Organic Disulfides and Related Substances. XXVI. Preparation and Oxidation of Cyclic Disulfides[1a-c]

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1,2-Dithiolane, 1,2-dithiane, and 1,2-dithiepane were prepared and oxidized to the corresponding dioxides and tetroxides, two of the dioxides and all the tetroxides being obtained for the first time. Alternative routes were compared in the hope that the information will prove useful in the class of cyclic disulfides as a whole. 1,2-Dithiolane seemed best prepared by oxidation with hydrogen peroxide at 75° of 1,3-propanedithiol in acetic acid containing potassium iodide or through depolymerization of its polymer, 1,2-dithiane by cyclization of 1,4-butanedithiol with *p*-toluenesulfonyl chloride or of the lead dithiolate with sulfur, and 1,2-dithiepane by a reported oxidation with ferric chloride. Oxidation of 1,2-dithiane to the 1,1-dioxide and 1,1,2,2-tetroxide was best achieved using hydrogen peroxide in acetic acid, as were oxidation of 1,2-dithiolane and 1,2-dithiepane to their 1,1-dioxides. The tetroxides of 1,2-dithiolane and 1,2-dithiepane, not obtainable directly from the cyclic disulfides, were prepared by oxidizing the dioxides. Oxidation with ozone of the cyclic disulfides gave mixtures of the corresponding dioxides and (presumed) sulfonic anhydrides. Neither ethyl disulfide nor its disulfide dioxide could be oxidized to the corresponding tetroxide.

In extension to 1,2-dithiacycloalkanes (and their oxidation products) of studies on the chemistry of disulfides,[1c] attention to synthesis was desirable first. 1,2-Dithiane seemed a good starting point for comparing and developing synthetic routes for the class as a whole, since it is relatively stable. Hopefully, a variety of routes to prototypes, and assessment of their relative merits, will facilitate syntheses where special limitations are imposed, *e.g.*, by functional groups.

Attention was focused first on development of methods for converting 1,4-butanedithiol into 1,2-dithiane. The approach shown in eq 1 involved conversion of the dithiol with *p*-toluenesulfonyl chloride into a monodisulfide dioxide, which could be attacked intramolecularly by the thiolate anion, displacing the *p*-toluenesulfinate ion and thus effecting cyclization. An earlier application of this approach failed, but the system seemed likely to have been atypical.[2] Use of either one or two molar proportions of pyridine with one each of the butanedithiol and sulfonyl chloride also failed, but the reaction cleanly gave the disulfide in 93% yield when the dithiol was mixed with somewhat more than two molar proportions of aqueous sodium hydroxide. After the reaction had succeeded, we became aware of the preparation of methyl 1,2-dithiolane-3-valerate by reaction of the corresponding dithiol with *p*-toluenesulfonyl chloride in ether containing solid potassium hydroxide;[3] similar conditions with 1,4-butanedithiol gave 1,2-dithiane in 87% yield.

$$\mathrm{HS(CH_2)_nSH + ArSO_2Cl \xrightarrow{2OH^-} [ArSO_2S(CH_2)_nS^-] \longrightarrow \overline{(CH_2)_nSS} + ArSO_2^-} \quad (1)$$

Three procedures developed for 1,2-dithiane by earlier workers were compared. Oxidation of the dithiol with aqueous iodine–potassium iodide[4] gave 1,2-dithiane in 72–77% yield (lit.[4] 92%), but the product polymerized when it melted at *ca.* 30°, behavior seemingly encountered earlier.[4] Preparation of stable 1,2-dithiane with iodine could be accomplished in 77% yield by a procedure of Isenberg, who obtained it in 96% yield by adding triethylamine to remove hydriodic acid.[5] The third procedure (90% yield) involved oxidation of the dithiol with *t*-butyl hydroperoxide in the presence of ferric chloride;[6] our yield was 81% but the dithiane again was stable. It should be remarked that 1,2-dithiane from syntheses other than that with I_2–KI occasionally polymerized capriciously, but there was no difficulty in keeping unpurified material of mp 20–30° as liquid under ambient conditions; since one sample polymerized after distillation, and seemingly pure solid occasionally polymerized when melted, impurities (thiol?) may stabilize the crude liquids.

