mate β and β' orbitals. Thus, the *endo* transition state (I) for this $4 + 2$ concerted cycloaddition reaction is stabilized *vis-a-vis* the *exo* alternative (II) by symmetry-controlled secondary orbital interactions. Similar circumstances obtain for all of the $4 + 2$ concerted cycloaddition reactions we have considered. For example, our extended Hückel calculations reveal that for maleic anhydride (V) and *p*-benzoquinone (VI), the relevant low-lying antisymmetric unoccupied dienophile orbitals are


V   VI
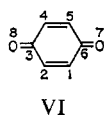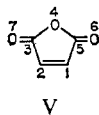
$$\chi_4 = 0.442(\psi_1 - \psi_2) + 0.506(\psi_5 - \psi_3) -$$
$$0.343(\psi_6 - \psi_7) \quad (V)$$

$$\chi_5 = 0.306(\psi_1 - \psi_2 - \psi_4 + \psi_5) +$$
$$0.461(\psi_6 - \psi_3) - 0.368(\psi_7 - \psi_8) \quad (VI)$$

The orbital symmetry relationships signalized here provide a simple quantum chemical basis for the large body of experience summarized in the Alder *endo* addition rule.[3] Our treatment differs from previous proposals, which have emphasized the roles of inductive forces,[4] electrostatic forces consequent upon charge transfer between diene and dienophile,[5] and maximum accumulation of unsaturation.[3] In particular it is now clear that in some cases the orbital interactions among unsaturated centers involved in a concerted cycloaddition reaction will be such as to raise, rather than lower, the energy of the *endo* transition state, and lead to a preference for *exo* addition, insofar as symmetry factors are dominant; inspection of the relevant orbital diagrams (VII and VIII) for the (as yet unobserved)
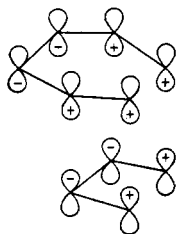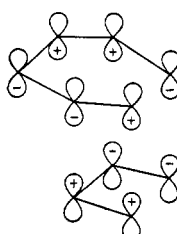
VII   VIII

symmetry-allowed $6 + 4$ combination[1] indicates that it is such a case. By contrast, the symmetry-allowed $8 + 2$ and $2 + 2 + 2$ cycloadditions[1] should resemble the $4 + 2$ process and proceed by preference through *endo* transition states; there is already evidence for that preference in one example of the latter process.[6]

The dimerization of cyclobutadiene is a special case of much interest, considered in the light of orbital symmetry relationships. If, as seems likely, there is substantial bond localization in that highly reactive

(3) K. Alder and G. Stein, *Angew. Chem.*, **50**, 514 (1937); K. Alder, *Ann.*, **571**, 157 (1951); K. Alder and M. Schumacher, *Fortschr. Chem. Org. Naturstoffe*, **10**, 1 (1953). For exceptions to the rule, *cf.* J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962).

(4) A. Wassermann, *J. Chem. Soc.*, 825, 1511 (1935); 432 (1936); *Trans. Faraday Soc.*, **35**, 841 (1939).

(5) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **66**, 645 (1944).

(6) R. C. Cookson, J. Dance, and J. Hudec, *J. Chem. Soc.*, 5416 (1964).

molecule, one can delineate, *a priori*, the possibilities of $2 + 2$, $2 + 4$, and $4 + 4$ cycloadditions. Our selection rules[1] require a preference for the concerted $2 + 4$ process, and indeed evidence that this path is favored has very recently been brought forward.[7] Examination of secondary orbital interactions along the lines set down in this communication reveals further that the *endo* process, leading to the *syn* dimer (IX), should be favored over the alternative *exo* combination, which
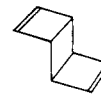
IX   X

would give the *anti* dimer (X). The formation of both *syn* and *anti* dimers in reactions initiated with a variety of possible cyclobutadiene precursors has been reported, but in those experiments in which there was the greatest likelihood of the transitory existence of a free cyclobutadiene the predicted *endo* process was observed.[8]

(7) G. Wittig and J. Weinlich, *Chem. Ber.*, **98**, 471 (1965).

(8) R. Criegee, *Angew. Chem.*, **74**, 703 (1962), and references therein; P. S. Skell and R. J. Peterson, *J. Am. Chem. Soc.*, **86**, 2530 (1964), and references therein.

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Orbital Symmetries and Orientational Effects in a Sigmatropic Reaction

Sir:

The 3,3 sigmatropic shift[1] (I → II) in hexa-1,5-dienes (the Cope rearrangement) has been shown[2] to proceed

I   II

more easily through a four-center chair-like transition state (III) than through the six-center boat-like alternative (IV).

III   IV

native (IV). It is the purpose of this communication to suggest that orbital symmetry relationships[1,3] play a predominant role in determining that preference.

A correlation diagram[3] for the molecular orbitals involved in the rearrangement is illustrated in Figure 1. The levels are classified as symmetric (S) or antisymmetric (A) with respect to the mirror plane in the boat-

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

(2) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962); *Angew. Chem.*, **75**, 27 (1963).

