addition. The solution was placed in a freezer at −28 °C overnight during which time a few clear, prismatic crystals grew.

Excess solvent was removed via syringe. An appropriately sized crystal was selected and rapidly mounted on the end of a glass fiber in a cold stream ($\cong$ −100 °C) of dry N_2 on the diffractometer. Preliminary rotation photographs were followed by X-ray data collection in the range $3.5° \leq \theta \leq 45°$. The X-ray diffraction experiment is summarized in Table I and in the supplementary material.[15]

THF-Solvated Potassium Enolate of 3,3-Dimethyl-2-butanone (4). A quantity of 3.99 g (20 mmol) of crystalline potassium hexamethyldisilazane[10] was placed in a reaction vessel and covered with heptane (4–6 mL). This suspension was cooled to 0 °C and a solution of 1.90 g (19 mmol) of 3,3-dimethyl-2-butanone and 1.44 g (20 mmol) of THF in heptane (5 mL) was added dropwise over a period of 30 min. Magnetic stirring was maintained throughout the addition. When the addition was complete a small quantity of THF ($\cong$0.5 mL) was added to dissolve the remaining solids. The solution was placed in a freezer at −28 °C overnight during which time the enolate crystals formed. No yield was determined.

Excess solvent was removed with a syringe. A crystal was selected and mounted on the diffractometer as with the previous compound. The parameters of the X-ray diffraction experiment are summarized in Table I and in the supplementary material.[15]

Acknowledgment. We thank J. H. Madaus (Callery Chem. Co.) for providing us with a generous supply of crystalline KHMDS and Dr. J. P. Springer (Merck, Sharpe and Dohme Research Labs) for a search of the Cambridge Crystallographic Database. We also thank Profs. D. Seebach (E.T.H.) and P. v. R. Schleyer (Erlangen-Nürnberg) for preprints of their work. Funds to support this work were provided by the BRSG grant administered through Brown University. The Nicolet X-ray crystallographic system was purchased with an instrument grant from the NSF (CHE-8206423).

Registry No. 1, 99016-93-0; **2**, 99016-94-1; **3**, 99016-95-2; *t*-$BuCOCH_2^- \cdot Li^+$, 70367-67-8; *t*-$BuCOCH_2^- \cdot Na^+$, 99016-96-3; *t*-$BuCOCH_2^- \cdot K^+$, 55440-76-1; 3,3-dimethyl-2-butanone, 75-97-8.

Supplementary Material Available: Crystallographic details including anisotropic thermal parameters, bond lengths, and angles for compounds **3** and **4** (14 pages). Ordering information is given on any current masthead page.

Deuterium Kinetic Isotope Effects in the 1,4-Dimethylenecyclohexane Boat Cope Rearrangement

Joseph J. Gajewski* and Jose Leonardo Jimenez[†]

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405.
Received February 25, 1985. Revised Manuscript Received October 1, 1985

Abstract: In order to examine the extent of bond making in the boat-like 3,3-sigmatropic shift transition states, *trans*-2,3-dimethyl-1,4-dimethylenecyclohexane (T) and its exomethylene tetradeuteria derivative (TXD) were prepared. The 3,3-shift of TXD at 305 °C results in interconversion of starting material, 5,5,6,6-tetradeuterio-*trans*-2,3-dimethyl-1,4-dimethylenecyclohexane (TND), and 2,2,3,3-tetradeuterio-*anti*-1,4-diethylidenecyclohexane (AD). A kinetic analysis of the first-order rate equations for the three-component system in both protio and deuterio species by numerical integration of the data and simplex minimization of the rate constants with symmetry and the assumption of no equilibrium or kinetic isotope effect on the TND-AD reaction gives a bond making kinetic isotope effect of 1/1.04 (0.04). The equilibrium isotope effects observed are 1/1.16 (0.04) so that the extent of bond formation in this boat-like bicyclo[2.2.2]octyl transition state is roughly 25%, a value to be compared with ca. 67% in chair-like acyclic 3,3-shift transition states. This rules out significant intervention of a bicyclo[2.2.2]octane-1,4-diyl intermediate or transition state.

Double allylic transposition of 1,5-hexadienes under thermal conditions is a subset in the category of 3,3-sigmatropic shifts. The general reaction type was discovered by Claisen with allyl vinyl ethers,[1] and Hurd first attempted to extend the reaction to dienes.[2] Cope provided numerous examples of the reaction in all carbon cases.[3] The reaction rate does not respond to changes in solvent polarity indicating a nonpolar mechanism. There is the strong suggestion that the reaction is concerted since the rate is far faster than what would be expected for cleavage to two allyl radicals; the pairwise interchange of C-1 and C-6 with C-3 and C-4 is also consistent with this hypothesis. There is evidence, from secondary deuterium kinetic isotope effects, that the transition-state structure, vis-à-vis the extent of C-3,C-4 bond breaking and C-1,C-6 bond making, is variable depending on the radical stabilizing ability and position of substituents.[4] Suggestions made by Dewar that a cyclohexane-1,4-diyl is an intermediate in the reaction[5] are not consistent with the isotope effects.

The Woodward–Hoffmann rules[6] suggest that there are four possible concerted transition states: chair, boat, twist, and plane. Recently Benner has shown that the latter two, which are antarafacial–antarafacial processes, may not be involved at temperatures below the cleavage temperature of 1,3,4,6-tetramethyl-1,5-hexadienes.[7] But the distinction between chair and boat was made much earlier by Doering and Roth, who examined the stereochemistry of the rearrangements of *threo*- and *meso*-3,4-dimethyl-1,5-hexadiene.[8] The boat pathway was ca. 6 kcal/mol higher in energy than the chair.

Goldstein examined the high-temperature rearrangement of a deuterated 1,5-hexadiene and also found evidence for a boat process 5.8 kcal/mol higher in energy.[9a] Further, he determined the activation enthalpy and entropy for the boat reaction to be

---

[†] Taken wholey from the Ph.D. Thesis of J.L.J., Indiana University, December 1984.

(1) For a review of the Claisen and Cope rearrangements see: Rhodes, S. J.; Rawlins, N. R. *Org. React.* **1970**, *22*, 1.

(2) Hurd, C. D.; Pollack, M. A. *J. Org. Chem.* **1939**, *3*, 550.

(3) (a) Cope, A. C.; Hardy, E. M. *J. Am. Chem. Soc.* **1940**, *62*, 441. (b) Cope, A. C.; Hofmann, C. M.; Hardy, E. M. *Ibid.* **1941**, *63*, 1852. (c) Cope, A. C.; Levy, H. *Ibid.* **1944**, *66*, 1684.

(4) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693.

(5) Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1973**, *95*, 290; **1977**, *99*, 4417. Dewar, M. J. S.; Healy, E. F. *Ibid.* **1984**, *106*, 7127 and references contained therein.

(6) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(7) Benner, C. W.; Ph.D. Thesis, Indiana University, Dec. 1984; paper in preparation.

(8) Doering, W. von E.; Roth, W. R. *Tetrahedron* **1962**, *18*, 67.

(9) (a) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 7149. (b) Shea, K. J.; Phillips, R. B. *Ibid.* **1980**, *102*, 3156.

0002-7863/86/1508-0468$01.50/0

Table I. Mole Percent T from Pyrolysis at 305.0 °C

time, s	T
0	100
5400	82.593 ± 0.2110
10800	67.4880 ± 0.2050
14400	60.3225 ± 0.1522
21600	51.8350 ± 0.3190
28800	43.2700 ± 0.2390
36000	37.8611 ± 0.2207
43200	33.0364 ± 0.2067
54000	28.1134 ± 0.1685
64800	23.1590 ± 0.0849
68400	22.9092 ± 0.2377
86400	19.0579 ± 0.1945
259200	14.5586 ± 0.3585

44.7 kcal/mol and −3.0 eu, respectively. These parameters stand in contrast to those usually observed in acyclic, chair-like 3,3-shifts where the activation enthalpy is ca. 36 kcal/mol and the activation entropy is −14 eu.[10] Subsequently Gajewski, Hoffman, and Shih found that 1,4-bis(dideuteriomethylene)cyclohexane underwent a necessarily boat-like 3,3-shift above 300 °C. While the activation free energy of the reaction was also 6 kcal/mol higher in energy than 3,3-shifts in acyclic systems, the activation parameters were similar to those for chair-like reactions.[11] Later Shea examined a 3,3-shift which was constrained to proceed by either a boat or a plane transition state and found an activation entropy similar to that reported by Goldstein.[9b] The kinetics of the 1,4-dimethylenecyclohexane rearrangement were redetermined by Doering and Troise, who found that the activation enthalpy is 43.9 kcal/mol and the activation entropy is −4.6 eu.[12] Reexamination of our data[10] indicates that only one rate constant deviates substantially from Doering's kinetics, suggesting that there was an error in reading the potentiometer which reported the voltage of the copper–constantan thermocouples used as that time. Thus the suggestion from the kinetics is that the boat-like transition state is "looser" than that involved in chair-like rearrangements. This paper tests this hypothesis by determining the secondary deuterium kinetic isotope effects at the terminal carbons of a 1,4-dimethylenecyclohexane.