Formation of disulfides by reaction of sulfur with lead thiolates is well known commercially for removal of thiols from gasoline.[7] Possible advantages of such a reaction in preparation of cyclic disulfides prompted study of the formation of the model lead thiolate of 1,4-butanedithiol and its reaction with sulfur. Negligibly different results were observed with the lead thiolate prepared at high dilution from that prepared merely by mixing solutions of lead acetate and dithiol, each method producing 1,2-dithiane in greater than 90% yield.

Although most of these methods thus gave 1,2-dithiane in relatively high yield, ease of execution and yield of product commends cyclization by eq 1.

Unfortunately, neither the cyclization of eq 1 nor of the lead dithiolate with sulfur were applicable in synthesis of 1,2-dithiolane. We obtained this in 26% yield by oxidizing 1,3-propanedithiol with iodine catalyzed by ferric chloride,[6] or with lead tetraacetate (21–40%). Since 1,2-dithiolane is quite unstable,[6] yields were determined in solution using an extinction coefficient at the highly characteristic absorption of 330 $m\mu$ estimated by Barltrop, Hayes, and Calvin.[8]

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[1] (a) This investigation was supported by the U. S. Army Medical Research and Development Command, Department of the Army, under Research Contract No. DA-49-193-MD-2030. (b) Taken mainly from the Ph.D. Dissertation of R. B. B., Vanderbilt University, Aug 1968; the dissertation may be consulted for greater detail. (c) Paper XXV: L. Field and J. D. Buckman, *J. Org. Chem.*, **33**, 3865 (1968). (d) Eastman Kodak Fellow, 1965–1966.

[2] R. R. Crenshaw and L. Field, *J. Org. Chem.*, **30**, 175 (1965).

[3] M. Ohara, K. Yamamoto, and A. Sugihara, Japanese Patent 7969 (1962); *Chem. Abstr.*, **59**, 5025 (1963).

[4] S. F. Birch, T. V. Cullum, and R. A. Dean, *J. Inst. Petrol.*, **39**, 206 (1953).

[5] N. Isenberg, Ph.D. Thesis, Rensselaer Polytechnic Institute, 1963.

[6] A. Schöberl and H. Gräfje, *Ann.*, **614**, 66 (1958).

[7] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. I, Chemical Publishing Co., Inc., New York, N. Y., 1958, pp 151–155.

[8] J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Amer. Chem. Soc.*, **76**, 4348 (1954).

Oxidation of the dithiol in acetic acid with hydrogen peroxide produced 1,2-dithiolane only in the presence of potassium iodide. Addition of peroxide to dithiol at 15° gave 1,2-dithiolane in 28% yield, and reversing the order gave only 8% yield. A third variation led to success. It began with simultaneous addition of the dithiol and peroxide to acetic acid to provide higher dilution; at 25° the yield was 35%. Previously, heating had been avoided by us because of the instability of the dithiolane ring,[6,8,9] but, when the peroxide and dithiol were introduced simultaneously at 75°, the yield of dithiolane doubled to 70% and with slight variations occasionally reached 84%; at 115°, no dithiolane was observed. A fourfold increase in potassium iodide was not helpful (70%); the time of addition could be varied from about 2 to 8 hr with little effect.[1b]

Although 1,2-dithiolane seems best prepared in acetic acid, it can be transferred to other solvents when desirable. For example, dilution of an acetic acid solution (0.21 to 0.02 M) with 10 volumes of water, and subsequent extraction, transferred the dithiolane to hexane (92% yield) or benzene (68% yield). This technique has been mentioned,[6,8] but is so useful that it deserves emphasis.

Since 1,2-dithiolane is highly subject to polymerization, it was important to determine whether the monomer could be generated from polymer. Barltrop, Hayes, and Calvin mentioned depolymerization by steam distillation from strongly alkaline sodium disulfide but gave no details.[8] Depolymerization of polymeric 1,2-dithiolane by Bergson and Claeson in molten camphor[10] suggested the possibility of slow depolymerization by heat alone.

