(2.0 mmol). The suspension was stirred at room temperature with periodic monitoring by capillary GC. After 3 h, the relative amounts of product and starting material remained constant, so 32 mg of zinc (0.5 mmol) was added. After 30 min, the starting material was consumed. The reaction mixture was filtered, and the solid was washed with several small portions of ether. The filtrate was washed with 1 N $NaHCO_3$, water, and brine, and then it was dried over $MgSO_4$ and filtered. Concentration provided 223 mg of **15** (75.2% yield) as a pale yellow liquid: GC/MS analysis, *m/e* (relative intensity) 149 (M^+, 0.3), 114 (2.2), 86 (100), 85 (74.3), 82 (41.9), 81 (18.3), 72 (67.9), 71 (9.5), 70 (10.0), 54 (22.1), 42 (43.6); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), the retention times of **15** were 5.71 and 6.88 min on columns B and A, respectively.

7-Chloro-6-[(methylsulfonyl)oxy]bicyclo[3.2.0]hept-2-ene-*1,2,3,4,4,5,6,7-d*$_8$ (16) was prepared from the d_7 ketone (215 mg), using 380 mg of sodium borodeuteride (9.08 mmol, Sigma, 98 atom % D), 3 mL of methanol-*d* (Aldrich, 99.5+ atom % D) for the reduction (64% yield), and 340 mg of methanesulfonyl chloride for the mesylation (99% yield): GS/MS analysis, *m/e* (relative intensity) 195 (0.1), 98 (15.0), 86 (20.5), 85 (4.4), 82 (15.9), 81 (4.2), 73 (5.1), 72 (100), 71 (11.9), 70 (8.0), 54 (7.9), 42 (18.6); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), the retention times of **16** were 11.72 and 13.34 min on columns B and A, respectively.

Bicyclo[3.2.0]hepta-2,6-diene-*1,2,3,4,4,5,6,7-d*$_8$ (8) was prepared by the method presented for the preparation of 1 with 50 mL of liquid NH_3, 420 mg of sodium (18.2 mmol), 210 mg of mesylate-d_8 (0.91 mmol), 3 mL of pentane, 6 mL of THF, and 8 mL of ether. A concentrated solution of 8 was obtained. Isolation and purification was accomplished by preparative GC: GC/MS analysis, *m/e* (relative intensity) 101 (2.3), 100 (M^+, 29.3), 99 (13.7), 98 (100), 97 (19.9), 73 (2.2), 72 (29.6), 71 (5.5), 70 (24.1), 54 (10.2), 42 (39.5), 40 (19.5); capillary GC analysis (45 °C), the retention times of 8 were 3.49 and 4.14 min on columns B and A, respectively.

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged.

Registry No. 1, 2422-86-8; **2**, 110097-50-2; **5**, 110097-51-3; **6**, 110097-52-4; **8**, 110097-53-5; **11**, 5307-99-3; **12** (isomer 1), 19296-96-9; **12** (isomer 2), 19296-95-8; **12-6-*d*** (isomer 1), 110097-55-7; **12-6-*d*** (isomer 2), 110171-08-9; **12-*1,2,3,4,4,5*-d_6** (isomer 1), 110097-61-5; **12-*1,2,3,4,4,5*-d_6** (isomer 2), 110171-09-0; **12**, *1,2,3,4,4,5,6*-d_7 (isomer 1), 110097-63-7; **12-*1,2,3,4,4,5,6*-d_7** (isomer 2), 110171-11-4; **13** (isomer 1), 110097-54-6; **13** (isomer 2), 110171-07-8; **13-*6*-*d***, 110097-59-1; **13-*1,2,3,4,4,5*-d_6** (isomer 1), 110097-62-6; **13-*1,2,3,4,4,5*-d_6** (isomer 2), 110171-10-3; **13-*1,2,3,4,4,5,6*,-d_7** (isomer 1), 110097-64-8; **13-*1,2,3,4,4,5,6*-d_7** (isomer 2), 110171-12-5; **14**, 110097-56-8; **15**, 110097-57-9; **16** (isomer 1), 110097-58-0; **16** (isomer 2), 110171-13-6; cyclopentadiene, 542-92-7; cyclopentadiene-d_6, 2102-16-1; dicyclopentadiene-d_x, 110097-60-4; dichloroacetyl chloride, 79-36-7.

A Stereochemical Study of the Thermolysis of *cis-anti-* and *trans*-1,2-Dimethyl-*cis*-3,4-dideuteriocyclobutane

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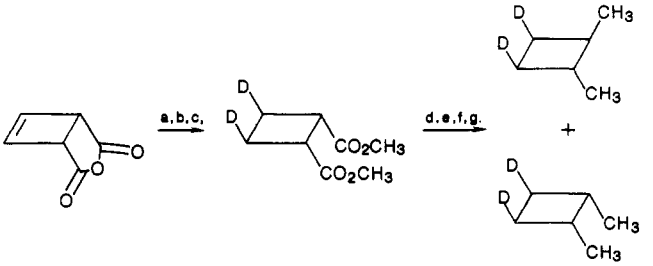
The stereochemistry of the fragmentation and isomerization of *cis-anti-* and *trans*-1,2-dimethyl-*cis*-3,4-dideuteriocyclobutane at 510 °C is reported. The cis-anti-cis isomer undergoes fragmentation to yield *cis/trans*-propene-d_1 (1.5/1, major pathway), *cis/trans*-2-butene (1.4/1), and *cis/trans*-ethylene-d_2 (1/1, minor pathway). Recovered *cis*-1,2-dimethylcyclobutane-d_2 contained approximately 40% of the double rotation product relative to the product of single methyl rotation, *trans-1,2-dimethylcyclobutane-*d_2. The trans isomer behaves similarly, yielding *cis/trans*-propene-d_1 (1/1, major pathway), *cis/trans*-2-butene (1/5), and *cis/trans*-ethylene-d_2 (1/1, minor pathway). Recovered *cis*-1,2-dimethylcyclobutane-d_2 from thermolysis of the trans isomer consists mainly of equal amounts of *cis-anti-cis-* and *cis-syn-cis*-1,2-dimethylcyclobutane-d_2 as analyzed by NMR. On the basis of product composition, the thermal chemistry of this system can be explained as proceeding through 2,5-hexanediyl (major pathway) and 3-methyl-1,4-pentanediyl (minor pathway). On the basis of the observed stereochemistry, it can be concluded that the lifetimes of both 2,5-hexanediyl and 3-methyl-1,4-pentanediyl are similar and of the same order as bond rotations at a radical center. This suggests that the gauche to trans conformational changes involving carbon–carbon bond rotation at carbons 2 and 3 of 1,4-diyls may not be competitive with fragmentation.

