

errors are 15–17 kcal/mol for the boat and 10–11 kcal/mol for the chair.

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### The Linear Analysis of Labeling Experiments. An Application to Sigmatropic Rearrangements of 1,5-Hexadiene<sup>1</sup>

Sir:

The increasingly complex labeling studies of pericyclic processes<sup>2</sup> suggest opportunities for a new and more general analysis than has hitherto been customary. Illustratively applied here to the sigmatropic rearrangements<sup>2f</sup> of 1,5-hexadienes, this analysis discovers all ambiguities in previous stereochemical deductions,<sup>3a,4</sup> defines the experiments that might resolve them, and indicates which of these might succeed.

We begin by generating the complete set of nine sigmatropic carbon skeleton rearrangements, first by subjecting the  $C_{2v}$  conformer of 1,5-hexadiene to its [3,3] alternatives (Figure 1). Sighting along each axis, first at the front and then from the rear, each rotation is classified as clockwise or counterclockwise.<sup>5</sup> The third mechanism, so generated, is here called "twist" (rather than "antara-antara"<sup>2f,6</sup>), in part because its most symmetric transition state shares  $D_2$  symmetry with the well-known twist conformer of cyclohexane.<sup>7,8</sup> In addition, the (hitherto unrecognized) "plane" transition state is also antara-antara but in an obviously different way.

All four [1,3] sigmatropic mechanisms (each implicitly fourfold degenerate in Figure 2) have been recognized,<sup>2</sup>

(1) Taken, in part, from the Ph.D. Thesis of M. S. Benzon, Cornell University, 1972.

(2) E.g., (a) M. R. Wilcott, III, and C. J. Boriack, *J. Amer. Chem. Soc.*, **93**, 2354 (1971); (b) J. J. Gajewski and L. T. Burka, *ibid.*, **94**, 2554 (1972); (c) W. E. Doering, M. Franck-Neumann, D. Hasselmann, and R. L. Kaye, *ibid.*, **94**, 3833 (1972), and references cited therein; (d) J. E. Baldwin and R. H. Fleming, *J. Amer. Chem. Soc.*, **94**, 2140 (1972), and references cited therein. For reviews, cf. (e) S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968); (f) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); (g) P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970); (h) J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970); (i) J. J. Gajewski, *Mech. Mol. Migr.*, **4**, 1 (1972); (j) M. R. Wilcott, R. L. Cargill, and A. B. Sears, *Progr. Phys. Org. Chem.*, **9**, 25 (1972).

(3) (a) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962); (b) W. von E. Doering, V. G. Toscano, and G. H. Beasley, *ibid.*, **27**, 5299 (1971).

(4) M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.*, **94**, 7147 (1972) (preceding communication).

(5) Cf. R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965), and ref 2f.

(6) (a) T. Miyashi, M. Nitta and T. Mukai *J. Amer. Chem. Soc.*, **93**, 3441 (1971); (b) J. E. Baldwin and M. S. Kaplan, *ibid.*, **94**, 1794 (1972), and references cited therein.

(7) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966, p 76; J. D. Dunitz, *J. Chem. Educ.*, **47**, 488 (1970).

(8) The possibility of less symmetric transition states is not precluded.

