

verted negative peaks. The region 4–7 ppm was still too congested and hence 50% C₆D₆ 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 I⁵ 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 Me₂SO-*d*₆ the ¹H NMR spectrum of **1** showed a conspicuous doublet at 6.92 ppm ($J = 8$ Hz, N²-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 D₂O. Such observations are only consistent with substitution of the N² 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 N² of guanine. An ion at m/e 342.1152 (1.9%, C₂₂H₁₆NO₃ = 342.1129) corresponds to cleavage between the C-2 and N² 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% C₂₀H₁₂NO = 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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- (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.
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- (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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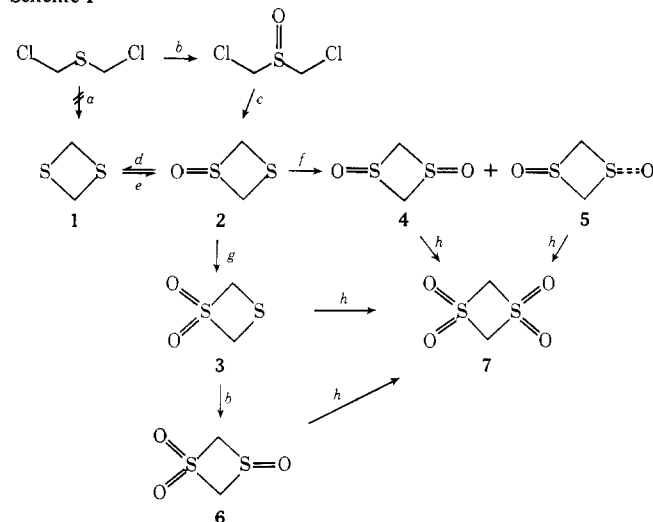
1,3-Dithietane

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,

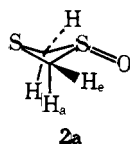
Scheme I



^a Na₂S·9H₂O, DMF, ^b CH₃CO₂H, CHCl₃, 0 °C. ^c Na₂S·9H₂O, 0.3 equiv of "Aliquat 336", H₂O, vigorously stirred. ^d 2 mol equiv of 1 M THF–BH₃, 24 h at 25 °C. ^e PhICl₂, CH₃CN, Et₃N, H₂O (or H₂¹⁸O). ^f PhICl₂, C₂H₅N, H₂O, -30 °C or *m*-ClC₆H₄CO₂H, CH₂Cl₂, 0 °C. ^g 0.67 mol equiv of KMnO₄, MgSO₄, acetone, -30 °C. ^h 30 mol equiv of CH₃CO₂H, 100 °C, 4 h.

bis(chloromethyl) sulfoxide⁵ in the presence of the phase transfer catalyst "tricaprylmethylammonium 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 H₂¹⁸O and triethylamine⁸ affords **2**-¹⁸O (required for microwave studies³). Treatment of **2** at –20 °C with KMnO₄/MgSO₄ in acetone⁹ 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 (¹⁸O, ³⁴S₀, ³⁴S, ¹³C, *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:



$r_{\text{S-O}} = 1.473$ (3) Å, $r_{\text{C-S}_0} = 1.81$ (2) Å, $r_{\text{C-S}} = 1.82$ (2) Å, $r_{\text{C-H}_a} = 1.13$ (4) Å, $r_{\text{C-H}_e} = 1.06$ (2) Å, $\angle \text{CS}_0\text{C} = 81.7$ (8)°, $\angle \text{CSC} = 81.1$ (5)°, $\angle \text{SC}_0 = 91.2$ (5)°, $\angle \text{CS}_0\text{O} = 112.4$ (7)°, $\angle (\text{H}_a\text{CS}_0) - (\text{CS}_0\text{O}) = 25.5$ (14)°, and $\angle (\text{H}_e\text{CS}_0) - (\text{CS}_0\text{O}) = -99.3$ (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, respectively¹⁴) 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: C₂H₄O₄S₂, *M* = 156.2; monoclinic, space group *P*2₁/*c*; *a* = 5.582 (2), *b* = 5.759 (2), *c* = 8.965 (4) Å, β = 116.84 (3)°; *d*_{meas} = 2.01 g cm^{–3}, *Z* = 2, *d*_{calcd} = 2.017 g cm^{–3}; *U* = 257.1 (2) Å³; one-half molecule in the asymmetric unit located about a center of symmetry; 1184 independent counter data were collected by the ω –2 θ 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 planar¹⁶ 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 $\angle \text{OSO}$, 119.2 (1)°, $\angle \text{HCH}$, 115 (3)°, $\angle \text{OSC}$, 111.2 (1)°,¹⁷ and $\angle \text{HCS}$, 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 interesting¹⁹ 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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- 1**: NMR (CDCl₃) δ 4.05 (s); ir (KBr) 1195 (m), 880 (m), 735 (w), 705 (m), 684 (m) cm^{–1}; uv (C₂H₅OH) λ_{max} 216 (860), 293 (38), 311 nm (sh, 20); MS 91.9760 (calcd for C₂H₄S₂ 91.9755). **2**: NMR (C₂D₆SO) δ 4.23 (m), (C₂D₆) AA'BB' system, δ_A 3.37, δ_B 3.73; ir (KBr) 1150, 1080, 1035 cm^{–1} (all s); uv (C₂H₅OH) λ_{max} 207 (674), 222 (578), 266 nm (101); MS 107.9708 (calcd for C₂H₄S₂O 107.9704). **3**: NMR (CF₃COOH or C₂D₆SO) δ 5.27 (s); ir (KBr) 1315 (s), 1200 (s), 1130 (s), 1393 (m), 555 (s), 440 (s) cm^{–1}; uv (C₂H₅OH) λ_{max} 217 (200), 245 nm (sh, 30); MS 123.9659 (calcd for C₂H₄S₂O₂ 123.9653). **4**: NMR (CF₃COOH) 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 C₂H₄S₂O₂ 123.9653). **5**: NMR (CF₃COOH) δ 4.97 (s); ir (KBr) 1342 (m), 1150 (m), 1055 (s); MS 123.9662 (calcd for C₂H₄S₂O₂ 123.9653). **6**: NMR (CF₃COOH) AA'BB' system, δ_A 5.47, δ_B 5.88, (C₂D₆SO) 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 C₂H₄S₂O₃ 139.9602). For **7** we find NMR (C₂D₆SO) δ 6.40 (s; lit.² δ 6.42).
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Thermolysis of Bicyclo[2.2.0]hex-2-ene

