verted negative peaks. The region 4–7 ppm was still too congested and hence 50% C_6D_6 was added to spread out the spectrum (Figure 1, bottom run). For further improvement, the 4.75 ppm HDO peak was moved upfield out of the range of overlap by warming the sample to 55 °C. As shown in Figure 1 (top run), the resulting spectrum was a dramatic improvement over the original (inset), and revealed almost all chemical shifts and coupling constants. This assignment is consistent with that of the trans opening of isomer I by guanine when compared with the cis and trans hydration products from isomer I[5] and was confirmed by showing that the 7-H doublet at 5.23 ppm (see insert, Figure 1) moves downfield to 6.60 ppm $J_{7,8}$ = 9 Hz in the per-*O*-acetate derivative (acetic anhydride–pyridine, room temperature 12 h).

The point of attachment of the guanosine moiety was proved as follows. When measured in Me_2SO-d_6 the ^1H NMR spectrum of **1** showed a conspicuous doublet at 6.92 ppm (J = 8 Hz, N^2-H of guanine), which collapsed to a singlet upon irradiation of the 10-proton at 5.93 ppm (overlapping with the 1′-H) and disappeared upon addition of D_2O. Such observations are only consistent with substitution of the N^2 of guanine at the 10-position of isomer I. The high resolution mass spectrum of the 5′,7-diacetate 2′,3′,8,9-diacetonide of **3**[6,7] also indicated that substitution had occurred through the N^2 of guanine. An ion at *m/e* 342.1152 (1.9%, $C_{22}H_{16}NO_3$ = 342.1129) corresponds to cleavage between the C-2 and N^2 positions of guanine and loss of acetone from the BP moiety. An additional loss of acetic acid from this ion was also observed: *m/e* 282.0930 (4.5% $C_{20}H_{12}NO$ = 282.0919).

Current investigations are directed towards the absolute configurations of **1** and **3** and other derivatives formed with RNA and DNA during metabolism of BP.[8]

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(3) The adducts were prepared by reacting isomer (±)-I with poly(G) (both at 1 mg/ml) in 2:1 acetone–water for 24 h at 37 °C. The unbound derivatives were removed by extraction with ethyl acetate and 1-butanol followed by precipitation of the poly(G) with ethanol. The modified polymer was hydrolyzed for 18 h at 37 °C with 0.3 N NaOH. The nucleotides were applied to a LH-20 Sephadex column (1.8 × 66 cm), eluting first with 20 mM NH_4HCO_3, pH 8.5, to remove GMP and then a gradient of 20–80% methanol which separated guanosine derivatives 1 and **3** as their monophosphates. The latter were treated with alkaline phosphatase and the nucleosides (1 and **3**) repurified by LH-20 Sephadex chromatography. Analysis of these derivatives by HPLC (Dupont Zorbax ODS column, 0.25 m × 6.4 mm; 2500 psi; 50 °C; 40% methanol in water) showed 1 (21 min) to be essentially pure and **3** (34 min) to be contaminated by about 10% with a third component **2** (25 min) (structure unknown). For detailed methods see S. H. Blobstein, I. B. Weinstein, D. Grunberger, J. Weisgras, and R. G. Harvey, *Biochemistry*, 14, 3451 (1975), and A. M. Jeffrey, S. H. Blobstein, I. B. Weinstein, and R. G. Harvey, *Anal. Biochem.*, 7**3**, 378 (1976).

(4) The CD spectra of **3** and 1 (50% water/methanol, Cary 60, JASCO J-40 instruments) showed weak extrema of same intensities but of opposite signs in the region 350–290 nm. Only the strong Cotton effects are listed. Compound **3** had the following $\Delta\epsilon$ at the indicated wavelengths: 280 nm, +31; 275 nm, −16; 249 nm, +115; and 240 nm, −53; Compound 1: 280 nm, −34; 273 nm, +4; 249 nm, −56; 240 nm, +25. The 5′,7-diacetate-2′,3′,8,9-diacetonides of **3** and 1 showed the following CD spectra **3:** 280 nm, +37; 275 nm, −26; 249 nm, +125; 236 nm, −63, 1: 280 nm, −38; 275 nm, +34; 249 nm, −121; 236 nm, +61.