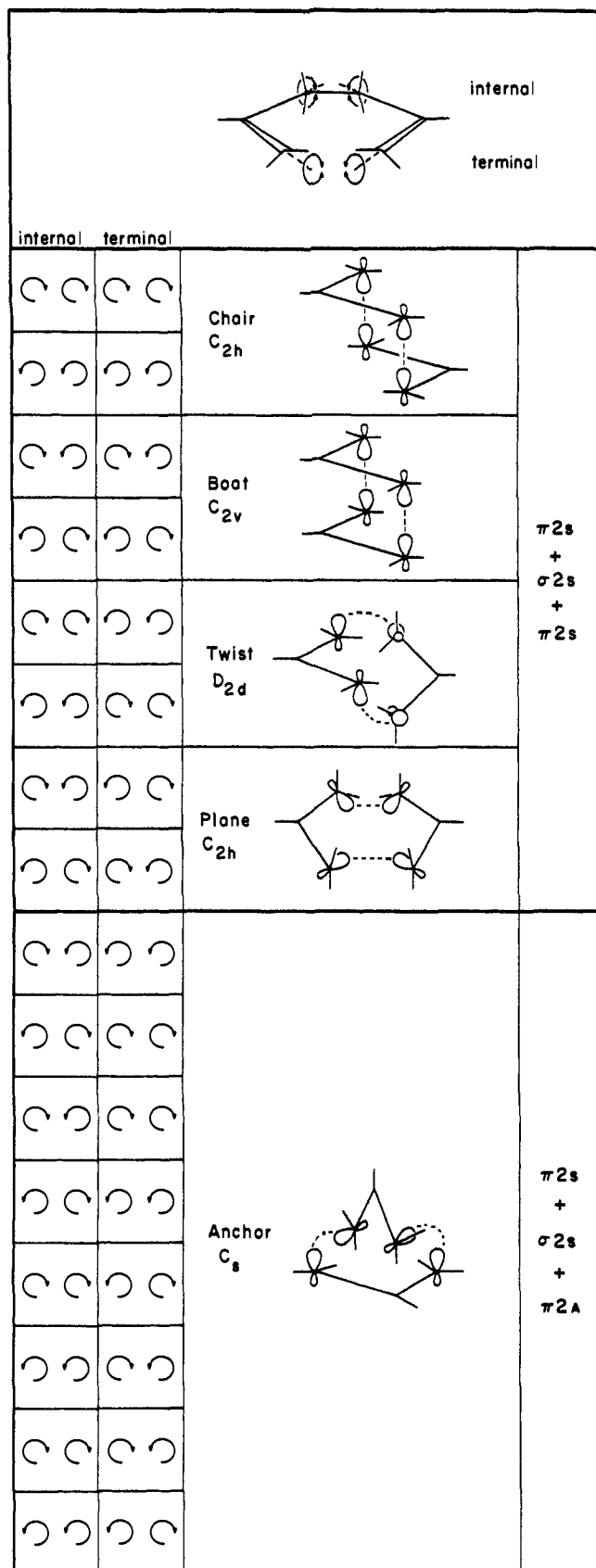


Figure 1. The complete set of [3,3] sigmatropic mechanisms.

if not by such names. These permit each first letter uniquely to label the appropriate mechanistic rate constant—e.g.,  $k_B$  for rearrangement through a boat transition state.

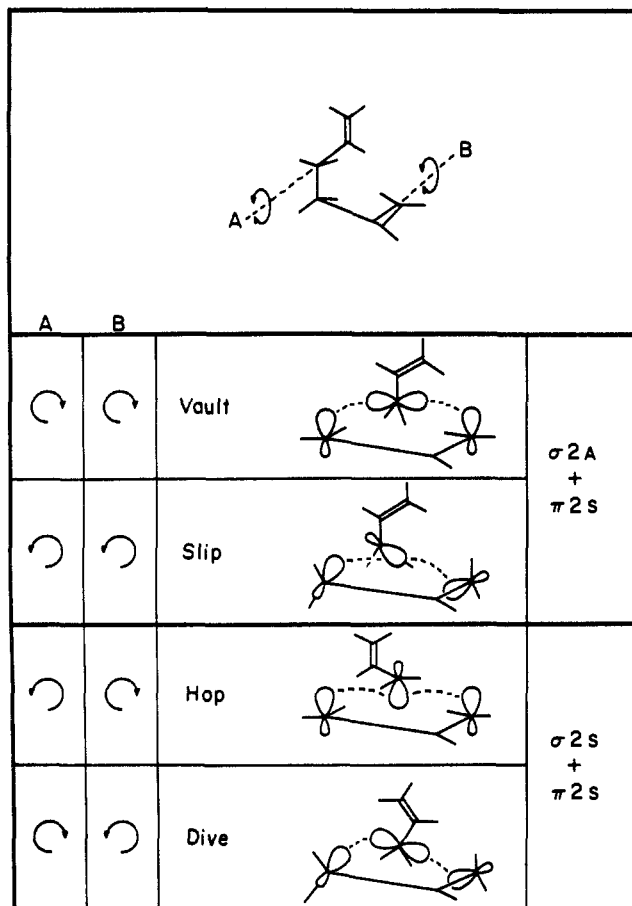


Figure 2. The complete set of [1,3] sigmatropic mechanisms.

