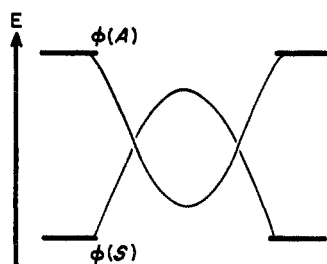
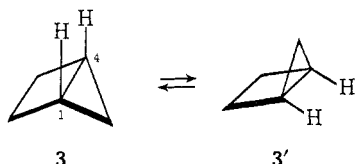


Figure 3. Abbreviated molecular orbital correlation diagram for the automerization of bicyclopentane (**3**).

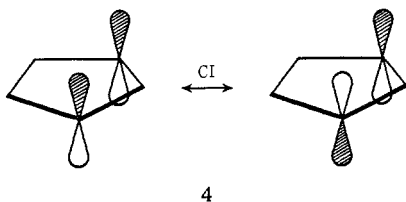
isomerizations they show. Indeed, a general rule has been proposed for thermal reactions whereby a low-lying excited state of the right symmetry is required for a low activation energy process.¹²

The linear correlation we observed earlier¹³ for a series of cyclic olefins between their lowest ultraviolet electronic transitions and the activation energies of their thermal isomerizations may be taken as a further indication of reactions being facilitated by low-energy virtual orbitals.

The bicyclo[2.1.0]pentane system provides another example in which single determinant wave functions are inadequate guides to chemical activity.



In the ground state of **3**, the C(1)–C(4) bonding orbital, symmetric with respect to the symmetry plane of the molecule, would be doubly occupied, and the corresponding antibonding and antisymmetric orbital would be unoccupied. Upon disrotatory ring-opening leading from **3** to a planar species, the $\phi(S)$ orbital would increase in energy as $\phi(A)$ decreased; they would be expected to cross, for in the planar form the antisymmetric nonbonding orbital would be on the order of 0.5 eV lower in energy than the $\phi(S)$ orbital (Figure 3).^{14,15}



The corresponding state correlation diagram would be as shown in Figure 4. The nonplanar activated complex and the planar intermediate would have singlet wave functions corresponding to linear combinations

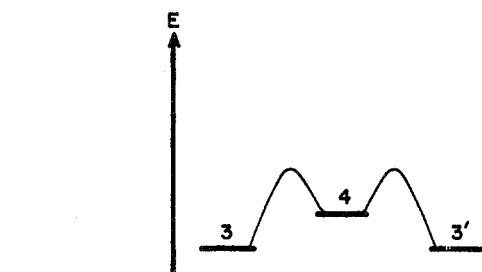
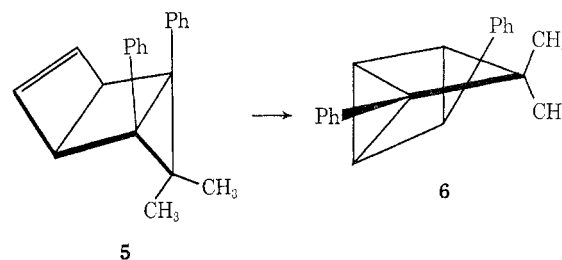


Figure 4. Abbreviated electronic state correlation diagram for the automerization of bicyclopentane (**3**).

of $\dots\phi(S)^2\phi(A)^0$ and $\dots\phi(S)^0\phi(A)^2$ configurations, as represented by structure 4. The partially flattened bicyclopentane or the planar intermediate could react in a manner appropriate to either type of C(1)–C(4) molecular orbital symmetry, for instance with an olefin in a cycloaddition reaction as a two-center two-electron A component or intramolecularly as an S orbital through collapse to bicyclopentane. An opportunity for "orbital inversion" is presented, but not required.

Substitution of conjugating groups at C(1) and C(4) of a bicyclo[2.1.0]pentane skeleton would make possible "orbital symmetry inversion" at a less planar geometry, and lower the activation energy required for either cycloaddition or the automerization of bicyclopentane.¹⁶ This is, we suggest, the factor accounting for the smooth conversion of the tricyclic hydrocarbon **5** to the quadracyclane derivative **6** at 100°^{17,18} when analogous systems lacking one or both phenyl groups undergo reaction more sluggishly.