(5) J. Keller, PhD Dissertation, Department of Chemistry, University of Wisconsin, Madison, Wis., 1976.

(6) The mass spectrum (Jeol JMS-01SG -2, EI mode, 70 eV, probe 290 °C, source 250 °C) showed ions mainly resulting from losses of acetic acid and/or acetone from the molecular ion *m/e* 749.2704 (1.1%, $C_{40}H_{39}N_5O_{10}$ = 749.2697); 384.1365 (5.9%, $C_{25}H_{20}O_4$ = 384.1362); 350.1099 (4.6%, $C_{14}H_{16}N_5O_6$ = 350.1100); 324.1158 (16%, $C_{23}H_{16}O_2$ = 324.1150); 284.0869 (30%, $C_{20}H_{12}O_2$ = 284.0837); 268.0876 (12% $C_{20}H_{12}$ = 268.0888); 256.0879 (12%, $C_{19}H_{12}O$ = 256.0888); 255.0825 (14%, $C_{19}H_{11}O$ = 255.0810); 239.0833 (13% $C_{19}H_{11}$ = 239.0860); 43 (100%).

(7) The authors wish to thank Dr. P. Roller, NCI, NIH, for the thorough analysis of the high resolution mass spectrum of the diacetate, diacetonide of **3.** This work was supported by NIH Grants CA-02332 and CA-11572, NCI Contracts E-72-3234 and CP-033385, and American Cancer Society Grant BC-132.

(8) Note Added in Proof: When reacted with poly(G), 7,12-dimethylbenz[*a*]anthracene-5,6-oxide has also been shown to link covalently via the 2-amino group of guanosine: A. M. Jeffrey, S. H. Blobstein, I. B. Weinstein, F. A. Beland, R. G. Harvey, H. Kasai, and K. Nakanishi, *Proc. Natl. Acad. Sci. U.S.A.*, **73,** 2311 (1976).

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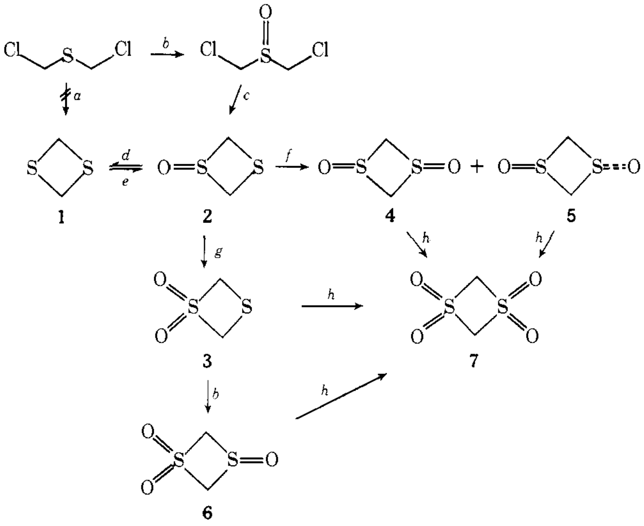
1,3-Dithietane

Sir:

Although derivatives of 1,3-dithietane (**1**) have been known for over 100 years,[1] the parent compound has until now remained unknown. We describe herein a simple synthesis of **1** from readily available starting materials. We also report the preparation of the previously unknown *S*-oxides of **1,** 1,3-dithietane 1-oxide (**2**), 1,3-dithietane 1,1-dioxide (**3**), *cis*- and *trans*-1,3-dithietane 1,3-dioxide (**4** and **5,** respectively), and 1,3-dithietane 1,1,3-trioxide (**6**), and the conversion in high yield of several of these compounds (**3, 4, 5, 6**) to the previously described sulfene dimer, 1,3-dithietane 1,1,3,3-tetraoxide (**7**).[2] We have initiated a detailed investigation of the reactions and structural features of these interesting heterocycles. Novel structural features of two of the above compounds are described in this communication while one aspect of the chemistry of **2,** namely, its facile pyrolytic conversion into sulfine and thioformaldehyde, is reported elsewhere.[3]

While bis(chloromethyl) sulfide fails to give monomeric product with sodium sulfide,[4] presumably due to the high reactivity of the former compound in displacement processes,