The thermolysis of *cis-* and *trans*-1,2-dimethylcyclobutane by Gerberich and Walters[1] is a classic kinetic study of cyclobutane decomposition. Since then, several different aspects of the thermal behavior of this chemical system have been reported. Scrinivasan and Hsu[2] have investigated the stereochemistry of recovered ethylene-d_2 from the thermolysis of *cis*-1,2-dimethyl-*anti-cis*-3,4-dideuteriocyclobutane and found extensive scrambling of stereochemistry. More recently, Dervan et al.[3] have investigated the thermal behavior of *cis-* and *trans*-3,4- and *cis-* and *trans*-3,6-dimethyl-3,4,5,6-tetrahydropyridazines and found similar product distributions from both 1,2-dimethylcyclobutane and 3,4- and 3,6-dimethyltetrahydropyridazine thermolyses. Starting off with different precursors, their analysis demonstrated that access to the

Scheme I. Synthesis of *cis-anti-* and *trans*-1,2-Dimethyl-*cis*-3,4-dideuteriocyclobutane[a]



[a] (a) D_2–Pd/C; (b) H_2O; (c) CH_2N_2; (d) CH_3ONa/CH_3OH; (e) LAH; (f) TsCl/pyridine; (g) LAH.

(1) Gerberich, H. R.; Walters, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 3935, 4884.
(2) Scrinivasan, R.; Hsu, J. N. C. *J. Chem. Soc., Chem Commun.* **1972**, 1213.
(3) Dervan, P. B.; Uyehara, T.; Santilli, D. S. *J. Am. Chem. Soc.* **1979**, *101*, 2069.

0022-3263/87/1952-4776$01.50/0

Table I. Thermolysis of 1,2-Dimethylcyclobutanes in a Flow System at 510 °C

run	propene	ethylene	2-butene		1,2-dimethylcyclobutane recovered		fraction reacted
			cis	trans	cis	trans	
			trans-1,2-Dimethycyclobutane				
1	26.8	7.8	1.3	6.6	2.0	55.5	0.3
2	26.5	8.1	1.3	6.8	1.9	55.5	0.3
			trans-1,2-Dimethylcyclobutane-d_2				
3	24.0	6.6	1.1	5.5	1.9	60.9	0.25
4	25.7	7.3	1.2	6.1	1.9	57.8	0.28
			cis-1,2-Dimethylcyclobutane				
5	48.2	7.1	4.4	2.8	30.9	6.7	0.55
			cis-1,2-Dimethylcyclobutane-d_2				
6	50.9	6.5	3.9	2.6	30.0	6.1	0.56
7	53.5	6.1	3.6	2.5	28.7	5.4	0.57

same potential energy surface was possible in this system. A similar conclusion was reached by Bach et al.,[4] who investigated the cycloaddition reactions of ethylene with *cis*- and *trans*-2-butene. The continued interest in 1,2-dimethylcyclobutane thermolyses and in the potential energy surface[5,6] that connects reactant with products prompts us to report some stereochemical results we have observed in the thermolysis of *cis-anti*- and *trans*-1,2-dimethyl-*cis*-3,4-dideuteriocyclobutane.

The title compounds were prepared according to Scheme I. Reduction of 3-cyclobutene-1,2-dicarboxylic anhydride with deuterium gas–5% Pd/C afforded *cis*-3,4-dideuteriocyclobutane-*anti*-1,2-dicarboxylic anhydride as the sole product. Hydrolysis followed by esterification with diazomethane afforded the dimethyl ester, which was partially epimerized by treatment with sodium methoxide. Complete reduction of the carbomethoxy groups afforded the desired hydrocarbons as a mixture, which were separated by preparative gas chromatography.

Exo deuteriation (>96%) of the cyclobutene to *cis*-3,4-dideuteriocyclobutane-*anti*-1,2-dicarboxylic anhydride was previously established by an NMR lanthanide shift study on the unlabeled anhydride.[7] Stereospecific cis addition of deuterium was confirmed by comparison of the NMR spectrum of labeled and unlabeled *cis*-1,2-dimethylcyclobutane. *cis*-1,2-Dimethylcyclobutane shows ring hydrogen resonances at δ 1.64, 2.14, and 2.47. Resonances at δ 2.14 are completely absent in the labeled material. In addition, labeling reduces the complexity of the resonances centered at δ 1.64 which are displayed as an inverted triplet with a 4.7-Hz separation between the outer lines. Irradiation of the multiplet at δ 2.47 leads to a collapse of the coupling at the methyl groups. Combination of the results of these experiments allows assignment of the resonances at δ 1.64, 2.14, and 2.47 to the hydrogens syn to the methyls, anti to the methyls, and to the methine positions, respectively. The NMR spectrum of labeled *trans*-1,2-dimethylcyclobutane was quite complex and was not particularly useful in providing any additional structural information.