The reaction **5** → **6** could well occur in a single step without intervention of a 1,3-diradical triplet-state intermediate susceptible to intramolecular trapping,¹⁷ and without prior rearrangement of the *cis,anti,cis* tricyclic substrate **5** to the corresponding *cis,syn,cis* isomer.^{16b,19}

Among mechanistic proposals for the facile thermal isomerization of *cis*-bicyclo[6.1.0]nona-2,4-6-triene to *cis*-3a,7a-dihydroindene are the two outlined in Scheme I.^{20,21} One or the other of the orbital-symmetry forbidden steps given by dashed arrows in this scheme

(12) R. G. Pearson, *Accounts Chem. Res.*, **4**, 152 (1971); *Pure Appl. Chem.*, **27**, 145 (1971).

(13) J. E. Baldwin and A. H. Andrist, *J. Amer. Chem. Soc.*, **93**, 3289 (1971).

(14) R. Hoffmann, *ibid.*, **90**, 1475 (1968); *Accounts Chem. Res.*, **4**, 1 (1971).

(15) E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **91**, 6766 (1969), ref 38.

(16) For reviews of bicyclopentane chemistry, see (a) K. B. Wiberg, *Advan. Alicycl. Chem.*, **2**, 185 (1968); (b) P. G. Gassman, *Accounts Chem. Res.*, **4**, 128 (1971).

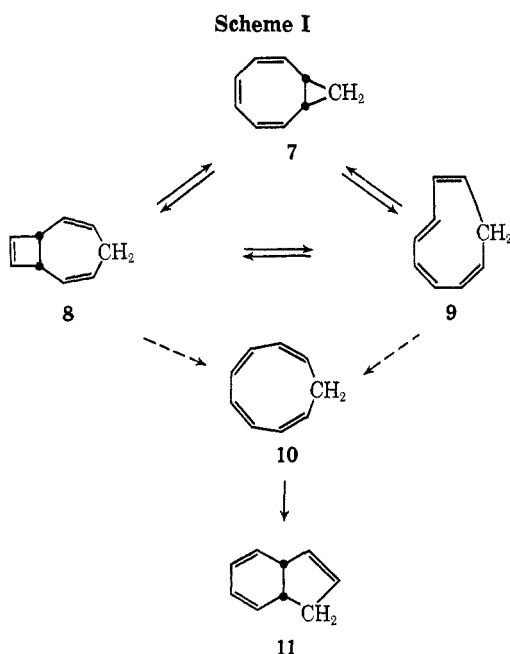
(17) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **92**, 1765 (1970); **93**, 5128 (1971).

(18) See also E. Druckrey, M. Arguelles, and H. Prinzbach, *Chimia*, **20**, 432 (1966); H. Prinzbach and M. D. Martin, *Helv. Chim. Acta*, **51**, 438 (1968).

(19) See also L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971).

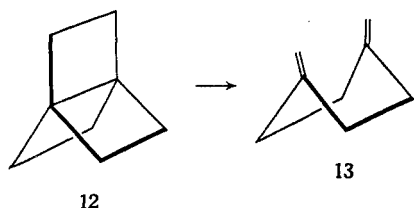
(20) S. W. Staley, *Intra-Sci. Chem. Rept.*, **5**, 149 (1971).

(21) J. E. Baldwin, A. H. Andrist, and R. Pinschmidt, Jr., *J. Amer. Chem. Soc.*, **94**, 5845 (1972).



seems a necessary postulate; simple molecular orbital analysis²¹ shows that a state-conservative and concerted isomerization, $8 \rightarrow 10$, is an excellent possibility, while the alternative, $9 \rightarrow 10$, is hardly plausible. The estimated energy at the transition state, defined by the projected crossing of ground and doubly excited molecular orbital configurations, is 2.5 times higher for $9 \rightarrow 10$ than for $8 \rightarrow 10$. The extent to which the actual activation energies would be lower than these crossing points could be estimated through configuration interaction calculations, but a reversal of the energetic ordering of the two activated complexes is most unlikely. We therefore now favor $8 \rightarrow 10$ in Scheme I as a reasoned and reasonable proposal and a possible break in the mechanistic opaqueness the rearrangement has sported over the past decade.