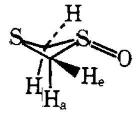
Scheme I



[a] $Na_2S\cdot 9H_2O$, DMF. [b] CH_3CO_3H, $CHCl_3$, 0 °C. [c] $Na_2S\cdot 9H_2O$, 0.3 equiv of "Aliquat 336", H_2O, vigorously stirred. [d] 2 mol equiv of 1 M THF–BH_3, 24 h at 25 °C. [e] $PhICl_2$, CH_3CN, Et_3N, H_2O (or $H_2{}^{18}O$). [f] $PhICl_2$, C_5H_5N, H_2O, −30 °C or *m*-$ClC_6H_4CO_3H$, CH_2Cl_2, 0 °C. [g] 0.67 mol equiv of $KMnO_4$, $MgSO_4$, acetone, −30 °C. [h] 30 mol equiv of CH_3CO_3H, 100 °C, 4 h.

bis(chloromethyl) sulfoxide[5] in the presence of the phase transfer catalyst "tricaprylylmethylammonium chloride" (General Mills "Aliquat 336") reacts rapidly and exothermically at room temperature with aqueous sodium sulfide affording **2**, mp 71–73.5 °C, in 36% yield[6,7] (Scheme I). Reduction of **2** with excess 1 M tetrahydrofuran-borane (Aldrich) at room temperature for 1 day gives **1**, mp 105–106 °C, in 70% yield.[7] Reoxidation of **1** with iodobenzene dichloride in acetonitrile containing $H_2{}^{18}O$ and triethylamine[8] affords **2**-^{18}O (required for microwave studies[3]). Treatment of **2** at −20 °C with $KMnO_4/MgSO_4$ in acetone[9] yields **3** (96%), mp 141–143 °C.[7] Oxidation of **2** with iodobenzene dichloride in aqueous pyridine at −30 °C or with metachloroperbenzoic acid in methylene chloride at 0 °C produces, respectively, a 3:1 or 2:3 mixture of **4**[7] (mp 260 °C dec) and **5**[7] (mp 203–205 °C dec), readily separable by fractional recrystallization from dimethylformamide.[10] Treatment of **3** in chloroform at 0 °C with peracetic acid gives **6**, mp 231–234 °C in 90% yield.[7] Finally, exposure of **3, 4, 5,** and **6** to excess peracetic acid at 100 °C for several hours gives in 71–86% yield compound **7** with spectral and physical properties in complete agreement with those previously reported for the sulfene dimer.[2] Compounds **1–7** are all colorless, nicely crystalline, sublimable solids.

The structure of **2** has been determined by the isotopic substitution method from its microwave spectrum and the spectra of eight isotopic modifications (^{18}O, $^{34}S_0$, ^{34}S, ^{13}C, d_1-a, d_1-e, d_3-aae, and d_4).[12] The ring is "puckered", the angle between the two CSC planes being 39.3 (2)°, with the oxygen equatorial as shown in **2a.**[13] Other structural parameters are:



2a

r S_0–O = 1.473 (3) Å, r C–S_0 = 1.81 (2) Å, r C–S = 1.82 (2) Å, r C–H_a = 1.13 (4) Å, r C–H_e = 1.06 (2) Å, $\angle CS_0C = 81.7$ (8)°, $\angle CSC = 81.1$ (5)°, $\angle SC_0 = 91.2$ (5)°, $\angle CS_0O = 112.4$ (7)°, $\angle(H_aCS_0) - (CS_0O) = 25.5$ (14)°, and $\angle(H_eCS_0) - (CS_0O) = -99.3$ (24)°. A novel feature of the structure of **2** is the short nonbonded S···S distance of 2.600 (7) Å (the nonbonded C···C distance is 2.37 (2) Å). Since the S–O distance in **2** is normal (the S–O distances in *cis*- and *trans*-3-*p*-bromophenylthietane 1-oxide are 1.482 (13) and 1.492 Å, respectively[14]) and **7** has been found to possess an even shorter S···S distance (see below), it seems unlikely that there is any substantial bonding between the sulfurs in **2.**[15]

If the ring of **1** were "puckered" as much as that of **2,** its dipole moment would probably be about 1 D, and this coupled with its high vapor pressure at room temperature would result in a rich microwave spectrum. The fact that no microwave absorptions are observed for **1** suggests that its ring is equilibrium planar, or very nearly so.