Thermolyses of labeled and unlabeled *cis*- and *trans*-1,2-dimethylcyclobutane were conducted in a flow system at 510 °C. The products were analyzed by gas chromatography. Recovered labeled dimethylcyclobutanes were separated into *cis*- and *trans*-1,2-dimethylcyclobutane-d_2, which in turn were analyzed by NMR. The C_2 and C_3 portions of the products were separated by standard vacuum line techniques and analyzed by IR. The data that were obtained are reported in Tables I and II. The relative amounts of reactant and products in the thermolyses, as analyzed by pressure and gas chromatographic measurements, are reported in Table I. Table II reports on the stereochemistry of recovered olefins, and the stereochemical results of this study are compared to previous work in Table III.

Table II. Stereochemical Composition of the C_2 and C_3 Fractions Isolated from *cis*- and *trans*-1,2-Dimethylcyclobutane-d_2 Using Infrared Spectroscopy

source	*trans*-/*cis*-ethylene-d_2 (843/989 cm^{-1})	*trans*-/*cis*-propene-d_1 (987/813 cm^{-1})
trans-1,2-dimethyl-cyclobutane-d_2	0.72 ± 0.03	0.69 ± 0.02
cis-1,2-dimethyl-cyclobutane-d_2	0.70 ± 0.03	1.13 ± 0.02
thermally equilibrated ethylene	0.71 ± 0.03	
1:1 *cis*-/*trans*-1-propene-d_1		0.70 ± 0.02

The results shown in Table I are quite similar to those previously reported in a static system. *cis*-1,2-Dimethylcyclobutane is more reactive than the trans isomer, with fragmentation to propene being the most probable reaction pathway regardless of the stereochemistry of the methyl groups. A similar regioselectivity is observed in the less reactive trans isomer. ^{1}H NMR analysis of the recovered cyclobutanes offered some additional information. The NMR spectrum of *cis*-1,2-dimethylcyclobutane recovered from the cis-anti-cis reactant at 56% reaction appeared unchanged at δ 1.64. Very weak absorptions at δ 2.14, similar in shape to those described below for *cis*-1,2-dimethylcyclobutane-d_2 isolated from *trans*-1,2-dimethylcyclobutane-d_2 could be detected. The NMR spectrum of the trans isomer recovered from *cis-anti-cis*-1,2-dimethylcyclobutane-d_2 isomer was similar and as complex as the trans starting material and was not very informative. The NMR spectrum of the trans isomer recovered from the trans reactant was similarly uninformative. The proton spectrum of the cis isomer recovered from the trans reactant, however, contained all the resonances of *cis-anti-cis*-1,2-dimethylcyclobutane-d_2 at δ 2.47 as well as a new triplet centered at δ 2.14 with a separation of 9.4 Hz between outer lines. We assign these lines to the cis-syn-cis isomer as described below.

The stereochemistry of the cis-syn-cis material is assigned on the basis of the sign of the long range coupling constant obtained by a Laocoon III simulation of the spectra of both *cis-anti-cis*- and *cis-syn-cis*-1,2-di-

(4) Scacchi, G.; Richard, C.; Bach, M. H. *Int. J. Chem. Kinet.* **1977**, *9*, 513. Scacchi, G.; Bach, M. H. *Ibid.* **1977**, *9*, 525.
(5) Hoffmann, R.; Swaminathan, S.; Odell, B.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 7091.
(6) Doubleday, R. N.; Camp, R. N.; King, H. F.; McIver, J. W.; Mullally, D.; Page, M. *J. Am. Chem. Soc.* **1984**, *106*, 447. Doubleday, R. N.; McIver, J. H.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 3768; **1985**, *107*, 7904.
(7) Doering, W. von E.; Guyton, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 3229.

Table III. Comparisons of the Stereochemical Composition of the Olefin Fraction in the Thermolysis of 1,2-Dimethylcyclobutane

compound	temp, °C	2-butene		ethylene-d_2		1-propene-d_1	
		cis	trans	cis	trans	cis	trans
cis-1,2-dimethylcyclobutane	510[a]	0.61	0.39				
	420[b]	0.63	0.37				
cis-1,2-dimethylcyclobutane-d_2	510[a]	0.60	0.40	0.50	0.50	0.38	0.62
	425[c]	0.56	0.44	0.52	0.48		
trans-1,2-dimethylcyclobutane	510[a]	0.16	0.84				
	430[b]	0.12	0.88				
trans-1,2-dimethylcyclobutane-d_2	510[a]	0.17	0.83	0.50	0.50	0.50	0.50

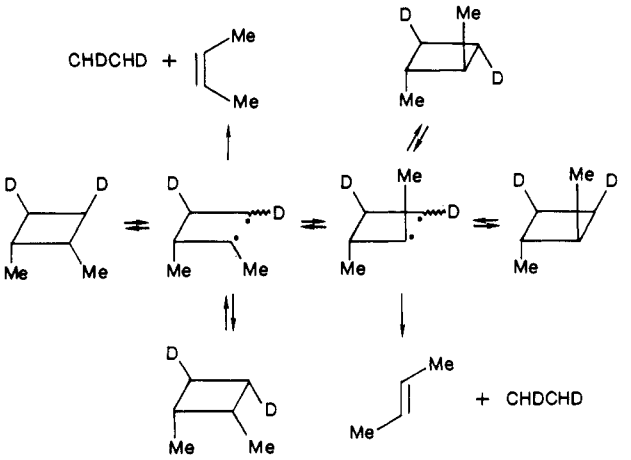
[a] This work; flow system; uncertainty in reported fractions, ±0.02. [b] Reference 1; static system. [c] Reference 2; static system.