As a basis vector ( $X$ ), we select the concentrations of the ten isomeric 1,3,4,6-tetradeuterio-1,5-hexadienes.<sup>4</sup> A matrix description<sup>9</sup> of the ten differential equations (1) also includes  $M$ , each of whose elements is an appropriate linear combination of the nine mechanistic rate constants.<sup>10</sup>  $M$  is first symmetrized by invoking

$$dX/dt = MX \quad (1)$$

microscopic reversibility<sup>9a</sup> and then diagonalized by exploiting isotopic permutational symmetry in close analogy with the traditional use of molecular symmetry in MO theory or in molecular spectroscopy.<sup>11</sup> Straight-forward integration then provides the ten equations (2)

$$x = x(0)e^{-\lambda t} \quad (2)$$

where  $x(0) \equiv x$  at  $t = 0$ . After cancelling constant factors, the eigenvectors are classified in Table I according to whether they are symmetric (s) or anti-symmetric (a) with respect to isotopic permutation—first at an internal carbon ( $R$ - $S$  inversion) and then at a terminal carbon ( $E$ - $Z$  isomerization).

Every experimentally determined rate constant must be one of the  $\lambda_i$  ( $i = 2 \rightarrow 10$ ).<sup>12</sup> Every experimental observation must be the product of a scalar and of a linear combination of  $\chi_i$ . For example, the ir analysis of the preceding communication<sup>4</sup> measures ( $\chi_9 - \chi_7$ ),

(9) (a) W. Jost, *Z. Naturforsch. A*, 2, 159 (1947); *Z. Phys. Chem.*, 195 (1950); (b) F. A. Matsen and J. L. Franklin, *J. Amer. Chem. Soc.*, 72, 3337 (1950); (c) J. Wei and C. D. Prater, *Advan. Catal.*, 13, 204 (1962).

(10) Although justified in this system, neither the assumption of first-order kinetics nor the neglect of isotope effects are mandatory prerequisites for such an analysis.

(11) F. A. Cotton, "Chemical Applications of Group Theory," 2nd ed, Wiley-Interscience, New York, N. Y., 1971.

(12)  $\chi_i = \chi_i(0)e^{-\lambda_i t}$  represents the conservation of matter.

Table I. Eigenvalues and Eigenvectors of  $M^a$ 

ss	$\lambda_1 = 0$	$16k_A$	$8k_H + 8k_D$	$ZRRZ + ZSSZ + ESSE + ERRE + ZRSZ + ERSE + ERSZ + ESRZ + ERRZ + ESSZ$
	$\lambda_5 =$	$8k_A + 4k_T$	$4k_H + 4k_D$	$ZRRZ + ZSSZ + ESSE + ERRE + ZRSZ + ERSE + ERSZ + ESRZ + ERRZ + ESSZ$
	$\lambda_7 =$	$4k_B + 4k_T$	$4k_H + 4k_D$	$ZRRZ + ZSSZ + ESSE + ERRE + ZRSZ + ERSE + ERSZ + ESRZ + ERRZ + ESSZ$
	$\lambda_9 =$	$4k_C + 4k_T$	$4k_H + 4k_D$	$ZRRZ + ZSSZ + ESSE + ERRE + ZRSZ + ERSE + ERSZ + ESRZ + ERRZ + ESSZ$
sa	$\lambda_3 =$	$2k_C + 2k_T$	$2k_B + 2k_S + 2k_H + 2k_D$	$ZRRZ + ZSSZ + ESSE + ERRE + ZRSZ + ERSE + ERSZ + ESRZ + ERRZ + ESSZ$
	$\lambda_6 =$	$2k_C + 2k_T$	$2k_B + 2k_S + 2k_H + 2k_D$	$ZRRZ + ZSSZ + ESSE + ERRE + ZRSZ + ERSE + ERSZ + ESRZ + ERRZ + ESSZ$
as	$\lambda_2 =$	$2k_C + 2k_T$	$2k_B + 2k_S + 2k_H + 2k_D$	$ZRRZ + ZSSZ + ESSE + ERRE + ZRSZ + ERSE + ERSZ + ESRZ + ERRZ + ESSZ$
aa	$\lambda_4 =$	$4k_C$	$4k_B$	$ZRRZ + ZSSZ + ESSE + ERRE + ZRSZ + ERSE + ERSZ + ESRZ + ERRZ + ESSZ$
	$\lambda_8 =$	$4k_C$	$4k_B$	$ZRRZ + ZSSZ + ESSE + ERRE + ZRSZ + ERSE + ERSZ + ESRZ + ERRZ + ESSZ$
	$\lambda_{10} =$	$2k_C + 2k_T$	$2k_B + 2k_S + 2k_H + 2k_D$	$ZRRZ + ZSSZ + ESSE + ERRE + ZRSZ + ERSE + ERSZ + ESRZ + ERRZ + ESSZ$