The structure of **7** has been determined by x-ray diffraction methods with the following crystal data: $C_2H_4O_4S_2$, M = 156.2; monoclinic, space group $P2_1/c$; $a = 5.582$ (2), $b = 5.759$ (2), $c = 8.965$ (4) Å, $\beta = 116.84$ (3)°; $d_{measd} = 2.01$ g cm^{-3}, $Z = 2$, $d_{calcd} = 2.017$ g cm^{-3}; $U = 257.1$ (2) Å^3; one-half molecule in the asymmetric unit located about a center of symmetry; 1184 independent counter data were collected by the ω–2θ scan technique. The structure was determined by direct methods and refined by full-matrix least squares (C, O, S anisotropic; H isotropic) to a discrepancy factor R_1 of 0.038. The four atom ring of **7** is planar[16] and almost square with SCS and CSC angles of 91.5 (1)° and 88.5 (1)°, respectively. Particularly notable is the extremely short nonbonded S···S distance of 2.590 (1) Å (to our knowledge, *the shortest yet reported*). Other pertinent structural features of **7** include: nonbonded C···C, 2.524 (4) Å, S–O 1.433 (2) Å,[17] S–C 1.808 (2) Å[17], C–H, 0.90 (3) Å,[17] ∠OSO, 119.2 (1)°, ∠HCH, 115 (3)°, ∠OSC, 111.2 (1)°,[17] and ∠HCS, 112 (2)°.[17,18]

We are actively investigating the chemical reactions of these intriguing lower homologues of 1,3,5-trithiane, with one objective being the synthesis of the theoretically interesting[19] molecule 2,4-dithiabicyclo[1.1.0]butane.

Acknowledgment. Support for this research from the donors of the Petroleum Research Fund, administered by the American Chemical Society (E.B.), the Research Corporation (R.E.P.), the University of Missouri—St. Louis, and the National Science Foundation under its Undergraduate Research Participation program is gratefully acknowledged. E.R.C. acknowledges use of x-ray facilities at Wayne State University during sabbatical leave. We thank Professor J. Gajewski for the high resolution mass spectrometric data.

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(6) For example, a vigorously stirred mixture of 0.2 mol of $(ClCH_2)_2SO$ and an equal weight of "Aliquat 336" in 200 ml of water was treated all at once with 0.26 mol of $Na_2S \cdot 9H_2O$. After 1 h, the aqueous layer was separated, saturated with salt, and extracted repeatedly with $CHCl_3$. Concentration, followed by recrystallization from CCl_4 gave **2.**

(7) **1:** NMR ($CDCl_3$) δ 4.05 (s); ir (KBr) 1195 (m), 880 (m), 735 (w), 705 (m), 684 (m) cm^{-1}; uv (C_2H_5OH) λ_{max} 216 (860), 293 (38), 311 nm (sh, 20); MS 91.9760 (calcd for $C_2H_4S_2$ 91.9755). **2:** NMR (C_2D_6SO) δ 4.23 (m), (C_6D_6) AA′BB′ system, δ_A 3.37, δ_B 3.73; ir (KBr) 1150, 1080, 1035 cm^{-1} (all s); uv (C_2H_5OH) λ_{max} 207 (674), 222 (578), 266 nm (101); MS 107.9708 (calcd for $C_2H_4S_2O$ 107.9704). **3:** NMR (CF_3COOH or C_2D_6SO) δ 5.27 (s); ir (KBr) 1315 (s), 1200 (s), 1130 (s), 1393 (m), 555 (s), 440 (s) cm^{-1}; uv (C_2H_5OH) λ_{max} 217 (200), 245 nm (sh, 30); MS 123.9659 (calcd for $C_2H_4S_2O_2$ 123.9653). **4:** NMR (CF_3COOH) AA′BB′ system, δ_A 4.78, δ_B 5.72; ir (KBr) 1342 (m), 1130, 1100, 1060, 995 (all s) cm^{-1}; MS 123.9662 (calcd for $C_2H_4S_2O_2$ 123.9653). **5:** NMR (CF_3COOH) δ 4.97 (s); ir (KBr) 1342 (m), 1150 (m), 1055 (s); MS 123.9662 (calcd for $C_2H_4S_2O_2$ 123.9653). **6:** NMR (CF_3COOH) AA′BB′ system, δ_A 5.47, δ_B 5.88, (C_2D_6SO) AA′BB′ system, δ_A 5.17, δ_B 5.72; ir (KBr) 1325, 1300, 1170, 1085 (all s) cm^{-1}; MS 139.9609 (calcd for $C_2H_4S_2O_3$ 139.9602). For 7 we find NMR (C_2D_6SO) δ 6.40 (s; lit.[2] δ 6.42).