methylcyclobutane-d_2. Gamba and Mondelli[8] have previously shown that cross-ring coupling (^4J) in cyclobutanes are positive, when the two interacting protons are cis and negative, (or small[9]) when they are trans to each other. Simulation of the triplets at δ 1.64 and 2.14 resulted in cross-ring coupling values of $^4J_{1,3} = -0.5 \pm 0.6$ Hz for the cis-anti-cis isomer and $^4J_{1,3} = 1.4 \pm 0.5$ Hz for *cis-syn-cis*-1,2-dimethylcyclobutane-d_2. On the basis of the agreement observed between calculated and experimental spectra at both δ 1.64 and 2.14 for *cis*-1,2-dimethylcyclobutane-d_2 recovered from *trans*-1,2-dimethylcyclobutane-d_2 and the relative magnitudes of the cross-ring coupling constants, we conclude that resonances observed at δ 2.14 are those of the cis-syn-cis isomer. In addition, it appears that these two *cis*-1,2-dimethylcyclobutane-d_2 isomers are the major thermolysis products of *trans*-1,2-dimethyl-*cis*-3,4-dideuteriocyclobutane which retain the integrity of the cyclobutane ring. On the basis of proton NMR integrations, they appear to be produced in equal amounts.

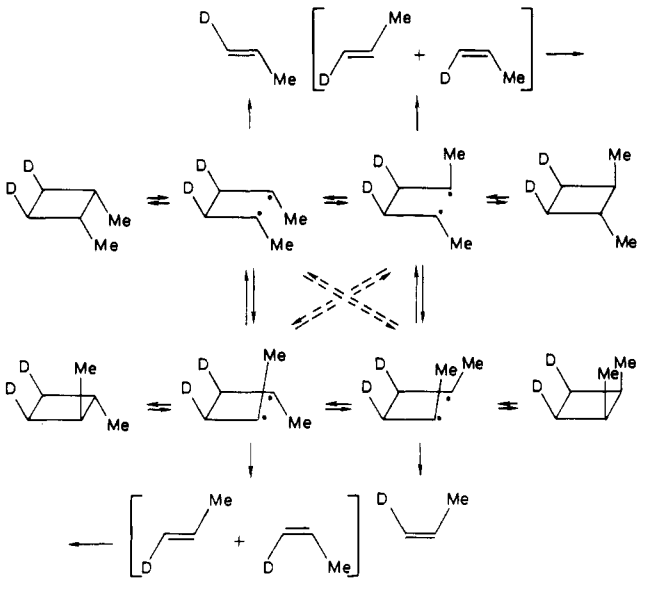
The stereochemical composition of the ethylene-d_2 and propene-d_1 recovered from thermolysis can be found in Table II. Both olefins recovered from *trans*-1,2-dimethylcyclobutane appear to be completely equilibrated with regards to cis-trans isomerization. Only the propene-d_1 isolated from the *cis-anti-cis*-1,2-dimethylcyclobutane-d_2 appears to have retained a portion of the original stereochemistry. Comparison of the relative infrared intensities characteristic of the cis and trans isomers of a completely equilibrated sample of propene-d_1, prepared independently, allowed us to estimate the cis-trans composition of the sample isolated as 38% cis and 62 ± 2% trans. Predominant formation of *trans*-propene-d_1 firmly establishes the anti relationship of deuterium to the methyl groups in *cis-anti-cis*-1,2-dimethylcyclobutane-d_2, thereby confirming both the original assignment of stereochemistry[7] and the assignment based on the sign of the long-range cross-ring NMR coupling constant.

Table III compares the stereochemical results of our experiments to those previously reported. In general we find slightly more stereomutation than previously reported. This is probably reflective of the higher temperatures employed in our thermolysis experiments. Only the results for 2-butene isolated from *cis-anti-cis*-1,2-dimethylcyclobutane appear less stereomutated than previously reported. Examination of the results reported in Tables I–III suggests that the fragmentation of 1,2-dimethylcyclobutane is proceeding by two pathways, one involving 2,5-hexanediyl and the other 3-methyl-1,4-pentanediyl. These pathways are summarized in Schemes II and III. On the basis of product composition and the NMR results described above, it is clear that these two independent

Scheme II. Thermolysis of *cis*- and *trans*-1,2-Dimethylcyclobutane-d_2 by way of 3-Methyl-1,4-pentanediyl (Minor Pathway)



Scheme III. Thermolysis of *cis*- and *trans*-1,2-Dimethylcyclobutane-d_2 by way of 2,5-Hexanediyl (Major Pathway)



pathways differ in their relative importance. Initial cleavage of most highly substituted carbon–carbon bond appears to be the most probable reaction pathway, both in *cis*- and *trans*-1,2-dimethylcyclobutane. In addition, the complete loss of stereochemistry in recovered ethylene-d_2 requires methylene rotation to be fast relative to fragmentation. The net retention of stereochemistry in propene-d_1 isolated from the cis-anti-cis reactant and the NMR results obtained on *cis*-1,2-dimethylcyclobutane-d_2 isolated from *trans*-1,2-dimethylcyclobutane reactant clearly eliminate 2,3-dimethyl-1,4-butanediyl from any

(8) Gamba, A.; Mondelli, R. *Tetrahedron Lett.* **1971**, 2133.
(9) The cross-ring coupling constants of cyclobutane have been deduced as $^4J_{cis} = 2.5$ Hz and $^4J_{trans} = 0.5$ Hz with an uncertainty of ±0.7 Hz. Meiboom, S.; Snyder, L. C. *J. Chem. Phys.* **1970**, *52*, 3857.

important role in the thermolysis reactions of 1,2-dimethylcyclobutane.