The possible isomerization of [2.2.2]propellane (**12**) to 1,4-dimethylenecyclohexane (**13**)^{22,23} represents another case where a symmetry-disallowed reaction may nevertheless occur in a facile and concerted manner, and where configuration interaction is essential for a decent theoretical treatment.



Conclusions

The original Woodward and Hoffmann communication² did not mention the word "concerted" or the concept of "concertedness"; neither does the most succinct and general formulation of their results, Chapter 4 in "The Conservation of Orbital Symmetry."⁴

(22) W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 779 (1972).

(23) M. D. Newton and J. M. Schulman, *ibid.*, **94**, 4391 (1972).

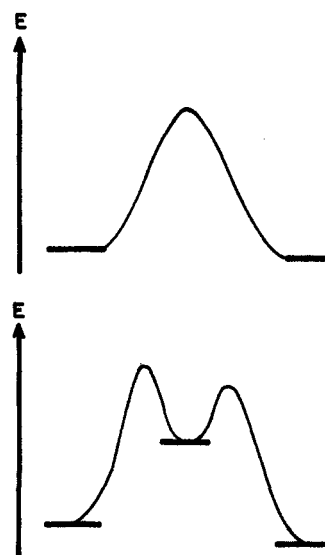


Figure 5. Energy vs. reaction coordinate profiles for an energetically concerted (above) and a nonconcerted process (below), one where an intermediate separates starting material and product.

Yet, the page-1 formulation⁴ "orbital symmetry is conserved in concerted reactions" has made it seem that, somehow, concerted reactions and orbital symmetry theory formed an intimate and exclusive duality, each dependent solely on the other.

When the term "concerted" is taken in an energetic sense, the energy profiles of Figure 5 may be viewed as representative of concerted and nonconcerted reactions.²⁴ Either profile may correspond to a symmetry-allowed reaction, for nothing in orbital symmetry theory requires the reaction profile to have a single maximum. Theory, rather, suggests that in some symmetry-allowed processes such as the Cope rearrangement there is a local energy minimum between reactant and product.^{25,26}

For reactions that are orbital symmetry forbidden, yet state conservative, the same two reaction profiles may obtain: calculations for the dihydropyrene isomerization $1 \rightleftharpoons 2$ correspond to the first alternative,¹⁰ those for the bicyclo[2.1.0]pentane inversion $3 \rightleftharpoons 3'$ to the second.²⁷

For state-conservative reactions, then, one cannot predict from the classifications "symmetry allowed" or "symmetry forbidden" whether a reaction will be concerted or not. The distinction between the two types of reaction profiles shown in Figure 5 may be attempted experimentally or theoretically, but not with absolute reliability through orbital-symmetry correlation diagrams alone. Orbital symmetry is conserved in some but not all concerted reactions, and not conserved in some but not all nonconcerted reactions.

(24) Compare J. E. Baldwin and R. H. Fleming, *Fortsch. Chem. Forschung*, **15**, 281 (1970).

(25) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968); *Chem. Brit.*, **5**, 449 (1969).

(26) See also L. Salem, *Accounts Chem. Res.*, **4**, 322 (1971).

(27) R. C. Spiker, Jr., L. Andrews, and C. Trindle, *J. Amer. Chem. Soc.*, **94**, 2401 (1972).

While detailed configuration interaction calculations are complex, the qualitative consequences of configuration interaction and the import of state-correlation diagrams are quite uncomplicated and accessible.