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(9) These conditions represent a modification of the useful procedure of H. B. Henbest and S. A. Khan, *Chem. Commun.*, 1036 (1968); also see S. A. Khan, J. B. Lambert, O. Hernandez, and F. A. Carey, *J. Am. Chem. Soc.*, **97,** 1468 (1975).

(10) The assignment of structure **4** to the mp 260 °C bis-sulfoxide and structure **5** to the mp 203 °C bis-sulfoxide follows from the NMR spectra of these isomers (the trans isomer showing a sharp *singlet* for the equivalent methylene protons) as well as the predominance of the mp 260 °C isomer or the mp 203 °C isomer under conditions involving respectively thermodynamic control ($PhICl_2$)[8] or kinetic control (RCO_3H).[11] Coupling of the S=O vibrations could account for the presence of *two* S=O bands in the ir spectrum of the symmetrical structure **4.**

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(12) Full details of the microwave study as well as novel features of deuterium incorporation in **2** and related compounds will be forthcoming.

(13) This is the first example of a *nonplanar* 1,3-dithietane derivative. *Planar* 1,3-diethietanes have previously been described by Durig,[1d] Middleton,[1f] and Krebs.[1h] Thietane 1-oxides are known from microwave[14a] or x-ray diffraction[14b,c] studies to be "puckered" with dihedral angles of 32–35° and with oxygen in the equatorial position.

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(17) Mean values.

(18) The structural data for 7 may be compared to corresponding data for 2,2-dimethylthietane 1,1-dioxide: S–O 1.459 (4) and 1.452 (4) Å, ∠CSC, 80.20°, ∠OSO, 117.59°; M. L. Ziegler, J. Weiss, H. Schildknecht, N. Grund, and H.-E. Sasse, *Justus Liebigs Ann. Chem.*, 1702 (1973).

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Thermolysis of Bicyclo[2.2.0]hex-2-ene

Sir:

The cyclodissociation of bicyclo[2.2.0]hex-2-ene[1] (**2ab**, Figure 1) bridges two long studied series of similar reactions. Common to both is a problem still unresolved in any general way. How does molecular strain enhance reactivity when a "least-motion" mechanism is symmetry-forbidden?

Bicyclo[2.2.0]hexane (**1b**) employs its strain to select a symmetry-allowed but otherwise unanticipated ($_{\sigma}2_s + {}_{\sigma}2_a$) path to hexa-1,5-diene.[2] Dewar benzene (**3b**), at least in part, crosses over to the benzene triplet surface.[3] Bicyclo[4.2.0]oct-7-ene (**4a**) is believed to choose a sequence of two symmetry-allowed steps—conrotatory ring opening to the cis-trans diene and then 1,5-hydrogen shift—to provide the isomeric cis-cis diene.[4,5] The more thoroughly investigated cyclodissociation of **1a** to cyclopentadiene[6] remains mechanistically the most obscure.[7]

Our approach, as elsewhere,[2,8] has been to generate a complete list of mechanistic alternatives, both "plausible" and otherwise. Then, through experiment, as many as possible are rigorously excluded.

In this case, product analysis (>97% cyclohexa-1,3-diene, uncontaminated by ^{1}H NMR- or GC-detectable impurities) and homogeneous first-order kinetic data (Table I)[9] rigorously excluded many C_6H_8 isomers as potential transient intermediates. Some are already known to provide other products (e.g., $\Delta^{1,4}$-bicyclo[2.2.0]hexene[10]) and/or to react too slowly at these temperatures (e.g., *trans*-hexa-1,3,5-triene,[11] cyclohexa-1,4-diene,[12] bicyclo[2.1.1]-[13] or bicyclo[3.1.0]hex-2-enes,[14] tricyclo[3.1.0.0^{2,6}]-[15] or *anti*-tricyclo[3.1.0.0^{2,4}]hexanes[16]). Still others (e.g., 2-vinylbicyclo[1.1.0]butane, tricyclo[2.2.0.0^{2,6}]hexane) may reasonably be presumed to fall into one or another of these two categories.[25] A particular effort was made to guarantee the absence (<1%) of *cis*-hexa-1,3,5-triene, both in residual reactant and in initial product. Otherwise, the reported rate of its transformation to cyclohexa-1,3-diene (10^5k = 0.22, 25.6 at 100°, 150°)[17] would strongly have implicated mechanism 1.