Net retention of stereochemistry in the recovered propene-d_1 also demonstrates the ponderal effect of methyl group substitution on the torsional frequency of a terminal methylene group in 1,4-butanediyl. The fact that carbon–carbon bond rotation about positions 2,3 and 4,5 in 2,5-hexanediyl are relatively slow in relation to its lifetime, suggests that rotation about the carbon–carbon bond at positions 3,4 is equally slow.[10] This necessitates 2,5-hexanediyl and presumably other acyclic 1,4-diyls to fragment predominantly through a gauche conformation, rather than through the anti form which is predicted by theory to be at lower energy.[5,6,11] Stereochemical results obtained on the thermolysis of *cis*- and *trans*-3,4-dideuterio-1,2-cyclobutanedione also appear to be consistent with this conclusion.[12]

As a test of the relative importance of synchronous double $CHCH_3$ rotation,[15,16] the NMR spectrum of recovered *cis*-1,2-dimethylcyclobutane-d_2 from run 6, Table I, was integrated at δ 2.14 and compared to the integration at δ 1.64. A relative ratio of $(0.08 \pm 0.03)/1$ was obtained. Assuming the total integration at δ 2.14 to be due to the cis-syn-cis isomer, the recovered *cis*-1,2-dimethylcyclobutane-d_2 can be estimated to contain about $7.4 \pm 2.5\%$ of the *cis-syn-cis*-1,2-dimethylcyclobutane-d_2. This converts to a value of 2.2 ± 0.8 based on the amount of recovered *cis*-1,2-dimethylcyclobutane-d_2 and is approximately 40% of the amount of the trans isomer recovered, 6.1. Double $CHCH_3$ rotation appears to be less important than single $CHCH_3$ rotation and given that 2,5-hexanediyl is the major precursor of both stereoisomers of 1,2-dimethylcyclobutane, this process alone cannot account for the observed stereochemistry. The value of 2.2 ± 0.8 is an estimate. It neglects the small amount of cis-syn-cis isomer which fragments. This is compensated in part by the assumption that all of integration at δ 2.14 is due to the cis-syn-cis isomer, which is clearly not the case. Contributions from the chemistry of 3-methyl-1,4-pentanediyl, although smaller, should also lead to other isomers of *cis*-1,2-dimethylcyclobutane-d_2 with resonances at this chemical shift. Some of the cis-syn-cis isomer may arise from consecutive rotations of alternate $CHCH_3$ groups or directly by double methyl rotation.

The stereochemical composition of the olefins recovered from both *cis*- and *trans*-1,2-dimethylcyclobutane-d_2 can be used as a measure of the rate of conformational equilibration in the intermediate diyls, if it is assumed that the rate of fragmentation is insensitive to the cis-trans orientation of the methyl groups in 3-methyl-1,4-pentanediyl.[13] Using the first-order rate equation for approach to cis–trans equilibrium and experimental *cis*/*trans*-2-butene values obtained from both 1,2-dimethylcyclobutane-d_2 isomers leads to an estimate of the cisoid and transoid conformers in 3-methyl-2,5-pentanediyl at equilibrium of 30% and 70%, respectively (Scheme II).[14] A comparison of the expected 2-butene composition at equilibrium with that isolated from both *cis*- and *trans*-1,2-dimethylcyclobutane (Table III), shows that approach to this equilibrium composition in the diyl has proceeded to about one half-life.

The cis/trans composition of propene-d_1 isolated from fragmentation of *cis-anti-cis*-1,2-dimethylcyclobutane-d_2 can likewise be used as a measure of the relative rate of bond rotation in 2,5-hexanediyl. The cis–trans composition of recovered propene-d_1 shows that stereomutation in 2,5-hexanediyl has proceeded through about two half-lives. When the statistical factor of two favoring $CHCH_3$ rotation in 2,5-hexanediyl is taken into account, the amount of rotation occurring before fragmentation in both 2,5-hexanediyl and 3-methyl-1,4-pentanediyl appears to be very similar and relatively small.

Previous reports in the literature have demonstrated that the same stereochemical behavior observed in the thermolysis of 1,2-dimethylcyclobutane, can also be observed in the cycloaddition of 2-butene and ethylene[4] and in the thermolysis of 3,4-(and 3,6-)dimethyl-3,4,5,6-tetrahydropyridazines.[3] Such agreement constitutes the experimental basis generally accepted for a "common intermediate". Whether this "intermediate" is best represented by a minimum or as a flat region[5,6] in the potential energy surface is not known. Although the results of the experiments reported here do not resolve this question, they do define some limits on the lifetime of this specie. In addition, similarities in the degree of stereomutation observed in the olefins obtained from fragmentation of 2,5-hexanediyl and 3-methyl-1,4-pentanediyl suggest that methyl substitution at position 3 of 1,4-pentanediyl does not have a very significant effect on the rate of cleavage of the second carbon–carbon bond. Deuterium substitution at positions 4 and 5 of 6-methylhept-1-ene-3,6-diyl has also been recently shown to have very little effect on the rate of carbon–carbon bond cleavage of 1,4-diyls.[17] The short lifetime of the diyl coupled with the apparent lack of substituent effects on carbon–carbon bond cleavage are not inconsistent with a surface for the diyl that is relatively flat.

Experimental Section

Infrared spectra (IR) were recorded on a Perkin-Elmer Model 337 grating infrared spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a T-60 and JEOL FX 100-MHz FT NMR. Nuclear magnetic resonance data are reported in the following order: chemical shift (multiplicity [s = singlet, d = doublet, t = triplet, m = multiplet], numbers of protons). Analytical and preparative vapor-phase chromatography were performed on a Varian Aerograph Model 920 chromatograph; helium carrier gas was used. The columns used were 12 ft (3/8 in.) and 18 ft ($^1/_4$ in.) squalane and Carbowax. Quantitative VPC analysis was performed by cutting out (in duplicate) and then weighing.