When polymer was heated in acetic acid at 80–85° for 7 days, the uv spectrum indicated 90–100% conversion into 1,2-dithiolane. Depolymerization may well be effective in most solvents which can be maintained at 75°. For example, after 2 days in acetonitrile at 75°, the polymer was converted in 80% yield into 1,2-dithiolane; a similar result seemingly occurred in diglyme. Both physical and chemical evidence confirmed that 1,2-dithiolane had been formed in large amounts in the acetic acid. Since 1,2-dithiolane readily polymerizes in light,[8] a sample of the solution was subjected to indirect sunlight; in less than 1 day, the uv absorption showed decrease in the amount by more than 90%. This instability of 1,2-dithiolane to light affords a convenient criterion for identity, 1,2-dithiolane in ethanol (0.1 M) being unchanged after 22 days at 25° when shielded from light. 1,2-Dithiane and 1,2-dithiepane appear to be quite stable in Pyrex vessels to light, it might be added, perhaps partly because of the screening effect of the glass and their lower λ_{max}; the infrared spectrum of the former showed no change after 2 months and that of the latter even after 9 months. Chemical evidence for presence of the monomer was obtained by oxidizing it in acetic acid to 1,2-dithiolane monoxide (76%),[11a] and thence to 1,2-dithiolane 1,1-dioxide (20%),[11a] which was well characterized (*vide infra*). The monoxide, first reported (without isolation) by Barltrop, Hayes, and Calvin,[8] showed the expected ir spectrum and good agreement with reported uv data.[8]

For the preparation of 1,2-dithiepane, the method of choice (54% yield) was that of Schöberl and Gräfje.[6] Other procedures effective with the dithiolane or dithiane gave the dithiepane in only 6–17% yield.

1,2-Dithiane again was selected as a prototype for studying cyclic oxidation products of the 1,2-dithiacycloalkanes to learn the effect of oxygenation on reactivity and also to provide the oxides as new tools for synthesis. Oxidants were sought which would selectively give intermediate oxidation products ($-SO_2$-S–, $-SO_2SO_2-$) with a minimum of sulfonic acid. The identity of three cyclic disulfide dioxides thus formed was established by analysis, ir spectrum, and a positive disulfide dioxide test.[12]

The best procedure for oxidizing 1,2-dithiane to the 1,1-dioxide was found to be that of Isenberg (hydrogen peroxide in acetic acid),[5] although our yield (66%) was less than his nearly quantitative one. Chlorine gave unpromising results by the Douglass–Farah procedure successful for alkyl and aryl disulfide dioxides,[1b,13] and potassium permanganate was too powerful (6% yield). Sodium metaperiodate gave the dioxide (16%) but the potassium salt was much better (67%). Peroximonosulfuric acid, *t*-butyl hydroperoxide (vanadium pentoxide catalyst), or chromium trioxide–sulfuric acid (Jones reagent)[14] gave the dioxide in only 19–31% yield. Nitrogen dioxide, which converts disulfides into the dioxides,[15] gave the dioxide in 43% yield, which only decreased under other conditions. 1,2-Dithiane could not be converted effectively into the dioxide or tetroxide by the following oxidants: ammonium persulfate, chlorine, chromium trioxide in acetic acid, chromium trioxide and pyridine, lead tetraacetate, manganese dioxide, nickel peroxide, nitric acid, selenium dioxide, or sodium peroxide. During this work, our attention was drawn to crystals in 1,4-butanedisulfinic acid which had decomposed during 3 years. Extraction separated 1,2-dithiane 1,1-dioxide (7% content); disulfide dioxide formation by the decomposition of sulfinic acids is well known.[16,17]

For the preparation of 1,2-dithiolane 1,1-dioxide, hydrogen peroxide was used exclusively. It was best added in acetic acid to 1,2-dithiolane and tungstic acid in acetic acid at 65°. Since 1,2-dithiolane in a concentration above 0.05 M tends to polymerize at room temperature,[18] the high temperature presumably favors the reaction by minimizing conversion into polymers. In any event, a low temperature (14°) during oxidation (with a 300% excess of peroxide) was detrimental; tungstic acid did not greatly aid the oxidation, which never exceeded 33% in yield.[1b] The stability of 1,2-

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[9] J. G. Affleck and G. Dougherty, *J. Org. Chem.*, **15**, 865 (1950).

[10] G. Bergson and G. Claeson, *Acta Chem. Scand.*, **11**, 911 (1957).

[11] (a) For many of the compounds described here and in later papers, the nomenclature will follow the flexible system recommended by Savige and Maclaren.[11b] Thus "thiolsulfinates" become disulfide monoxides, "thiolsulfonates" become disulfide 1,1-dioxides, and "α-disulfones" become disulfide tetroxides. (b) W. E. Savige and J. A. Maclaren in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed. Pergamon Press, New York, N. Y., 1966, p 394.