Results

The product from the 3,3-sigmatropic shift of *trans*-2,3-dimethyl-1,4-dimethylenecyclohexane (T) is *anti*-1,4-diethylidenecyclohexane (A) as judged by its ^{1}H NMR spectrum. The ring methylenes appear as a AA′BB′ spectrum with coupling constants consistent with the two sets of protons being on adjacent carbons. This ^{1}H NMR stands in contrast to that obtained from the product of 3,3-shift of *cis*-2,3-dimethyl-1,4-dimethylenecyclohexane (C) which consists of two proton singlets for the ring methylenes, indicating that this material is *syn*-1,4-diethylidenecyclohexane (S). These results reinforce not only one another but also the boat-like nature of this 3,3-shift which apparently is concerted since no 1,3-shift products are formed. This observation is consistent with those provided by Hoffman, who degraded the product mixture from 1,4-bis(dideuteriomethylene)cyclohexane and found only 3,3-shift deuterium isomers.[11]

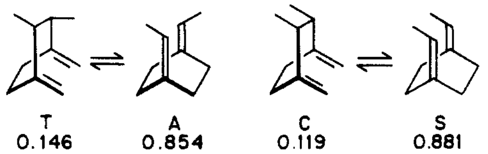


Table II. Mole Percents from Pyrolysis of TXD at 305.0 °C

time, s	TND	TXD	AD
0	0.0	100.0	0.0
5400	6.3481 ± 0.0699	75.9438 ± 0.3241	17.7081 ± 0.2697
10800	9.6019 ± 0.1545	60.6923 ± 0.3102	29.7058 ± 0.3794
21600	12.5667 ± 0.1095	36.8510 ± 0.1458	50.5824 ± 0.1978
28800	13.0290 ± 0.1445	32.5115 ± 0.2953	54.4592 ± 0.2803
32400	13.0643 ± 0.1372	26.0072 ± 0.2493	60.9285 ± 0.3850
39600	12.5401 ± 0.0676	19.7232 ± 0.1652	67.7366 ± 0.2329
46800	11.6123 ± 0.1220	15.8031 ± 0.1546	72.8546 ± 0.2758
50400	11.6455 ± 0.1405	14.9192 ± 0.2142	73.4352 ± 0.2987
54000	12.0309 ± 0.1573	14.3831 ± 0.4131	73.5400 ± 0.4773
86000	9.2394 ± 0.0867	8.5534 ± 0.0942	82.2072 ± 0.1789
284000	7.6095 ± 0.1502	6.5728 ± 0.1640	85.8184 ± 0.3121

Table III. Mole Percent C from Pyrolysis at 305.0 °C

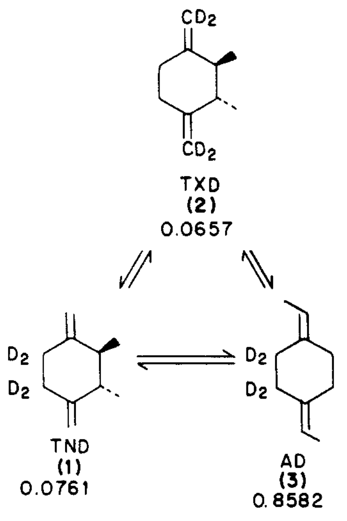
time, s	CD
0	100.0
10800	78.7400 ± 0.0173
21600	68.9985 ± 0.2804
43200	48.0293 ± 0.4165
93600	24.6508 ± 0.0509
259200	11.8722 ± 0.2198

Table IV. Mole Percent CD from Pyrolysis at 305.0 °C

time, s	CD
0	100.0
10800	82.5876 ± 0.6238
54000	40.5581 ± 0.5407
86400	26.0141 ± 0.1214
259200	10.9950 ± 0.0801

The equilibrium concentrations and constants for the interconversions of T and A and of C and S at 305 °C are given below the structures and indicate the usual stability of the more highly substituted double bond isomers.

At 305 °C the reaction of *trans*-2,3-dimethyl-1,4-(dideuteriomethylene)cyclohexane (TXD) led to an additional peak in the GC whose retention time was very close to that of starting material. This peak was assigned the structure *trans*-2,3-dimethyl-5,5,6,6-tetradeuterio-1,4-dimethylenecyclohexane (TND). Given the reversibility of the T to A interconversion, this third material must be present. What is remarkable is the efficiency of the DB-5 capillary column. This good fortune allows high precision quantification of the three components of the reaction mixture and avoids the difficulty inherent in a ^{1}H NMR analysis on small samples obtained from each of the many kinetic runs. Importantly, the relative equilibrium concentration of TXD and TND is that expected for an equilibrium isotope effect at this temperature (see scheme below). The kinetic data for reaction of T, TXD, C, and CD at 305 °C are given in Tables I, II, III, and IV, respectively.



---

[10] Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981.

[11] Gajewski, J. J.; Hoffman, L. K.; Shih, C. N. *J. Am. Chem. Soc.* **1974**, *96*, 3705.

[12] Troise, C. A. *Diss. Abstr. Int. B* **1979**, *39*, 5936. Doering, W. von E.; Troise, C. A. *J. Am. Chem. Soc.*, submitted. We thank Prof. Doering for a preprint of this paper. Indeed, it prompted submission of this manuscript which appears here in almost exactly the same form as J.L.J.'s Thesis which was written before Doering's manuscript was made available to us.

To standardize the kinetic analysis, the reaction schemes from both T and TXD were treated as three-component reversible systems. In the former case, two of the components, designated **1** and **2** in the scheme, were starting material, each with starting mole fractions equal to 0.500; the product A is designated as **3**; and the two rate constants $k_{1,3}$ and $k_{2,3}$ must be equal. In these schemes, equilibrium constants are necessary boundary conditions, and the set determined from T and from TD had the following values:

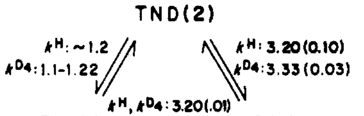
$$[K^H/K^D](1,2) = 1/1.16\ (0.04) \rightarrow 1/1.16$$

$$[K^H/K^D](1,3) = 1/1.04\ (0.04) \rightarrow 1.00$$

$$[K^H/K^D](2,3) = 1/1.11\ (0.04) \rightarrow 1/1.16$$

From the structures, no equilibrium isotope effect (EIE) would be expected for $K(1,3)$, and the EIE for $K(1,2)$ should equal that for $K(2,2)$. Indeed, this is the case within the standard deviation in the concentrations. Thus, the starting point for the kinetic analysis is the adjusted equilibrium concentrations to reflect the expected EIE as indicated by the arrows in the equations above.

The experimental data were submitted to the SMPLXKS program (see Appendix) with the adjusted equilibrium constants. Since there was more data at longer reaction times, the residuals from the data at very early reaction times were weighted twice as much as those from data near equilibrium to allow the simplex response function (sum of the squares of the residuals) to respond to data that determine the rate constants not the equilibrium constants. When starting with T, the rate constant $k_{1,2}$ could be varied from 1.0 to 1.5 × 10^{-5} s^{-1} without any effect on $k_{1,3}$ and $k_{2,3}$. However, $k_{1,3}$ and $k_{2,3}$ could vary only from 3.10 to 3.30 × 10^{-5} s^{-1} without effect on the average residual of each concentration (0.013). Beyond these rate constant limits, the average residual increased sharply, again independent of $k_{1,2}$. Given that there should be no kinetic isotope effect on the **1** to **3** conversion for the same reason that there should be no equilibrium IE, $k_{1,3}$ (from TND (**2**)) was fixed at values from 3.10 to 3.30 × 10^{-5} s^{-1} giving values of $k_{1,2}$ = 1.10 to 1.22 × 10^{-5} s^{-1} and $k_{2,3}$ = 3.31 to 3.36 × 10^{-5} s^{-1}, all without any noticeable change in the average residual (0.012). When all ks were allowed to "float" in the minimization of the data from TXD, k_{23} = 3.30 × 10^{-5} s^{-1} and k_{12} = 1.10 × 10^{-5} s^{-1}. Thus the kinetic isotope effect on k_{23} (TXD to AD) is $k^H/k^{D_4} = 1/1.04\ (0.04)$. If the assumption of no EIE on $K(1,3)$ is not made, the KIE becomes 1/1.08 (0.04). Because the value of $k_{1,2}$ from T is virtually indeterminant, it is not reasonable to estimate the KIE on this path. From $k_{1,2}$ (for TXD), however, it is clear that T indeed undergoes a direct 3,3-shift to itself at roughly one-third the rate of its 3,3-shift to A.