Preparation of *trans*-1,2-Dimethylcyclobutane. *trans*-1,2-Dimethylcyclobutane was synthesized from *trans*-1,2-cyclo-

(10) To the extent that rotational barriers are significant in diradicals, barriers to rotation at radicals sites are lower than those in the corresponding alkanes. Fischer, H. In *Free Radicals*; Kochi, J., Ed.; Wiley: New York, 1973; Vol 2, pp 435–491.

(11) The stereochemical results obtained in the thermolysis of *exo*-2,3,5,6-tetradeuteriobicyclo[2.2.0]hexane, if interpreted in terms of 1,4-cyclohexanediyl, is a unique example of a case where dialkyl-substituted C–C bonds rotate faster than the corresponding fragmentation into 1,5-hexadiene-d_4. Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 5120.

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(13) The relative rates of fragmentation to cyclization in 3-methyl-1,4-pentanediyl have been found to be insensitive to the stereochemistry of the methyl groups.[3,4]

(14) The equilibrium composition in 3-methyl-1,4-pentanediyl was estimated by simultaneous solution for A_e in the first-order rate expression for approach to cis-trans equilibrium in the diyl, $\ln [(A_o - A_e)/(A - A_e)] = (k_f + k_r)t$, from both *cis*- and *trans*-1,2-dimethylcyclobutane-d_2. A_o is the initial concentration of either the cis or trans conformer as determined by the composition and stereochemistry of the starting material, and A_e is the corresponding equilibrium concentration. The composition of cis and trans conformers in 3-methyl-1,4-butanediyl at time t, A was determined by experimental *cis*/*trans*-2-butene values and Scheme II.

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butanedimethanol (99%, Aldrich). The diol was esterified with *p*-toluenesulfonyl chloride/pyridine. A solution of TsCl (32.6 g) in pyridine (150 mL) was cooled to 0 °C, and *trans*-1,2-cyclobutanedimethanol (3.7 g) was added. The solution was kept in a refrigerator for 3 days, until no additional crystallization of pyridinium hydrochloride was evident. The mixture was poured with stirring into ice–water (500 g). The tosylate crystallized after 30 min of stirring. The crystals were filtered, washed with cold water, and dried in vacuum at room temperature overnight. The tosyl ester (14.2 g) was collected in a 92% yield. NMR ($CDCl_3$) δ 1.50–1.84 (m, 4), 2.24–2.5 (m, 2), 2.47 (s, 6), 3.17 (d, 4), 7.50 (d, 4), 7.93 (d, 4).

The tosyl/ester (7 g) was reduced with $LiAlH_4$ (0.19 g) in ether (150 mL). After 4 h, the mixture was hydrolyzed by dropwise addition of 2 mL of water and 2 mL of 15% sodium hydroxide, followed by 6 mL of water and left to stir overnight. The precipitate was filtered and the filtrate fractionated on a 60-cm column; the ether fraction was collected at 32–34 °C. *trans*-1,2-Dimethylcyclobutane was separated from the residue by bulb-to-bulb distillation and purified by gas chromatography. NMR (C_6D_6) δ 1.04 (d, 6), 1.2–1.6 (m, 2), 1.7–2.1 (m, 4); mass spectrum (*m/e*) calcd 84, found 84; IR (gas phase) δ_{max} 2925, 1450, and 1100 cm^{-1}.

Preparation of *cis*-1,2-Dimethylcyclobutane. Cyclobutane-1,2-dicarboxylic anhydride (10.1 g) was reduced with $LiAlH_4$ (3.99 g) in ether (100 mL). After 4 h, the mixture was hydrolyzed as previously reported for the ditosyl ester of cyclobutanedimethanol. The solution was concentrated and *cis*-1,2-cyclobutanedimethanol was obtained in a yield of 72% (6.65 g) by simple distillation (bp 76–90 °C at 50 μm). NMR ($CDCl_3$) δ 1.4–2.2 (m, 4), 2.42–3.08 (m, 2), 3.83 (d, 4), 3.78 (s, 2); IR (neat) 3300 and 2925 cm^{-1}. The cis diol (3.87 g) was converted to the ditosyl ester in a 52.6% yield (7.3 g). NMR ($CDCl_3$) δ 1.5–1.84 (m, 4), 2.67 (s, 6), 2.74–3.0 (m, 2), 3.1 (d, 4), 7.5 (d, 4), 7.93 (d, 4). The ditosyl ester was converted to *cis*-1,2-dimethylcyclobutane as previously reported for the synthesis of *trans*-1,2-dimethylcyclobutane. NMR (100 MHz, C_6D_6) δ 0.98 (d, 6), 1.44–1.7 (m, 2), 1.99–2.2 (m, 2), 2.2–2.58 (m, 2), ($CDCl_3$) δ 1.0 (m, 6), 1.64 (m, 2), 2.14 (m, 2), 2.47 (m, 2); mass spectrum (*m/e*), calcd 84, found 84; IR (gas phase) δ_{max} 2925, 1450, and 1100 cm^{-1}.