Table I. Gas Phase (240–420 Torr) Kinetic Data

Temp, °C	10^5k[a]	*R* factor[b]
102.5	.417 ± 0.006	0.011
110.9[c]	1.06 ± 0.06	0.032
123.4	3.89 ± 0.18	0.019
137.4	20.5 ± 1.0	0.038
151.6[c]	72.8 ± 2.5	0.018
$\Delta H^{\ddagger}$ [d]	32.15 ± 0.09	0.071
$\Delta S^{\ddagger}$ [d]	2.4 ± 0.2	
E_a[d]	32.95 ± 0.09	0.071
A[d]	(7.4 ± 0.8) × 10^{13}	

[a] Uncertainties are standard deviations. [b] W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y., 1964, p 157. [c] Insensitive to a sixfold increase in surface area. [d] Each set derives from concurrent nonlinear least-squares fitting of integrated GC area ratios obtained at all temperatures between 3 and 87% reaction.

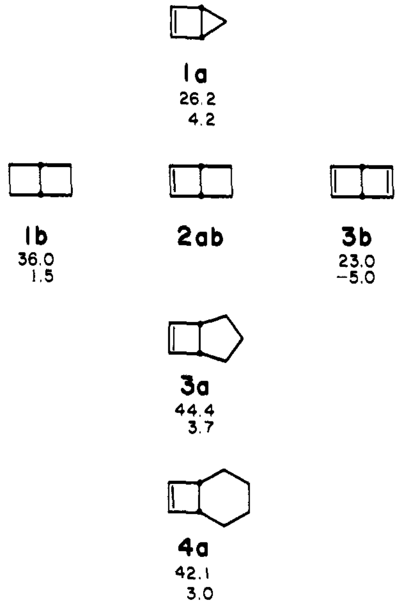
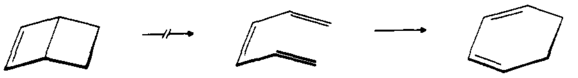
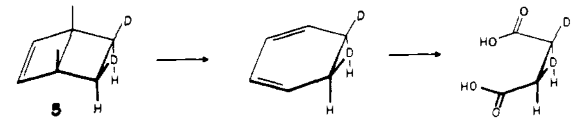


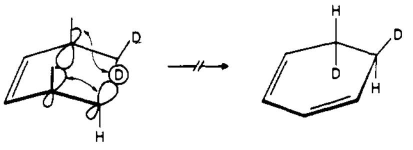
Figure 1. Hitherto available thermolysis $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ data.


(1)

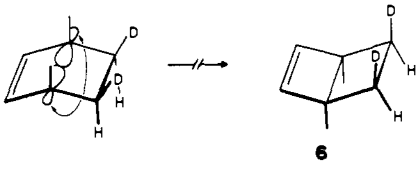
Next, cyclohexa-1,3-diene-d_2, obtained from the 5-exo,6-exo-d_2 substrate **5**, was oxidized to *meso*-dideuteriosuccinic acid of >95% isotopic and diastereomeric purity. In this way, the absence of the ($_{\sigma}2_a + {}_{\sigma}2_s$) – ($_{\pi}2_s + {}_{\pi}4_s$) variant of eq 1 is



confirmed. More generally excluded is any mechanism that might violate the stereochemical integrity of the two adjacent methylene groups. Among these, eq 2 is analogous to the (more difficult) transformation of bicyclo[2.1.0]pentane to cyclopentene.[18] Finally, the absence of >1.3% of **6** or of >0.2% of **7** in residual reactant requires that neither eq 3 nor 4 effectively compete with cyclodissociation.[19]



(2)



6
(3)