k(i<j)s in units of 10^{-5} $^{-1}$ at 305.0 °C

Discussion

Hoffman examined the product distribution and activation parameters for the degenerate rearrangement of 1,4-bis(dideuteriomethylene)cyclohexane at temperatures above 300 °C.[11] Degradation of the product mixture revealed only 3,3-shift reactions and no 1,3-shifts. The activation enthalpy was 39.0 kcal/mol and the activation entropy was −13.8 eu. The activation free energy for this necessarily boat-like reaction is 6 kcal/mol higher than that generally observed in 3,3-shifts of acyclic 1,5-dienes which proceed via chair-like transition states. While not important for any conclusions drawn from the observations, the very low activation entropy and enthalpy was surprising. Every other boat-like rearrangement examined has higher activation parameters[9,11] which are consistent with a very loose transition state–one that more resembles two allyl radicals than a cyclohexane-1,4-diyl which is the extreme result of complete C-1,C-6 bond making and no C-3,C-4 bond breaking.[4]

Fortunately, the kinetics of the rearrangement were redetermined in Prof. Doering's laboratory and found to have roughly the same activation entropy as that in the other boat-like rearrangements.[12]

The current study was initiated in order to test the hypothesis derived from activation parameters that boat 3,3-shifts indeed had transition states that were "looser" than chair-like 3,3-shifts. In simple acyclic systems, the secondary deuterium kinetic isotope effects on the terminal methylenes of 1,5-dienes are inverse, as expected, and are roughly two-thirds the magnitude of the effect predicted from the equilibrium isotope effects for the same compounds. Since it is very difficult to measure the rate of a truly degenerate rearrangement (one with no labels), the 2,3-dimethyl-1,4-dimethylenecyclohexanes were chosen for study. Since the rate constant for interconversion of the cis isomer and *syn*-1,4-diethylidenecyclohexane could be determined with only moderate precision for reasons that are not obvious, the *trans*-dimethyl isomer and its exocyclic tetradeuterio derivative were prepared. An unanticipated bonus was the capillary GC separation of the two deuterio isomers, TXD (starting material) and TND. This provided relatively high precision data for subsequent numerical analysis. Unfortunately, the small amount of TND formed precluded its structural identification to beyond any doubt; however, this material must be formed in the reaction, and the only other reasonable products are the 1,3-shift products which would have to be formed from the deuterated derivative but not from the protio starting material. Further, at equilibrium there should be formed two 1,3-shift isomers, not just one.

The numerical integration coupled with a simplex minimization started not with the average equilibrium mole fractions from the GC analysis but with mole fractions that provided no equilibrium isotope effect on the TND to AD interconversion. The adjusted equilibrium mole fractions were, however, within experimental error of the average values. The justification for little, if any, equilibrium isotope effect comes from the numerous calculations of deuterium isotope fractionation factors by Shiner which indicate little effect of β substituents and none by γ substituents.[13]

Given these slightly adjusted equilibrium mole fractions, the only other assumption is that of little kinetic isotope effect on the TND to AD interconversion. The justification for this assumption is the same as that for the EIE. It is necessary to note that while the $k_{1,3}$ (TND to AD) in the protio case is fairly precisely determined, $k_{1,3}$ in TND to AD itself is poorly determined, but varying its value over a large range had little effect (1%) on $k_{2,3}$, the TXD to AD rate constant. Thus the value of $k_{2,3}$ does not depend strongly on the assumption of no kinetic isotope effect on $k_{1,3}$. Similarly, the rate constants $k_{2,3}$ and $k_{1,3}$ in the protio case can be determined with good precision since they do not depend on $k_{1,2}$, which cannot be determined with any precision since a 1:1 mixture of **1** and **2** (a necessary division of T to apply the same scheme) is present. Further, the requirement that $k_{2,3}$ and $k_{1,3}$ be equal further restricts the values of these rate constants. This is accompanied by fixing all of the equilibrium constants with $K_{2,3} = K_{1,3}$ and $K_{1,2} = 1.0$ in the protio case. Finally, it is not unreasonable that $k_{1,3}$ in the deuterio case be determined only poorly by the data. This is because starting material is **2**. The lack of sensitivity of $k_{2,3}$ in the deuterio case testifies to this expectation.

Given the indeterminacy of $k_{1,2}$ in the protio case and the necessarily imprecise determination of $k_{1,3}$ in the tetradeuterio case, the only pathway whose rate constants can be determined in both cases is **2** to **3** (TXD to AD), and the kinetic isotope effect here is inverse and is only 25 ± 25% of the equilibrium isotope effect. Given the assumption that factors affecting the kinetic isotope effect are no different than those affecting the EIE, the conclusion is that, indeed, the transition state is looser in this boat-like 3,3-shift. The assumption of similar factors affecting KIEs and EIEs is generally valid so long as a hydrogen (or

---

[13] Hartshorn, S. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 9002. Also more recent unpublished results.

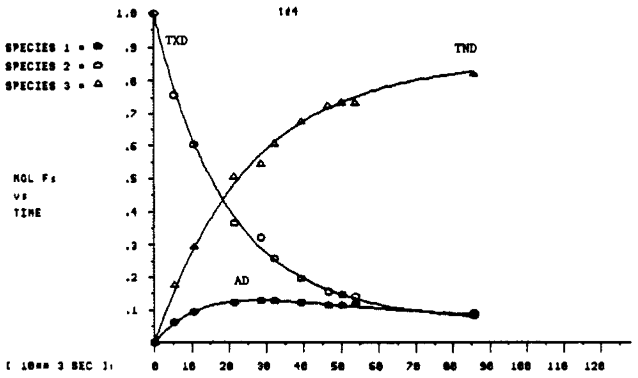


Figure 1. Conversion of TND, TXD, and AD at 305.0 °C.

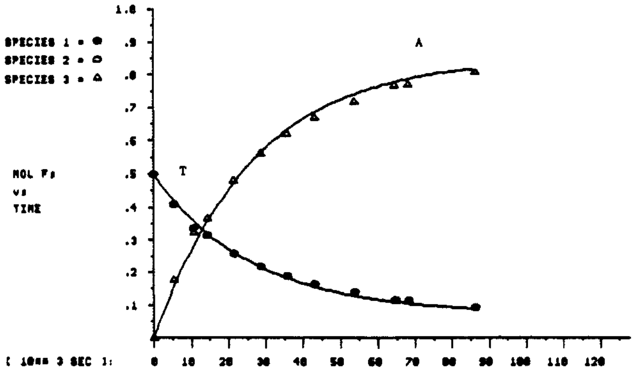
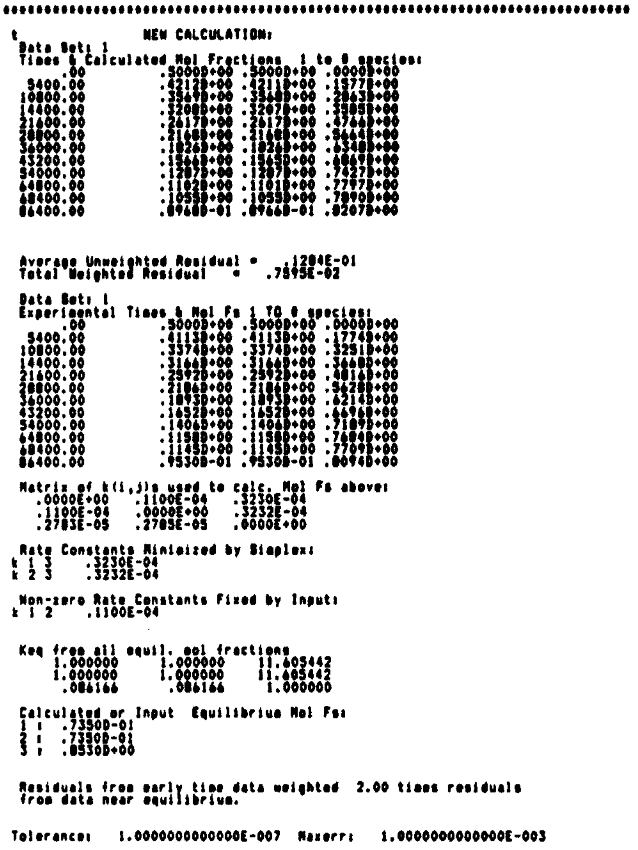