Sir:

The cyclodissociation of bicyclo[2.2.0]hex-2-ene¹ (**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 ($\sigma_{2s} + \sigma_{2a}$) 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 cyclopentadiene⁶ 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 ¹H NMR- or GC-detectable impurities) and homogeneous first-order kinetic data (Table I)⁹ rigorously

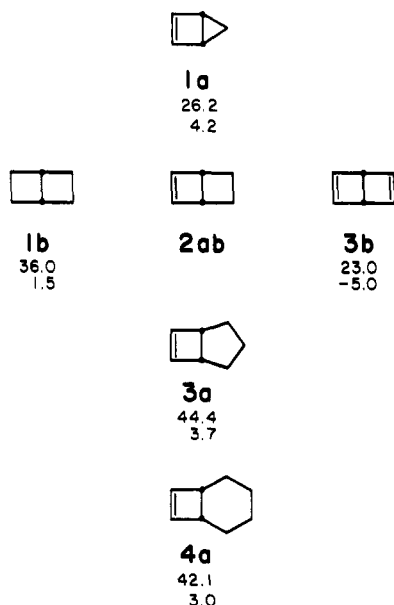


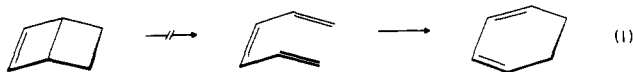
Figure 1. Hitherto available thermolysis ΔH^\ddagger and ΔS^\ddagger data.

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

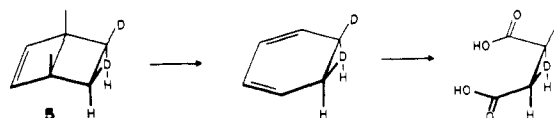
Temp, °C	$10^5 k^a$	R factor ^b
102.5	4.17 ± 0.006	0.011
110.9 ^c	1.06 ± 0.06	0.032
123.4	3.89 ± 0.18	0.019
137.4	20.5 ± 1.0	0.038
151.6 ^c	72.8 ± 2.5	0.018
$\Delta H^\ddagger d$	32.15 ± 0.09	
		0.071
$\Delta S^\ddagger d$	2.4 ± 0.2	
E_a^d	32.95 ± 0.09	
		0.071
A^d	$(7.4 \pm 0.8) \times 10^{13}$	

^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.

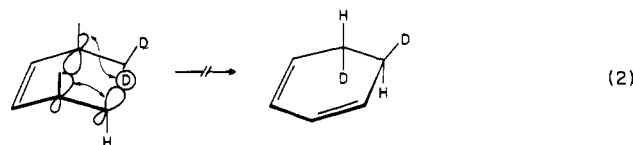
excluded many C₆H₈ isomers as potential transient intermediates. Some are already known to provide other products (e.g., $\Delta^{1,4}$ -bicyclo[2.2.0]hexene¹⁰) and/or to react too slowly at these temperatures (e.g., *trans*-hexa-1,3,5-triene,¹¹ cyclohexa-1,4-diene,¹² bicyclo[2.1.1]-¹³ or bicyclo[3.1.0]hex-2-ene,¹⁴ tricyclo[3.1.0.0.2.6]-¹⁵ or *anti*-tricyclo[3.1.0.0.2.4]hexanes¹⁶). 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 ($10^5 k = 0.22, 25.6$ at 100°, 150°)¹⁷ would strongly have implicated mechanism 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 ($\sigma_{2a} + \sigma_{2s}$) - ($\pi_{2s} + \pi_{4s}$) 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 cyclo-



pentene.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