(3) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965); *cf.* also H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).
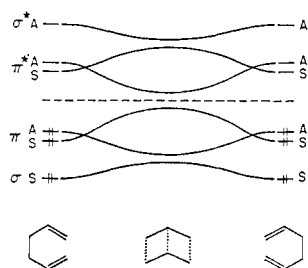
Figure 1.

like transition state or the twofold rotation axis in the chair-like form. The scheme shown is for the former case, and the diagram for the latter is qualitatively similar. The correlation of reactant bonding levels with product bonding levels, characteristic of a symmetry-allowed thermal reaction, should be noted. At the half-way mark in the reaction the level ordering is recognizable as that of two interacting allyl radicals. The actual behavior of the levels along the reaction coordinate is abstracted from extended Hückel calculations.[4]

If the correlation diagrams are qualitatively similar for four- and six-center reactions, where does the observed preference come from? An explanation requires the construction of a further correlation diagram (Figure 2) for the hypothetical process of two allyl radicals
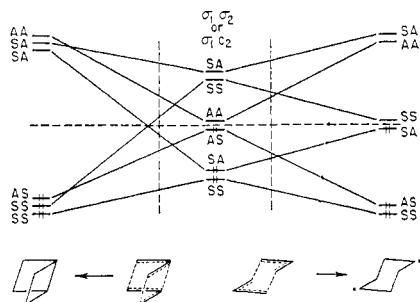

Figure 2.

approaching each other from infinity, in parallel planes, so as to pass through the symmetrical half-way points in the reaction surface for the actual Cope rearrangement. In these motions there are two symmetry elements: (1) σ_1, the plane passing through carbons 2 and 5, and (2) in the boat form a plane, σ_2, parallel to and half-way between the planes of the approaching radicals, in the chair form a twofold axis C_2 perpendicular to σ_1. To complete the correlation one must specify the end products of this hypothetical motion; these are a bicyclohexane in the boat approach, a cyclohexyl biradical in the chair pathway. Among the occupied levels the essential difference in the two pathways is in the behavior of the occupied SA level, which in the boat approach correlates to an antibonding σ orbital while in the chair form it goes over to a nonbonding radical level. The crucial point of the argument now is that reactions proceeding as in Figure 1 must pass at the half-way point through some point

(4) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and subsequent papers.

in the correlation diagrams of Figure 2, and that this point is approximately the same horizontal distance along in the two alternate pathways of Figure 2 (marked by vertical dashed lines). Further, at any such point the chair-like transition state is at lower energy as a result of the difference in correlation properties of the SA orbital. Or to rephrase the situation in terms of Figure 1, the occupied A level, which is 1–6 and 3–4 antibonding and consequently decreases in energy on approaching the transition state, decreases less in the boat form than in the chair. In this sense, the argument represents a further development of the simple orbital repulsion effect suggested by Doering and Berry.[2]

For the 5,5 sigmatropic shift, a variety of transition state conformations is available. Considerations similar to those given for the Cope rearrangement lead to the conclusion that of all these arrangements a chair-like transition state derived from a *cis,cis*-decatetraene (V) is clearly preferred.[5]

V
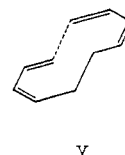
It should be emphasized that the effects discussed here are, not unexpectedly, small ones, and that in systems possessing special geometrical restraints which necessitate a boat-like transition state 3,3 sigmatropic changes take place with no special difficulty.[6]

(5) D. H. Gibson and R. Pettit, *J. Am. Chem. Soc.*, **87**, 2620 (1965), find evidence for homolytic cleavage and radical recombination in the pyrolysis of a *trans,trans*-decatetraene. The desired geometry (V) could not be attained in this case.

(6) J. M. Brown, *Proc. Chem. Soc.*, 226 (1965); W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); R. Merényi, J. F. M. Oth, and G. Schröder, *Ber.*, **97**, 3150 (1964); H. A. Staab and F. Vögtle, *Tetrahedron Letters*, 54 (1965).

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The Cycloheptatrienide Dianion Radical

Sir:

We wish to report the preparation of the first aromatic dianion radical.

The Hückel energy levels for the cycloheptatrienyl system are shown in Figure 1. The low-energy antibonding molecular orbitals ($E = \alpha - 0.44\beta$) are only half-filled in the cycloheptatrienide anion, the preparation of which was recently reported.[1] The possibility of addition of further electrons to the system is obvious. Reaction of tropyl methyl ether with a sodium mirror in purified tetrahydrofuran on a vacuum line[2] quickly gives the deep blue diamagnetic anion reported by Dauben and Rifi. Further reaction (20–40

(1) H. J. Dauben, Jr., and M. R. Rifi, *J. Am. Chem. Soc.*, **85**, 3041 (1963).

(2) The reaction vessel was of the usual type[3] except that it had five capillary side arms into which samples could be decanted at intervals for e.s.r. analysis. Pure alkali metal mirrors were distilled from a side arm and pure solvents were distilled from storage over potassium benzophenone. Reactions were run at room temperature.

(3) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964).