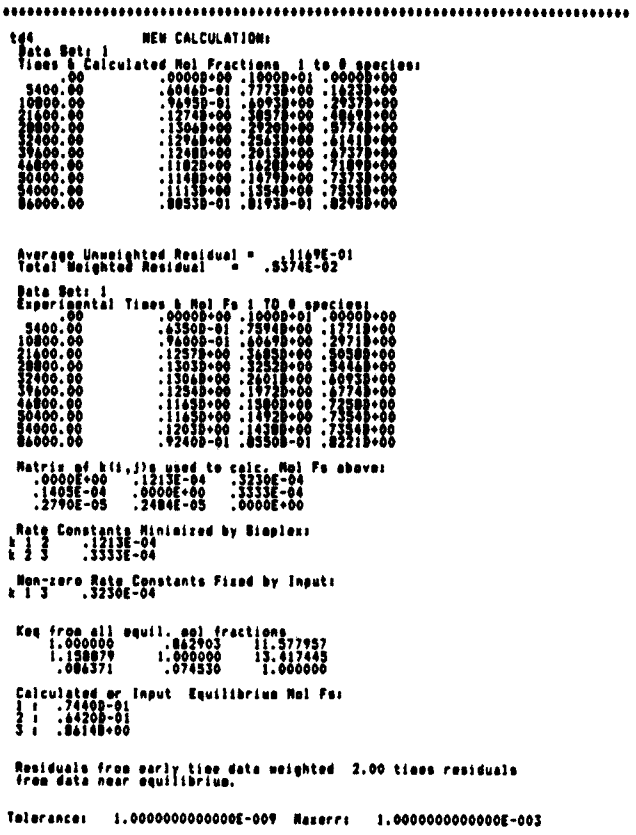
Figure 2. Conversion of T to A at 305.0 °C.



```
****************************************************************************

t                NEW CALCULATION:
 Data Set: 1
 Times & Calculated Mol Fractions  1 to 8 species:
      .00              .5000D+00 .5000D+00 .0000D+00
  5400.00              .4212D+00 .4211D+00 .1577D+00
 10800.00              .3569D+00 .3568D+00 .2863D+00
 14400.00              .3208D+00 .3207D+00 .3585D+00
 21600.00              .2617D+00 .2617D+00 .4766D+00
 28800.00              .2168D+00 .2168D+00 .5664D+00
 36000.00              .1826D+00 .1826D+00 .6348D+00
 43200.00              .1566D+00 .1565D+00 .6869D+00
 54000.00              .1287D+00 .1287D+00 .7427D+00
 64800.00              .1102D+00 .1101D+00 .7797D+00
 68400.00              .1055D+00 .1055D+00 .7890D+00
 86400.00              .8966D-01 .8966D-01 .8207D+00


 Average Unweighted Residual =  .1284E-01
 Total Weighted Residual   =   .7595E-02

 Data Set: 1
 Experimental Times & Mol Fs 1 TO 8 species:
      .00              .5000D+00 .5000D+00 .0000D+00
  5400.00              .4113D+00 .4113D+00 .1774D+00
 10800.00              .3374D+00 .3374D+00 .3251D+00
 14400.00              .3166D+00 .3166D+00 .3668D+00
 21600.00              .2592D+00 .2592D+00 .4816D+00
 28800.00              .2186D+00 .2186D+00 .5628D+00
 36000.00              .1893D+00 .1893D+00 .6214D+00
 43200.00              .1652D+00 .1652D+00 .6696D+00
 54000.00              .1406D+00 .1406D+00 .7189D+00
 64800.00              .1158D+00 .1158D+00 .7684D+00
 68400.00              .1145D+00 .1145D+00 .7709D+00
 86400.00              .9530D-01 .9530D-01 .8094D+00

 Matrix of k(i,j)s used to calc. Mol Fs above:
   .0000E+00   .1100E-04   .3230E-04
   .1100E-04   .0000E+00   .3232E-04
   .2783E-05   .2785E-05   .0000E+00

 Rate Constants Minimized by Simplex:
k 1 3    .3230E-04
k 2 3    .3232E-04

 Non-zero Rate Constants Fixed by Input:
k 1 2    .1100E-04


 Keq from all equil. mol fractions
     1.000000      1.000000     11.605442
     1.000000      1.000000     11.605442
      .086166       .086166      1.000000

 Calculated or Input  Equilibrium Mol Fs:
 1 :  .7350D-01
 2 :  .7350D-01
 3 :  .8530D+00


 Residuals from early time data weighted  2.00 times residuals
 from data near equilibrium.


Tolerance:   1.0000000000000E-007  Maxerr:   1.0000000000000E-003
```

Figure 3. Conversion of T and A at 305.0 °C.

deuterium) is not involved in reaction coordinate motion which would superimpose a primary KIE on the secondary one being examined. Since no hydrogen transfers are involved here, a fact further supported by Hoffman's degradation and subsequent mass spectral analysis of the deuterated parent material, one possible objection can be countered. With respect to the other, it is important to recognize that rotation of methylene groups in the transition state will also superimpose a primary KIE on a reaction. This is the case in reactions examined by Dolbier,[14] by Crawford,[15]



```
****************************************************************************

t44              NEW CALCULATION:
 Data Set: 1
 Times & Calculated Mol Fractions  1 to 8 species:
      .00              .0000D+00 .1000D+01 .0000D+00
  5400.00              .6046D-01 .7773D+00 .1623D+00
 10800.00              .9695D-01 .6093D+00 .2937D+00
 21600.00              .1274D+00 .3857D+00 .4869D+00
 28800.00              .1306D+00 .2920D+00 .5774D+00
 32400.00              .1296D+00 .2563D+00 .6141D+00
 39600.00              .1248D+00 .2015D+00 .6737D+00
 46800.00              .1182D+00 .1628D+00 .7189D+00
 50400.00              .1148D+00 .1479D+00 .7373D+00
 54000.00              .1113D+00 .1354D+00 .7533D+00
 86000.00              .8853D-01 .8193D-01 .8295D+00


 Average Unweighted Residual =  .1169E-01
 Total Weighted Residual   =   .8374E-02

 Data Set: 1
 Experimental Times & Mol Fs 1 TO 8 species:
      .00              .0000D+00 .1000D+01 .0000D+00
  5400.00              .6350D-01 .7594D+00 .1771D+00
 10800.00              .9600D-01 .6069D+00 .2971D+00
 21600.00              .1257D+00 .3685D+00 .5058D+00
 28800.00              .1303D+00 .3252D+00 .5446D+00
 32400.00              .1306D+00 .2601D+00 .6093D+00
 39600.00              .1254D+00 .1972D+00 .6774D+00
 46800.00              .1165D+00 .1580D+00 .7258D+00
 50400.00              .1165D+00 .1492D+00 .7354D+00
 54000.00              .1203D+00 .1438D+00 .7354D+00
 86000.00              .9240D-01 .8550D-01 .8221D+00

 Matrix of k(i,j)s used to calc. Mol Fs above:
   .0000E+00   .1213E-04   .3230E-04
   .1405E-04   .0000E+00   .3333E-04
   .2790E-05   .2484E-05   .0000E+00

 Rate Constants Minimized by Simplex:
k 1 2    .1213E-04
k 2 3    .3333E-04

 Non-zero Rate Constants Fixed by Input:
k 1 3    .3230E-04


 Keq from all equil. mol fractions
     1.000000       .862903     11.577957
     1.158879      1.000000     13.417445
      .086371       .074530      1.000000

 Calculated or Input  Equilibrium Mol Fs:
 1 :  .7440D-01
 2 :  .6420D-01
 3 :  .8614D+00


 Residuals from early time data weighted  2.00 times residuals
 from data near equilibrium.


Tolerance:   1.0000000000000E-009  Maxerr:   1.0000000000000E-003
```

Figure 4. Conversion of TND, TXD, and AD at 305.0 °C.

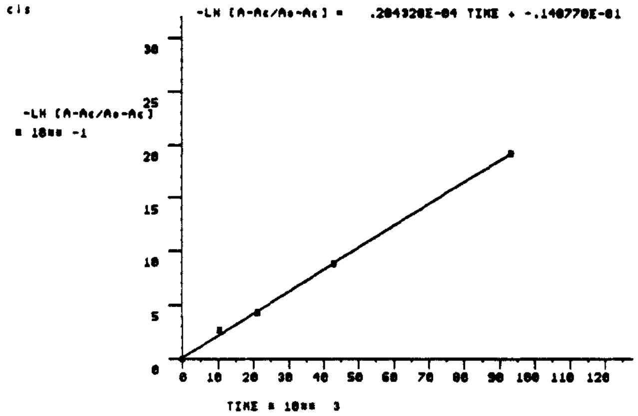


Figure 5. Conversion of C to S at 305.0 °C.