<sup>a</sup> Enclosing brackets for the concentration components of the  $\chi_i$  have been omitted for simplicity.

the molar discrepancy between those isomers that yield *meso*-dideuteriosuccinic acid and those that yield racemic. Since  $\chi_9(0) = 0$ , the observed "high-temperature rate constant" is  $\lambda_7$ . Its components include, but are not limited to,  $k_B$ . Three more critical deductions from Figure 1 and Table I<sup>1</sup> are: (a) the "low-temperature rate constant,"  $\lambda_9 = 4(k_C + k_T)$ , (b) the Doering-Roth experiments<sup>3a</sup> could not distinguish chair from twist mechanisms, and (c) either of these would have sufficed for the *ESRZ/ERSZ* structure proof.<sup>4,13</sup>

A more promising use of Table I is in the design of new experiments to remove such ambiguities. For example, at temperatures where only  $k_C$  and/or  $k_T$  are significant, their relative contributions could be evaluated by measuring either of two rate constants—that for racemizing an optically active mixture containing only *ERSZ* and/or *ESRZ* ( $\chi_4 - \chi_8$ ) or for equilibrating any experimentally convenient members of the *ZRRZ*, *ZSSZ*, *ESSE*, and *ERRE* quartet ( $\chi_4 + \chi_8$ ).<sup>14</sup> In either case, the experimental rate constant ( $4k_C$ ) could then be compared with the known value of  $\lambda_9$ ,  $4(k_C + k_T)$ .<sup>3b</sup>

A comparably complete resolution of  $\lambda_7$  is significantly more difficult and, perhaps, impossible. The relative contribution of [1,3] and [3,3] components is accessible by comparing  $\lambda_7$  with  $8(k_V + k_S + k_H + k_D)$ , the eigenvalue obtained by equilibrating a 1,4-disubstituted 1,5-hexadiene with its 1,6 and 3,4 isomers.<sup>15</sup> Further progress would then either require that  $k_C < \lambda_7$  (which seems unlikely) or  $\lambda_5 > 0$  (in violation of orbital symmetry control).<sup>2f</sup> Otherwise,  $k_C$  would dominate all other possible eigenvalues of both doubly and quadruply labeled 1,5-hexadienes. No further information could then be obtained.

Obviously, the utility of such an analysis in no way disparages the suggestive power of more empirically justified mechanistic criteria.<sup>16</sup> It does, however, emphasize that many, still unrealized, mechanistic distinctions can be made with complete rigor. Others cannot.

**Acknowledgment.** We are grateful for the partial financial assistance provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (GP 15863) and for the careful criticism of R. C. Fay.

(13) M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.*, **94**, 5119 (1972).

(14) Gajewski<sup>21</sup> has independently discovered the equivalent of one such possibility.

(15) Algebraic details of the analysis of doubly and quadruply labeled 1,5-hexadienes have been made available to the Editor and referees of this manuscript and will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number JACS-72-7149. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(16) For example,  $\Delta S^\ddagger \approx 4$  is more consistent with a "vault" or "slip" than with a "boat" or "plane" transition state. An extended search for the "twist" has (thus far) yielded no authentic examples,<sup>6b</sup> nor do we know of an authentic symmetry-forbidden thermal reaction of any hydrocarbon.