In some circumstances the dichotomy between orbital symmetry allowed and disallowed reactions may be more profitably replaced by a dichotomy based on how state-conservation may be achieved. Thus the rearrangements leading to dihydroindene treated above, $7 \rightarrow 8 \rightarrow 10 \rightarrow 11$, might be described as a sequence of three state-conservative isomerizations, $[\pi 2_s + \sigma 2_s + \pi 2_s]$ (OS), $[\pi 2_s + \sigma 2_s]$ (CI), and $[\pi 2_s + \pi 2_s + \sigma 2_s]$ (OS), giving in each case the stereochemistry of utilization of the two-electron components and a label (OS or CI) for the way in which state conservation may be realized. Tables giving orbital symmetry allowed and disallowed reaction types might be usefully relabeled "state-conservative through OS" and "state-conservative through CI." Compounds having no low-energy OS-dominated state-conservative path, but having electronic structural features appropriate for a low activation energy conversion (describable through effective configuration interaction), might be expected to show the CI-dominated reaction path.

The recognition of delocalization accompanying progress along a reaction coordinate as a great facilitator of effective configuration interaction and thus

a patron of state-conservative CI dominant processes may also provide an understanding of how calculations based on thermochemical data and radical models may be so successful in predicting activation energies²⁸ even for hydrocarbon rearrangements that seem to be entirely nonradical. Parallels between estimated radical stabilization and bond delocalization capacities for various substituents would not be surprising.

Better calculations of reacting systems including configuration interaction, and a wider appreciation of its energy-influencing and "orbital-symmetry inverting" manifestation, may contribute to a new stage of work on cycloadditions, one in which the concepts of orbital symmetry conservation and energetic concertedness are separate and independent. Experiments testing for the energetic concertedness of reactions and for the characteristics of short-lived singlet intermediates, suggested by this new conceptual framework, may well prove rewarding.

We gratefully acknowledge financial support for our studies on cycloaddition chemistry contributed by the National Science Foundation, and by The Cities Service Oil Co., The Du Pont Co., and Hoffmann-LaRoche Inc.

(28) S. W. Benson, "Thermochemical Kinetics," John Wiley, New York, N. Y., 1968; S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS 21, U.S. Government Printing Office, Washington, 1970.

Orbital-Symmetry-Forbidden Reactions

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The organic chemist, for all his modern sophistication, remains fundamentally a maker of compounds. Heritage, training, and experience teach him that syntheses of complex molecules are laborious and require construction of most of the bonds one at a time. This accounts, as much as any other factor, for his abiding fascination with concerted reactions, in which two or more bonds are made or broken simultaneously.

The traditional criteria of concert follow directly from the idea that bonding of the reactive sites is maintained throughout. Thus, the recovery of part of the cost of bond breaking by bond making should depress the activation energy below that expected for a rate-determining complete rupture of any of the relevant bonds of the reactant. Since the reactive sites must

remain in close proximity to preserve bonding, concerted reactions would tend to be stereospecific. Moreover, the same proximity requirement often would result in a low Arrhenius preexponential term or low entropy of activation because of the conversion of internal rotational to vibrational degrees of freedom in the transition state.

Not many thermal reactions clearly satisfy both the kinetic and the stereochemical criteria of concert. In the bimolecular group, perhaps the best known example is the Diels-Alder reaction,¹ while the unimolecular cases include the cyclobutene \rightarrow butadiene electrocyclic reaction,² the Claisen and Cope rearrangements,³ and the retroene reaction that converts *cis*-2-methyl-1-vinylcyclopropane to *cis*-1,4-hexadiene.⁴

(1) A. Wassermann, "Diels-Alder Reactions," Elsevier, New York, N. Y., 1965.

(2) (a) E. Vogel, *Justus Liebig's Ann. Chem.*, **615**, 14 (1958); (b) R. Criegee and K. Noll, *ibid.*, **627**, 1 (1959); R. Criegee, D. Seebach, R. E. Winter, B. Boretzen, and H.-A. Brune, *Chem. Ber.*, **98**, 2339 (1965), and references cited therein.

(3) S. J. Rhoads in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 11; (b) W. von E. Doering, V. G. Toscano, and G. H. Beasley, *Tetrahedron*, **7**, 25299 (1971).

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Additions and Corrections

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Page 403. The drawing at lower left should be inverted.

Page 405. Reference 27 should read: F. S. Collins, J. K. George, and C. Trindle, *J. Amer. Chem. Soc.*, **94**, 3732 (1972).