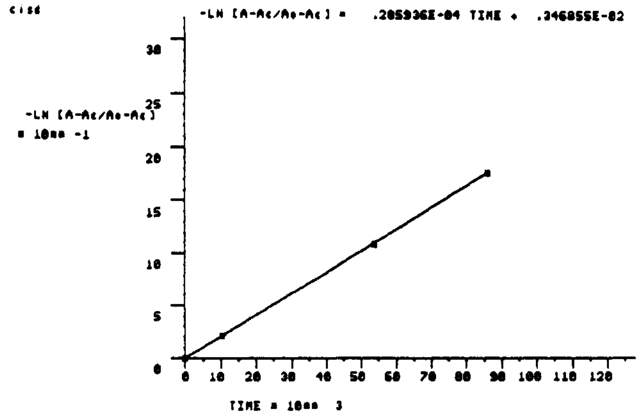


Figure 6. Conversion of CD to SD at 305.0 °C.

and by this group.[16] However, examination of molecular models quickly reveals that no methylene rotation should occur in the transition state for the degenerate 3,3-sigmatropic rearrangement of 1,4-dimethylenecyclohexane. Thus, it would appear that, indeed, the transition-state structure involves substantially less bonding between the exomethylenes in the 1,4-dimethylenecyclohexane degenerate, boat-like 3,3-sigmatropic shift than in acyclic, chair-like 3,3-shifts.

Experimental Section

General nuclear magnetic resonance spectra (NMR) were recorded on Varian HR-220 or EM-390 and Nicolet NT-360 spectrometers. The chemical shifts are given in parts per million (ppm) downfield from Me_4Si in δ. High-resolution mass spectral analyses were performed with a KRATOS MS-80. Purification and separation of substances were accomplished on a Varian Aerograph Model A-90-P3 instrument equipped with thermal conductivity detector and with helium as the carrier gas. For analytical vapor-phase chromatography, a Varian 3700 instrument equipped with a flame ionization detector and a DB-5 capillary column was used. Relative areas were measured with a Varian CDSII integrator. Melting points were obtained with a Thomas-Hoover melting point apparatus and are uncorrected. Reagent grade chemicals were used without additional purification.

***endo*-2,3-Dimethylbicyclo[2.2.2]oct-5-ene (4).** This material could be obtained by two different methods from the bis *p*-toluenesulfonate of *endo*-2,3-bis(hydroxymethyl)bicyclo[2.2.2]oct-5-ene;[17-21] however, method A proved to be adequate only on a small scale.

Method A.[22] An oven-dried, 250-mL, three-necked flask, fitted with a silicone rubber stopper, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler, was cooled to room temperature under a dry stream of nitrogen. Tetrahydrofuran was introduced followed by 5.9 g (12.4 mmol) of the ditosylate. The mixture was cooled to 0 °C. To this stirred mixture, 50 mL (50 mmol) of a 1 M solution of lithium triethylborohydride in tetrahydrofuran was added via syringe, and the ice bath was removed. The mixture was stirred for 22 h at 25 °C. The excess of hydride was decomposed by the careful addition of 1.5 mL of water. The borane was oxidized with 20 mL of 3 N NaOH solution and 20 mL of 30% H_2O_2. The tetrahydrofuran layer was separated and the aqueous layer was extracted with pentane. The combined organic extracts were washed with water to remove the ethanol produced in the reaction. The organic extract was dried ($MgSO_4$) and distilled under vacuum to give 1.20 g (71%) of *endo*-2,3-dimethylbicyclo[2.2.2]oct-5-ene.

Method B.[23] To a suspension of 2.1 g (1303 mmol) of LiH and 7.61 g (201 mmol) of $LiAlH_4$ in 127 mL of dry tetrahydrofuran was added, drop by drop, 39 g (81 mmol) of the ditosylate dissolved in 200 mL of dry THF. The excess of hydride was decomposed by the addition of 2 mL of water, 8 mL of 15% NaOH solution, and 24 mL of water. Normal workup gave 4.9 g (44% yield) of alkene **4**. NMR ($CCDCl_3$, 90 MHz) δ 6.1 (m, 2 H), 2.2 (m, 2 H), 1.8 (m, 2 H), 1.1–1.6 (m, 4 H), 0.7 (d, *J* = 7.5, 6 H).

***cis*,*cis*,*cis*-2,3-Dimethyl-1,4-cyclohexanedicarboxylic Acid (5).** Alkene **4** (2.7 g (20 mmol)) was ozonized in a mixture of 50 mL of methanol-methylene chloride (1:1) at −70 °C. After 40 min the reaction was stopped. The solvent was removed in vacuo, leaving 5.6 g of a syrup-like material. This material was dissolved in 14 mL of 90% formic acid and 7 mL of 30% hydrogen peroxide and carefully warmed on a water bath at 60%. After the vigorous reaction has ceased (20 min) the mixture was heated for 6 h at 75 °C. After being cooled, excess formic acid was removed to give 3.9 g (98%) of diacid **5**, mp 210–212 °C dec; NMR ($CDCl_3$, 90 MHz) δ 1.80 (d, 6 Hz, 6 H), 1.0–1.40 (m, 2 H), 1.5–2.1 (m, 4 H), 2.1–3.5 (m, 4 H).

Dimethyl *cis*,*cis*,*cis*-2,3-Dimethyl-1,4-cyclohexanedicarboxylate (6). The procedure for the esterification of carboxylic acids described by Kadaba[24] was used. A reaction mixture consisting of acid **5** as described above, 3.9 g, boron trifluoride etherate (5.62 mL), and methanol (16 mL) was stirred at reflux under nitrogen for 24 h. After the mixture was cooled, excess methanol was removed under vacuum, and the reaction mixture was quenched by the addition of 15 mL of water. The ether solution was washed with a saturated solution of $NaHCO_3$ and then with brine and was dried over $MgSO_4$. After concentration under reduced pressure and distillation through a 19-cm Vigreaux column, 2.9 g (66%) of the diester was obtained as a colorless liquid: bp 142–144, 85–87 °C (0.1 mmHg); NMR ($CDCl_3$, 90 MHz) δ 0.8–1.1 (m, 6 H), 1.8–2.0 (m, 4 H), 2.2 (m, 2 H), 2.4 (m, 2 H), 3.55 (s, 6 H).

***cis*,*cis*,*cis*-2,3-Dimethyl-1,4-bis(hydroxymethyl)cyclohexane (7).** To a solution of 0.396 g (10.4 mmol) of lithium aluminum hydride in 50 mL of dry ether, under a nitrogen atmosphere, was added 1.62 g (7.1 mmol) of diester **6** dissolved in 15 mL of ether over a 40-min period. The reaction mixture was heated at reflux for 36 h. The excess of $LiAlH_4$ was destroyed by the successive addition of 0.5 mL of water, 0.5 mL of 15% NaOH solution, and 1.5 mL of water. The workup was similar to the one employed with **2**. Diol **7** was obtained: 1.20 g (98% yield); mp 58–59 °C; NMR ($CDCl_3$, 90 MHz) δ 0.80 (d, *J* = 6 Hz, 6 H), 1.00–1.40 (br m, 2 H), 1.60–2.10 (br m, 4 H), 2.10–3.50 (m, 4 H).

Bis *p*-Toluenesulfonate of *cis*,*cis*,*cis*-2,3-Dimethyl-1,4-bis(hydroxymethyl)cyclohexane (8). To a 0 °C stirred solution of diol **7** (1.44 g, 8 mmol) in 8 mL of dry pyridine was added 3.96 g (21 mmol) of *p*-toluenesulfonyl chloride in a minimum volume of dry pyridine. After workup, 3.76 g of white crystals were obtained (mp 112–114 °C, 94%): NMR ($CDCl_3$, 90 MHz) δ 7.80 (d, *J* = 8 Hz, 4 H), 7.30 (d, *J* = 8 Hz, 4 H), 3.90 (d, *J* = 6 Hz), 4 H), 2.50 (s, 6 H), 150–220 (br m, 4 H), 1.20–1.50 (br m, 4 H), 0.73 (d, *J* = 8 Hz, 6 H).