Preparation of *cis*-1,2-Dimethyl-*anti*-*cis*-3,4-dideuteriocyclobutane and *trans*-1,2-Dimethyl-*cis*-3,4-dideuteriocyclobutane. 3-Cyclobutane-1,2-dicarboxylic anhydride (15.3 g) was reduced by deuteriation (D_2) in anhydrous ethyl acetate (100 mL) and 5% Pd/C (0.83 g) as catalyst with stirring for 2 h. *cis*-3,4-Dideuteriocyclobutane-*anti*-1,2-dicarboxylic anhydride (14.7 g) was obtained in a 94% yield (mp 74–75 °C). NMR ($CDCl_3$) δ 2.47 (d, 2), 3.57 (d, 2); IR (Nujol) 1750 and 1370 cm^{-1}. The anhydride (9.8 g) was hydrolyzed by heating in water to corresponding dicarboxylic acid (9.9 g) and esterified by treating with diazomethane in ether. The cis dimethyl ester (8.4 g) was obtained in a yield of 82%. NMR ($CDCl_3$) δ 2.37 (d, 2), 3.41 (d, 2), 3.71 (s, 6); IR (gas phase) δ_{max} 1725 cm^{-1}.

The cis ester (6.12 g) was partially isomerized to the trans ester by stirring with sodium methoxide for 24 h. Neutralization with 0.1 M HCl (20 mL), treatment with saturated NaCl (20 mL), and extraction three times with ether (20 mL) afforded a cis–trans mixture.[18] The ethereal solution was dried with anhydrous $MgSO_4$, and distilled. The cis–trans mixture (4.5 g) was collected at 32–36 °C at 25–30 μm. The mixture (4.3 g) was reduced with $LiAlH_4$ (2.05 g) to an isomeric diol mixture (2.3 g) and converted to the tosylate ester (4.4 g) in a yield of 55% as previously reported. Additional ditosyl ester of *cis*-*anti*-*cis*-3,4-dideuteriocyclobutanedimethanol (4.0 g), prepared from dideuterio-1,2-cyclobutanedicarboxylic acid, was added to the above mixture and reduced to dideuterio-1,2-dimethylcyclobutane. The solution was fractionated very carefully in a 50-cm column, and the ether was collected at 32–34 °C. The *cis*- and *trans*-dideuteriodimethylcyclobutanes were removed from the residue by bulb-to-bulb distillation and separated by preparative gas chromatography (squalane, 18 ft × $^1/_4$ in.) at room temperature. *cis*-1,2-Dimethylcyclobutane-d_2 (0.11 g) and *trans*-1,2-dimethylcyclobutane-d_2 (0.67 g) were isolated.

***cis*-1,2-Dimethylcyclobutane-d_2.** NMR (100 MHz, C_6D_6) δ 0.98 (m, 6) 1.64 (t, 2), 2.38–2.5 (m, 2): mass spectrum (*m/e*), calcd 86, found 86; IR (gas phase) δ_{max} 2925, 2185, 1450, and 1100 cm^{-1}.

***trans*-1,2-Dimethylcyclobutane-d_2.** NMR (100 MHz, C_6D_6) δ 1.00 (m, 6) 1.61 (m, 2), 2.02–2.18 (m, 2); mass spectrum (*m/e*), calcd 86, found 86; IR (gas phase) δ_{max} 2925, 1750, 1450, and 1370 cm^{-1}.

***cis*/*trans*-Propene-d_1 (1:1).** An equal molar mixture of *cis*- and *trans*-propene-d_1 was prepared by the pyrolysis of *n*-propyl-d_1 acetate at 510 °C. Propionaldehyde (4 g) was reduced with $LiAlD_4$ (1.02 g) in ether (20 mL). The mixture was hydrolyzed as previously reported. The ether extract (3 × 20 mL) was dried ($MgSO_4$) and carefully concentrated. The residue was treated with acetic anhydride (12 mL) and 2 drops of concentrated H_2SO_4 and refluxed for 6 h. The reaction product was poured into cold water, neutralized with $NaHCO_3$, and extracted with ether. Careful removal of the ether followed by preparative gas chromatography of the residue (Carbowax column, 35 °C) afforded *n*-propyl-d_1 acetate. NMR ($CDCl_3$) δ 1.0 (t, 3), 1.6 (q, 2), 2.0 (s, 3), 3.9 (t, 1). Pyrolysis of propyl-d_1 acetate (20 mm × 78.5 mL) at 510 °C afforded propene-d_1 (15.5 mm × 78.5 mL). The infrared spectrum showed peaks at 987 and 813 cm^{-1} and was identical with that of propene-d_1 isolated from *trans*-1,2-dimethylcyclobutane-d_2.

Preparation of *cis*- and *trans*-Ethylene-d_2.[19] An equal molar mixture of *cis*- and *trans*-ethylene-d_2 was made by thermolysis of *trans*-ethylene-d_2 at 510 °C in a quartz tube until the ratio of cis band (843 cm^{-1}) to the trans band (987 cm^{-1}) in the infrared no longer changed (reaction time, 1 day).

Thermolysis Experiments. The flow system consisted of a 35-cm quartz tube (16 mm o.d.) surrounded by a brass sheath and heated by asbestos-insulated nichrome wire and controlled to ±5 °C. The temperature was monitored by an iron–constantan thermocouple kept inside the tube. Flow rates were measured at the exhaust of the vacuum pump and were kept at about 0.35 mL/s. A carrier gas of nitrogen (142 mm) was used. For each thermolysis, 52 mg (50 mm × 78.5 mL) of sample was used.

Typical Analysis of the Thermolysis Products of 1,2-Dimethylcyclobutane. After thermolysis, ethylene was separated from the other products by bulb-to-bulb distillation on the vacuum line. About 5 mg (2 mm × 78.5 mL) of ethylene-d_2 was collected for each reaction. The cis-trans composition of ethylene-d_2 was determined by infrared spectroscopy in a 5-mL (5-cm path) gas cell, equipped with KBr windows. The infrared cell contained a conical shaped aluminum sheath to reduce the dead volume. The 1-propene-d_1 was also separated from the other products by the same procedure. About 9 mg (20 mm × 78.5 mL) was separated from mixture. The cis-trans composition of 1-propene-d_1 was also determined by infrared spectroscopy in a 19.6-mL (8-cm path) gas cell, equipped with KBr windows. The composition of *cis*- and *trans*-2-butene was determined by VPC (squalane, 18 ft × $^1/_4$ in.) at room temperature. The recovered *cis*- and *trans*-1,2-dimethylcyclobutane-d_2 mixture was analyzed and separated by VPC (squalane, 12 ft × $^3/_8$ in.) at room temperature.