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## Mechanisms of Photochemical Reactions in Solution. LXXII.<sup>1</sup> Electronic Pathways in the Photodissociation of 3-Methyl-1-phenoxybut-2-ene

Sir:

We recently reported evidence that photorearrangement of phenyl acetate to *o*- and *p*-hydroxyacetophenones<sup>2</sup> occurs *via* homolysis of the O-C(acyl) bond followed by radical recombination or hydrogen abstraction,<sup>2</sup> and not by concerted intramolecular pathways as had been previously suggested.<sup>3</sup> The electronic steps which lead to dissociation have not yet been elucidated, although Shizuka, *et al.*,<sup>4,5</sup> have proposed that acetanilide and phenyl acetate dissociate *via* (predissociative) triplet states of the N-C(acyl) or O-C(acyl) bonds. A similar mechanism had earlier been advanced by Porter<sup>6,7</sup> to explain the formation of benzyl radicals in the photolysis of toluene. Even though such a transition is spin forbidden, Porter concluded that the quantum yield was sufficiently low (*ca.*  $10^{-2}$ ) to be in qualitative agreement with known rates of intersystem crossing. In applying this same model to their studies, Shizuka, *et al.*, have concluded that the considerably larger quantum yields for photodissociation of acetanilide and phenyl acetate (0.25 and 0.51, respectively) result from enhanced intersystem crossing due to vibronic coupling of the aromatic  $S_1(\pi, \pi^*)$  and carbonyl  $T_1(n, \pi^*)$  states. In a sense this invokes some of the characteristics which usually lead to efficient crossing of  $S_1(n, \pi^*)$  states of simple carbonyl compounds to triplets.

Analogous photorearrangements of phenyl allyl ethers are of interest since there is no obvious basis for expecting interchromophoric coupling to enhance the rate of an  $S_1(\pi, \pi^*) \rightarrow {}^3\sigma(O-C)$  intersystem crossing (*vide infra*). We therefore chose  $\gamma, \gamma$ -dimethylallyl phenyl ether (3-methyl-1-phenoxybut-2-ene) (1) for photochemical study.<sup>8</sup>

Irradiation of 1 at 254 nm in either isopropyl alcohol or cyclohexane solution at room temperature led to the formation of six products. The quantum yields for the disappearance of 1 and for the appearance of products 2-7 are shown in Table I.<sup>10</sup>

We also irradiated 1 at 254 nm at atmospheric pressure in a gas-phase flow system, which has been previously described.<sup>2</sup> Products 2-7 were observed in relative yields not greatly different from those seen in solution. Addition of 25 Torr partial pressure of nitric oxide quenched the formation of products 3-7; some phenol and several uncharacterized products were detected by glpc.

Product ratios obtained both in solution and in the vapor phase, as well as the total quenching of 3-7

(1) Part LXXI: Y. L. Baharel, D. J. MacGregor, T. L. Penner, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 637 (1972).

(2) J. W. Meyer and G. S. Hammond, *ibid.*, **92**, 2187 (1970).

(3) D. Bellus, *Advan. Photochem.*, **8**, 109 (1971).

(4) H. Shizuka and I. Tanaka, *Bull. Chem. Soc. Jap.*, **42**, 909 (1969), and references therein.

(5) H. Shizuka, T. Morita, Y. Mori, and I. Tanaka, *ibid.*, **42**, 1831 (1969).

(6) G. Porter, *Chem. Soc., Spec. Publ.*, No. 9, 139 (1957).

(7) G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 1595 (1958).

(8) Kelly, Pinhey, and Rigby reported<sup>9</sup> that the compound undergoes photochemical rearrangement, although their study lacked the quantitative character needed for our purposes.

(9) D. P. Kelly, J. T. Pinhey, and R. Rigby, *Aust. J. Chem.*, **22**, 977 (1969), and references therein.

(10) Details of product isolation and quantum yield determinations will be reported later.