***cis*,*cis*,*cis*-2,3-Dimethyl-1,4-bis(iodomethyl)cyclohexane[25] (9).** A mixture of 3.76 g (7.8 mmol) of ditosylate **8** and 4.22 g (28 mmol) of sodium iodide in 24 mL of dry acetone was heated at reflux for 9 h. After being cooled the reaction mixture was filtered. The solid was washed with hot acetone. The acetone was removed from the filtrate by distillation at reduced pressure, and the residue was treated with dry ether. After filtration to remove suspended solids, the filtrate was washed with dilute sodium thiosulfate solution then with water and was dried over Na_2SO_4. After removal of the ether on a rotary evaporator, 3.0 g (98%) of a clear liquid diiodide was obtained. No attempt was made to purify this material before elimination.

***cis*-2,3-Dimethyl-1,4-dimethylenecyclohexane (C) (10).** Diodide **9**, 3.0 g, was treated with 32 mL of a 1 N solution of potassium *tert*-butoxide in dimethyl sulfoxide.[26] A few minutes after addition, the reaction mixture turned dark red. The mixture was stirred at room temperature for 12 h and then it was quenched with ice-cold water and pentane. The aqueous layer was saturated with sodium chloride. After the mixture was shaken, the organic layer was separated, and the aqueous layer was extracted three times with pentane. The combined organic phases were washed with saturated brine and dried over anhydrous sodium sulfate. After filtration of the pentane solution through an alumina column, the solvent was distilled away at atmospheric pressure to give 1 g of a mixture of hydrocarbons which was separated by preparative GC on a 10 ft × 0.25 in. 15% EGTCP on Chromosorb P column at 130–140 °C with a flow rate of 42 mL/min. The retention time of the major product was 10 min. Further purification on a 10 ft × 0.25 in. 15% SE-30 column at 100 °C and a flow rate of 30 mL/min (retention time was 40 min) gave 99.9% pure *cis*-2,3-dimethyl-1,4-dimethylcyclohexane: NMR ($CDCl_3$) δ 4.718 (d, *J* = 1.44 Hz, 2 H), 4.659 (d, *J* = 1.44 Hz, 2 H), 2.390 (m, 2 H), 2.322 (m 2 H), 2.119 (m, 2 H), 0.925 (d, *J* = 6.5 Hz, 6 H); MS, *m/e* 136.1259 (calcd for $C_{10}H_{16}$ 136.1253).

***cis*,*cis*,*cis*-2,3-Dimethyl-1,4-bis(dideuteriohydroxymethyl)cyclohexane (11).** The deuterated diol was prepared in the same fashion as the protio compound **7** from 0.91 g (21.7 mmol) of lithium aluminum deuteride in 40 mL of ether and 4.51 g (19.7 mmol) of diester **6**. The yield was 3.45 g (99%) of a clear viscous liquid: NMR ($CDCl_3$, 90 MHz) δ 0.8–1.10 (m, 6 H), 1.20–2.0 (br m, 8 H).

***cis*,*cis*,*cis*-2,3-Dimethyl-1,4-bis(dideuteriohydroxymethyl)cyclohexane Ditosylate (12).** The deuterated ditosylate was prepared in the same fashion as the protio compound[17-21] with 3.45 g (19.5 mmol) of tetradeuterio diol **11** and 13.4 g (70 mmol) of *p*-toluenesulfonyl chloride in 34 mL of dry pyridine. The yield was 2.21 g after extensive recrystallization from ether (23%) of a white solid (mp 97–99 °C dec): NMR ($CDCl_3$, 90 MHz) δ 7.35 (d, *J* = 8 Hz, 4 H), 7.80 (d, *J* = 8 Hz, 4 H), 1.8 (m, 4 H), 2.4 (s, 6 H), 1.2 (m, 4 H), 0.65 (d, 6 H).

***cis*,*cis*,*cis*-2,3-Dimethyl-1,4-bis(iododideuteriomethyl)cyclohexane (13).** The deuterated iodide was prepared in the same fashion as the protio compound **9** with 2.21 g (4.5 mmol) of ditosylate **12** and 2.47 g (16.5 mmol) of sodium iodide in 14 mL of dry acetone. The yield was 1.78 g (100%) of a light yellow liquid. No attempt was made to purify the iodide before elimination.

***cis*-2,3-Dimethyl-1,4-bis(dideuteriomethylene)cyclohexane (CD) (14).** The deuterated alkene was prepared in the same fashion as the protio

---

(14) Dolbier, W. R., Jr.; Dai, S. H. *J. Am. Chem. Soc.* **1972**, *94*, 3946.

(15) Crawford, R. J.; Cameron, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 2589.

(16) Gajewski, J. J.; Benner, C. W.; Stahly, B. N.; Hall, R. F.; Sato, R. I. *Tetrahedron* **1982**, *38*, 853.

(17) Bailey, W. J.; Lawson, W. B. *J. Am. Chem. Soc.* **1957**, *79*, 1444.

(18) J. B. Rose, British Patent 796 133 (1958).

(19) Pettit, F.; Pecque, M.; Blanchard, M. *Bull. Soc. Chim. Fr.* **1972**, 747.

(20) Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 1197.

(21) Birtch, S. F.; Hunter, N. J.; Allan, D. T. *J. Org. Chem.* **1956**, *21*, 970.

(22) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1973**, *95*, 1670.

(23) del C. Salazar, J. Ph.D. Dissertation, Indiana University, 1979.

(24) Kadaka, P. K. *Synthesis* **1972**, 628.

(25) Alder, K.; Dortmann, H. A. *Chem. Ber.* **1954**, *87*, 1492.

(26) Wood, N. F.; Chang, F. C. *J. Org. Chem.* **1964**, *30*, 2054.

compound with 1.78 g (4.5 mmol) of iodide **13** and 20 mL of a solution of potassium *tert*-butoxide in Me_2SO. The yield was 0.20 g (31%): NMR ($CDCl_3$, 360 MHz) δ 0.857 (d, J = 6.5 Hz, 6 H), 2.075 (m, 2 H), 2.2250 (m, 2 H), 2.399 (m, 2 H); MS, *m/e* 140.1504, found 140.1511 (0.0008), ca. 5% d_3 present.

***trans*-2,3-Bis(chloroformyl)bicyclo[2.2.2]oct-5-ene (15).** The general procedure for Diels–Alder reactions with fumaryl chloride described by Blomquist and Wislow[27] was used. A solution of 10.0 g (0.125 mL) of 1,3-cyclohexadiene in 12.5 mL of anhydrous ether was stirred and cooled at 0 °C, and a solution of 19.0 g (0.125 mol) of fumaryl chloride in 17.5 mL of anhydrous ether was added dropwise, under nitrogen, over a 27-min period. The flask was allowed to come to room temperature, and after the mixture was stirred for 23 h the ether and the unreacted 1,3-cyclohexadiene were removed on a rotary evaporator. Distillation of the liquid residue through a 15-cm vigreaux column gave 24.5 g (84%) of acid chloride **15** as a light-yellow liquid: bp 135–136 °C (9 mmHg); IR (neat) 3530, 3050, 2950, 2910, 2870, 1780 cm^{-1}; H NMR ($CDCl_3$, 90 MHz) δ 1.1–1.7 (m, 4 H), 3.2–3.7 (m, 4 H), 6.1–6.5 (p, J = 7.5 Hz, 2 H).

***trans*-2,3-Dicarbomethoxybicyclo[2.2.2]oct-5-ene (16).** To 24.5 g (0.15 mol) of acid chloride **15** cooled to 5 °C with stirring was added 10 mL (0.23 mol) of absolute methanol dropwise under nitrogen atmosphere. After 1 h at 5 °C and overnight at room temperature, the mixture was dissolved in 50 mL of ether, washed with dilute sodium carbonate solution and then water, and dried ($MgSO_4$). The ether was removed under vacuum. The residue was vacuum distilled to give 20.4 g (86%) of diester **16** as a colorless liquid: bp 138–140 °C (9 mmHg); IR (neat) ν^{max} 2940, 2860, 1720, 1430, 1270, 1170 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.2–1.7 (m, 4 H), 2.8–3.0 (m, 2 H), 3.0–3.2 (m, 2 H), 3.6–3.7 (d, J = 6 Hz, 6 H), 6.1–6.4 (p, J = 9 Hz, 6 H); MS, *m/e* 224.20 (calcd for $C_{12}H_{16}O_4$).

***trans*-2,3-Bis(hydroxymethyl)bicyclo[2.2.2]oct-5-ene (17).** This diol was prepared by the general method of Nystrom and Brown.[20] A mixture of 4.5 g (0.12 mol) of lithium aluminum hydride in 230 mL of anhydrous ether was stirred and cooled at 0 °C as 20.4 g (0.09 mol) of dimethyl ester **16** was added dropwise under nitrogen atmosphere over a 2-h period. The excess of $LiAlH_4$ was decomposed cautiously by the dropwise addition of 4.5 mL of water, then 4.5 mL of 15% sodium hydroxide solution, and 13.5 mL of water. The white solid was removed by vacuum filtration and was washed with hot THF. The combined organic filtrates were dried (Na_2SO_4). The solvent was removed under vacuum to give 15.0 g (98%) of diol **17** as white crystals: mp 68–70 °C; IR (KBr) ν^{max} 3280, 3015, 2905 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.0–1.5 (m, 6 H), 2.4 (s, 2 H), 3.1 (t, J = 9 Hz, 1 H), 6.35 (t, J = 9 Hz, 1 Hz).