The yields of ethylene and propene were determined by pressure measurements on the isolated materials relative to the total pressure of recovered material. The amount of 2-butene was determined from the amount of ethylene recovered. Recovered 1,2-dimethylcyclobutane was evaluated by difference. Uncertainties in composition between C_2, C_3, C_4, and C_6 fractions are larger than the uncertainties within each fraction.

Control Experiments. *cis*- and *trans*-ethylene-d_2 and *cis*- and *trans*-2-butene were found to be stable under the experimental conditions. A nonequilibrated mixture of *cis*- and *trans*-1-propene-d_1 isolated from *cis*-1,2-dimethylcyclobutane-d_2 was also found to be stable under the same conditions.

NMR Simulations. The NMR resonances of *cis*-*anti*-*cis*- and *cis*-*syn*-*cis*-1,2-dimethylcyclobutane-d_2 at δ 1.64 and 2.14 were displayed as distorted triplets and could be simulated as A,A',B,B' systems. The spacings of the outer lines of both triplets were found to be very sensitive to the sum of the coupling constants

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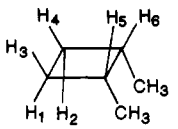
between protons at carbons 1 and 3 and 2 and 3. This allowed us to set the sum of $J_{1,5} + J_{1,6}$ to 4.7 Hz for the cis-anti-cis compound and $J_{3,5} + J_{3,6}$ to 9.4 Hz for the cis-syn-cis compound. Values for the other coupling constants (in Hz) used in the simulations include the following: $J_{1,2} = 8.9$, $J_{1,5} = 5.5$, $J_{1,6} = -0.8$, $J_{5,6} = 9.4$ for the cis-anti-cis isomer; $J_{3,4} = 8.0$, $J_{3,5} = 8.0$, $J_{3,6} = 1.4$ for the cis-syn-cis isomer. The use of values for $J_{1,6}$ and $J_{3,6}$ outside the range of uncertainty quoted in the text, resulted in spectra which were different from experiment; variations in the other J values were not sufficient to produce acceptable simulations. The chemical shifts used for the protons in *cis*-1,2-dimethylcyclobutane were δ 1.64, 2.14, and 2.47 ($CDCl_3$). The methyl resonances at δ 1.0 were not used in the simulations.



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Registry No. *cis*-1,2-Dimethyl-*anti*-3,4-dideuteriocyclobutane, 39768-31-5; *trans*-1,2-dimethyl-*cis*-3,4-dideuteriocyclobutane, 110221-72-2.

Notes

Synthesis of Nitro-Substituted 2,3,4,8-Tetraphenylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decanes

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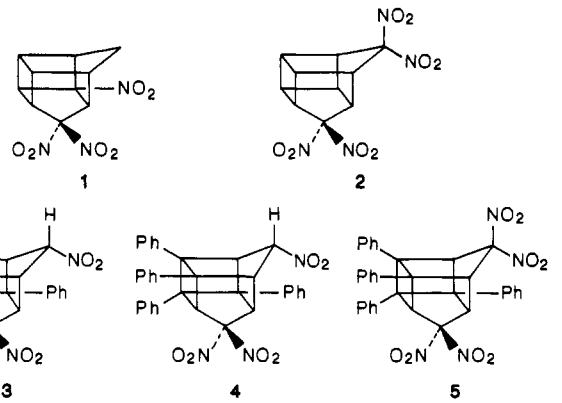
There is considerable current interest in the synthesis and chemistry of energetic polycyclic "cage" compounds.[1-5] The title compounds are novel, strained energetic materials that have been prepared as part of an ongoing program involved with the synthesis of new polynitro-1,3-bishomocubanes. Two such systems, a trinitro- and a tetranitro-1,3-bishomocubane (**1**[3] and **2**[4], respectively) have been prepared in our laboratory, and their respective structures have been determined via single-crystal X-ray crystallography.[6,7]

Three compounds, a dinitro- (**3**), a trinitro- (**4**), and a tetranitro-2,3,4,8-tetraphenylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (**5**), have been prepared in the present study. The



route employed for synthesizing **3**–**5** is shown in Scheme I. The starting material for this reaction sequence is the known[8,9] 2,3,4,8-tetraphenylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]-decane-6,10-dione **6** (Scheme I). Subsequent conversion of the ketone functionalities in **6** into $CHNO_2$ and into $C(NO_2)_2$ groups was accomplished by using previously published procedures.[3,4]

Trifluoroperacetic acid oxidation of bis(oxime) **7** (derived[10] from cage dione **6**) afforded a gross mixture of isomeric 2,3,4,8-tetraphenyl-6,10-dinitropentacyclo-[5.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decanes. Careful fractional recrystallization of this mixture from methanol afforded a single isomer, **3**. Analysis of the proton and carbon-13 NMR spectra of **3** suggests that it contains a twofold symmetry element. While this result rules out the syn-6, anti-10 isomer, it is consistent with either of two possible structures for **3**, i.e., the syn-6, syn-10 or the anti-6, anti-10 isomer. Careful fractional recrystallization of this material from methanol afforded only a poor quality single crystal for use in single-crystal X-ray structural analysis. The quality of refinement of the crystallographic data obtained for this crystal was correspondingly poor (see Experimental Section). Nevertheless, the results thereby obtained

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