Bis *p*-Toluenesulfonate of *trans*-2,3-Bis(hydroxymethyl)bicyclo[2.2.2]oct-5-ene (18). A solution of 15.2 g (0.09 mol) of diol **17** in 60 mL of dry pyridine was stirred and cooled at 0 °C as 38.0 g (0.2 mol) of *p*-toluenesulfonyl chloride was added in small portions over a 20-min period at such a rate that the temperature did not exceed 20 °C. After the addition, the entire mixture was placed in the refrigerator for 24 h. After the reaction mixture was poured onto a mixture of 94 mL of concentrated hydrochloric acid and 286 g of ice, the ditosylate crystallized. The solid was collected on a chilled Buchner funnel, washed with water, and dried in vacuo to give 41.5 g (96%) of a white solid: mp 122–125 °C; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.0–1.5 (m, 4 H), 2.5 (s, 10 H), 3.5–3.7 (d, J = 7.5 Hz, 2 H), 3.8–4.1 (m, 2 H), 5.9 (t, J = 7.5 Hz, 1 H), 6.2 (t, J = 7.5 Hz, 1 H), 7.2–7.8 (symm m, 8 H).

***trans*-2,3-Dimethylbicyclo[2.2.2]oct-5-ene (19).** The procedure for the reduction of tosylates described by Salazar[23] was used. A solution of 2.46 g (0.31 mol) of lithium hydride and 7.83 g (0.21 mol) of lithium aluminum hydride in 200 mL of THF was stirred and cooled at 0 °C as a solution of 40.4 g (0.08 mol) of ditosylate **18** in 250 mL of dry THF was added dropwise under nitrogen atmosphere. After the addition, the reaction mixture was heated with stirring for 36 h. The THF solvent and some of the hydrocarbon formed was removed under reduced pressure and condensed in dry ice cooled traps. Ether (0.5 L) was added to the reaction mixture and the excess of hydride was decomposed by the successive addition of 10 mL of water, 10 mL of 15% NaOH solution, and 35 mL of water. Normal workup gave 9.3 g (80%) of alkene **19** as a clear liquid: bp 90–91 °C (566 mm) (lit.[19] bp 164 °C (760 mmHg); IR (neat) ν^{max} 3020, 1620, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 0.9 (d, J = 3 Hz, 3 H), 1.0–1.2 (m, 7 H), 1.25–1.75 (m, 2 H), 2.1–2.3 (dm, 2 H), 6.1 (t, J = 7.5 Hz, 1 H), 6.3 (t, J = 7.5 Hz, 1 H); MS, *m/e* 136.10 (calcd for $C_{10}H_{16}$ 136.1253).

***trans*-2,3-Dimethyl-*cis*-1,4-cyclohexanedicarboxylic Acid (20).** The method of Miller and Greenlee[28] was used with some modifications. A mixture of 5.12 g (0.038 mol) of alkene **19**, 3.39 g (0.032 mol) of sodium carbonate, and 10 mL of *tert*-butyl alcohol in 440 mL of acetone was stirred and cooled at 0 °C as 17.25 g (0.11 mol) of potassium permanganate was added in small portions such that the temperature of the flask never exceeded 10 °C. After the addition was complete, the mixture was stirred overnight at room temperature. Then 5.4 g of Celite was added to the mixture. After vacuum filtration, the filtrate was removed under reduced pressure. No residue was left upon evaporation of the filtrate. The manganese dioxide–Celite cake was washed with five 100-mL portions of 5% sodium carbonate solution and two 200-mL portions of water. The basic extracts were concentrated to ca. 100 mL under reduced pressure. The residue was acidified with 240 mL of 10% hydrochloric solution. The precipitated solid was collected on a chilled Buchner funnel, washed with 40 mL of cold water, and dried in vacuo to give 5.00 g (66%) of diacid **20** as white crystals: mp 190–191 °C; IR (KBr) ν^{max} 3300–2500, 1680 cm^{-1}; ^1H NMR (Me_2SO-d_6, 90 MHz) δ 0.8–1.0 (unsymmetrical 4-line pattern, 6 H), 1.1–2.0 (m, 4 H), 2.5 (m, 4 H).

Dimethyl *trans*-2,3-Dimethyl-*cis*-1,4-cyclohexanedicarboxylic (21). The procedure for the esterification of carboxylic acids described by Kadaba[24] was used. A solution of 5.0 g (0.025 mol) of diacid **20**, 7.0 mL of boron trifluoride–etherate, and 24 mL of anhydrous methanol was stirred and heated at reflux for 24 h. After the mixture was cooled, excess methanol was removed under vacuum and the reaction mixture was quenched by the addition of 120 mL of 5% of sodium carbonate solution, and the resulting solution was extracted with four 30-mL portions of ether. The combined ethereal phases were washed with two 20-mL portions of brine, dried over $MgSO_4$, concentrated under reduced pressure, and distilled through a 15-cm Vigreaux column to give 5.07 g (89%) of diester **21** as a colorless liquid: bp 115–117 °C (0.1 mmHg); IR (neat) ν^{max} 3940, 1725 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.8–1.1 (m, 6 H), 1.2–2.1 (m, 6 H), 2.5–2.7 (m, 2 H), 3.6 (s, 6 H); MS, *m/e* 228.1359 (calcd for $C_{12}H_{20}O_4$ 228.1362).

***trans*-2,3-Dimethyl-*cis*-1,4-bis(hydroxymethyl)cyclohexane (22).** To a solution of 1.07 g (0.028 mol) of lithium aluminum hydride in 50 mL of dry ether, under a nitrogen atmosphere, was added 5.0 g (0.022 mol) of diester **21** dissolved in 50 mL of ether over a 1-h period. The reaction mixture was heated at reflux for 23 h. The excess of $LiAlH_4$ was destroyed by the successive addition of 1 mL of 15% sodium hydroxide solution and 3 mL of water. The mixture was filtered and the solid filtrate was washed several times with hot THF. The combined washings and the ether filtrate were dried on Na_2SO_4 and evaporated in vacuo to give 3.41 g (89%) of diol **22** as white crystals: mp 91–92 °C; IR (KBr) ν^{max} 3500–3000, 1350 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.9–1.0 (d, J = 6 Hz, 6 H), 1.1–2.0 (m, 8 H), 3.5–3.7 (m, 4 H).

Bis *p*-Toluenesulfonate of *trans*-2,3-dimethyl-*cis*-1,4-bis(hydroxymethyl)cyclohexane (23). A solution of 1.98 g (0.11 mol) of diol **22** in 10 mL of dry pyridine was stirred and cooled at 0 °C as 5.45 g (0.029 mol) of *p*-toluenesulfonyl chloride was added in small portions. The reaction mixture was kept at 0 °C overnight. After the reaction mixture was poured onto a mixture of 12 mL of concentrated hydrochloric acid and 37 g of ice, the resulting solution was extracted with three 50-mL portions of ether. The combined ethereal phases were washed with two 15-mL portions of 10% hydrochloric acid solution then with one 15-mL portion of 5% sodium carbonate solution and dried over K_2CO_3. The solvent was removed on a rotary evaporator to give 4.85 g (87%) of a white solid: mp 78–80 °C; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.7–0.9 (m, 6 H), 1.0–2.0 (m, 8 H), 2.4 (s, 6 H), 3.9–4.1 (m, 4 H), 7.2–7.8 (symmetrical m, 8 H). It was not possible to successfully eliminate both tosylate groups or both iodides from the corresponding diodide; the second elimination is apparently much too slow.

***trans*-2,3-Dimethyl-1,4-dimethylenecyclohexane (T) (24).** To a well-stirred solution of diol **22** (1.25 g, 7.3 mmol) in 25 mL of dry tetrahydrofuran containing 3.95 g (17.3 mmol) of *o*-nitrophenyl selenocyanate was added dropwise 3.69 g (17.3 mmol) of tri-*n*-butylphosphine at room temperature under a nitrogen atmosphere.[29] After being stirred for 26 h the reaction mixture was cooled to 0 °C and 15 mL (17 mmol) of 30% hydrogen peroxide was added dropwise.[30] After the mixture was removed from the ice bath and stirred for an additional 45 h at room temperature, it was diluted with 30 mL of water and then was extracted with five 50 mL portions of pentane. The combined organic extracts were successively washed with two 30-mL portions of an aqueous sodium carbonate solution and two 20-mL portions of brine and were dried over magnesium sulfate. After filtration and careful removal of solvent by distillation at atmospheric pressure a dark red oil resulted. After filtration through Silica gel (60G E Merck, 50 g, hexane was the eluent) and removal of the solvent at atmospheric pressure, a colorless liquid

---

[27] Blomquist, A. T.; Winslow, E. C. *J. Org. Chem.* **1945**, *10*, 149.

[28] Miller, H. N.; Greenlee, K. W. *J. Org. Chem.* **1961**, *26*, 3734.

[29] Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485.

[30] Sharpless, K. B.; Young, M. *J. Org. Chem.* **1975**, *40*, 947.

remained which was purified by preparative GC on a 20 ft × 0.25 in. 15% carbowax 20M on Chromosorb p column at 140 °C to give 0.273 g (27%) of the diene: NMR ($CDCl_3$, 360 MHz) δ 1.067 (d, J = 6.5 Hz, 6 H), 2.020–2.180 (m, 4 H), 2.257–2.365 (m, 2 H), 4.72 (d, J = 1.81 Hz, 2 H), 4.687 (d, J = 1.8 Hz, 2 H); MS, *m/e* 136.1249 (calcd for $C_{10}H_{16}$ 136.1253).

***trans*-2,3-Dimethyl-*cis*-1,4-bis(dideuteriohydroxylmethyl)cyclohexane (25).** The deuterated diol was prepared from 2.91 g (12.7 mmol) of ester **21** with 0.638 g (16.3 mmol) of lithium aluminum deuteride by employing the same method as used for conversion of **21** to protio diol **22**. A total of 2.20 g (98%) of deuterio diol **25** was obtained: mp 89–90 °C; NMR ($CDCl_3$, 90 MHz) δ 0.9–1.0 (d, J = 6 Hz, 6 H), 1.1–2.0 (br m, 8 H).

***trans*-2,3-Dimethyl-1,4-bis(dideuteriomethylene)cyclohexane (TXD) (26).** The deuterated diene was prepared from 1.28 g (7.3 mmol) of deuterio diol **25**, 3.93 g (17 mmol) of *o*-nitrophenyl selenocyanate, and 3.68 g (17 mmol) of tri-*n*-butylphosphine in the same way as diene **24** was prepared from diol **22** to give 0.223 g (22%) of material. NMR ($CDCl_3$, 360 MHz) δ 1.069 (d, J = 6.9 Hz, 6 H), 2.020–2.179 (m, 4 H), 2.257–2.345 (m, 2 H); MS, *m/e* 140.1515 (calcd for $C_{10}H_{12}D_4$ 140.1504).

Pyrolysis of *trans*-2,3-Dimethyl-1,4-dimethylenecyclohexane to *anti*-1,4-Diethylidenecyclohexane (A). Samples of 3 μL of T were pyrolyzed at 305 °C for 12 h. The combined, recovered pyrolysates were analyzed by NMR with the spectrum of starting T subtracted by computer. The resulting spectrum in $CDCl_3$ at 360 MHz is δ 5.209 (q, J = 6.86, 2 H), 2.188 (t, J = 5.42 Hz, 4 H), 2.115 (t, J = 5.42 Hz, 4 H), 1.59 (d, J = 6.14 Hz, 6 H).

Pyrolysis of *cis*-2,3-Dimethyl-1,4-dimethylenecyclohexane to *syn*-1,4-Diethylidenecyclohexane (S). Samples of 3 μL of C were pyrolyzed at 305 °C for 12 h. The combined, recovered pyrolysates were analyzed by NMR with the spectrum of starting C subtracted by computer. The resulting spectrum in $CDCl_3$ at 360 MHz is δ 5.201 (q, J = 6.50 Hz, 2 H), 2.17 (s, 4 H), 2.118 (s, 4 H), 1.605 (d, J = 6.5 Hz, 6 H).

Gas-Phase Pyrolyses. The reaction vessel consisted of a 2-L Pyrex round-bottomed flask which was treated with dimethylchlorosilane and then with dimethylamine. This flask was connected to a vacuum line fitted with a spiral trap and the usual arrangement to allow the introduction of the sample into the system. The flask was immersed in a molten potassium nitrate–sodium nitrate (10:7) bath heated by a 500-W Vycor immersion heater. The fine adjustment of the temperature was accomplished with a Bayley controller Model 76-8 connected to a 125-W Vycor immersion heater. The temperature was measured with an Omega platinum resistance thermometer probe and the readout was performed with an Omega temperature indicator, Model 410A-PT3-C. The temperature reported was measured at the middle point of the reactor. Temperature variation across the vessel was less than 0.5 °C, and it was constant to 0.1 °C.

Acknowledgment. We thank the National Science Foundation for generous financial support as well as the Venezuelan Government for a Fellowship to J.L.J.

Appendix

SMPXKS is a Fortran 77 program written for the IBMPC by K. E. Gilbert with modifications of I/O by J. J. Gajewski. It utilizes the Gear algorithm for numerical integration of first-order differential rate equations and varies specified rate constants to obtain the best fit to experimental mole fractions by the Simplex algorithm. The response function to be minimized is the sum of the squares of the residuals of each concentration. Any number of *k*s can be fixed and all (or some) K_{eq}s can be entered so that the $k_{j,i}$s can be determined by the set of $k_{i,j}$s and $K_{i,j}$s. The residuals can be weighted according to the extent of reaction by a factor that is user selectable. The program will accept data sets starting with one or all isomers, does the integration, and calculates the sum of the squares of the residuals to be minimized from all data sets. The data output and plots reported for the interconversions of T with A and TXD with TND and AD are provided by the program. This and other kinetics programs are available from SERENA SOFTWARE.

Chemiluminescence from Free-Radical Sources. Excited States from Thermolysis of Hyponitrite Esters

E. M. Y. Quinga and G. D. Mendenhall*

Contribution from the Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, Michigan 49931. *Received July 15, 1985*

Abstract: Chemiluminescence was observed from the thermolysis of 11 symmetrical *trans*-alkyl hyponitrites (RON=NOR), in which the alkyl groups contained α-hydrogen atoms, in solutions containing aromatic fluorescers. The excited-state production occurs by disproportionation of alkoxyl radicals within the solvent cage, possibly by a mechanism involving spin inversion in the caged radical pair followed by reaction on a triplet surface. The reactions are characterized by large T_1/S_1 ratios in the carbonyl products and exited-state yields that were more sensitive to changes in the alkyl structure than to changes in the solvent. The approximate total quantum yields in *tert*-butylbenzene varied from 3.3×10^{-3} (R = PhCHMe) to 5×10^{-6} (R = Me) einsteins/mol of hyponitrite.

Studies of chemiluminescence have traditionally focused on reactions which produce high quantum yields. For many of the visible examples of these reactions, an electron-transfer, charge-recombination and high yields of singlet excited states are a common feature.[1] The rate constants for excited state production in some bimolecular chemiluminescent reactions can be related directly to the redox potentials of one reactant.[2]

1,2-Dioxetanes, on the other hand, generally show high specifically for the generation of excited triplet states, and the quantum yields are a sensitive function of substituents.[3]

The chemiluminescent thermolysis of hyponitrites in solution gives excited states via cage dismutation of alkoxyl radicals. We have studied this reaction because (1) the transition state for alkoxyl self-reaction exhibits a formal similarity to the 1,4-bis(alkoxyl) biradical postulated as an intermediate from 1,2-diox-

---

(1) (a) Lytle, F. E.; Hercules, D. M. *Photochem. Photobiol.* **1971**, *13*, 123–133. (b) Faulkner, L. R. *Int. Rev. Sci.: Phys. Chem., Ser. 2*, **1976**, *9*, 213–263. (c) Schuster, G. B.; Schmidt, S. P. *Adv. Phys, Org. Chem.* **1984**, *18*, 187–234. (d) Chandross, E. A.; Sonntag, F. I. *J. Am. Chem. Soc.* **1964**, *86*, 3179–3180. (e) McCapra, F. *Q. Rev. Chem. Soc. (London)* **1966**, *20*, 485–510.

(2) Dixon, B. G.; Schuster, G. B. *J. Am. Chem. Soc.* **1979**, *101*, 3116–3118.

(3) Review of dioxetanes: Adam, W.; Yang, F. In "The Chemistry of Heterocyclic Compounds"; Hassner, A., Ed.; Wiley: New York, 1985; Vol. 42, Part 3, pp 351–430.

0002-7863/86/1508-0474$01.50/0