[12] D. Barnard and E. R. Cole, *Anal. Chim. Acta*, **20**, 540 (1959).

[13] *Cf.* L. Field and T. F. Parsons, *J. Org. Chem.*, **30**, 657 (1965).

[14] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[15] W. L. Fierce and R. L. Weichman, U. S. Patent 3,153,078 (1964); *Chem. Abstr.*, **62**, 488 (1965). However, N. Kunieda and S. Oae reported only sulfonic anhydrides in use of dinitrogen tetroxide with alkyl or aryl disulfides [*Bull. Chem. Soc. Jap.*, **41**, 233 (1968)].

[16] H. J. Barber and S. Smiles, *J. Chem. Soc.*, 1141 (1928).

[17] C. S. Marvel and R. S. Johnson, *J. Org. Chem.*, **13**, 822 (1948).

[18] R. B. Whitney and M. Calvin, *J. Chem. Phys.*, **23**, 1750 (1955).

dithiolane 1,1-dioxide is noteworthy in comparison with 1,2-dithiolane. The melting point remained at 20–25° for more than 1 month, behavior which compares favorably with that of 1,2-dithiane 1,1-dioxide.

1,2-Dithiepane was oxidized to the 1,1-dioxide essentially like 1,2-dithiane but in much lower yield (17%). An explanation for this marked difference might shed light on the oxidation of disulfides, but no very attractive one is apparent. 1,2-Dithiepane 1,1-dioxide compared favorably in stability with its five- and six-membered homologs; the ir spectrum and melting point were unchanged after more than 10 months of standing.

For the next phase, study of the tetroxides, 1,2-dithiane again was chosen as a model. Oxidants mentioned above other than hydrogen peroxide were disregarded, because even their use in excess had led to none of the easily isolable tetroxide.

The most convenient oxidation of 1,2-dithiane to 1,2-dithiane 1,1,2,2-tetroxide ultimately seemed to be by use of eight molar proportions of hydrogen peroxide in dioxane–acetic acid containing sulfuric acid (35% yield). Structural evidence for the tetroxide was afforded by analysis, molecular weight, strong ir absorption at the positions expected of sulfones, formation from the 1,1-dioxide (69% yield), use of the tetroxide in synthetic applications,[19] and independent synthesis by oxidative cyclization of 1,4-butanedisulfinic acid. The cyclization of the sulfinic acid was achieved using potassium permanganate (1% yield), a procedure known to produce acyclic disulfide tetroxides, albeit also in poor yield;[20] lead tetraacetate or potassium periodate failed, but manganese dioxide gave the tetroxide in 6% yield.

Oxidation of 1,2-dithiane with hydrogen peroxide, in a mixture of acetic, hydrochloric, and tungstic acids (tungsten trioxide monohydrate),[13] resulted in 1,4-butanedisulfonyl chloride (36–51% yield), as did oxidation with potassium permanganate–hydrochloric acid (49%). Oxidation in dioxane–acetic acid with four molar proportions of hydrogen peroxide gave the tetroxide in only 1% yield, and use of a little sulfuric acid gave none at all although acid catalyzes peroxide oxidations.[21] However, eight molar proportions of hydrogen peroxide in the presence either of tungstic or sulfuric acid gave the tetroxide in 35% yield and, with both present, in 40% yield. Variations in amounts of tungstic or sulfuric acid did not increase the yield above 40%. Tungsten trioxide, its monohydrate, or its dihydrate were nearly equivalent, as was use of pertungstic acid (33%).[22] Low (0°) or high (60°) temperatures reduced yields to 15–20%.[1b] Phosphoric acid[23] instead of sulfuric acid resulted in a yield of 14%. Other systems gave no yields much in excess of 40%: thus hydrogen peroxide in acetic acid–acetic anhydride, water, formic acid, or acetone gave yields of 2–30%, and use of peracetic, peroxytrifluoroacetic, or *m*-chloroperbenzoic acid, of 29–42%; 1,4-butanedisulfonyl iodide was not cyclized by zinc or with irradiation, nor was lead 1,4-butanedisulfinate by sulfur or iodine (*cf.* Experimental Section or ref 1b).

1,2-Dithiane 1,1-dioxide with hydrogen peroxide in dioxane–acetic acid (containing sulfuric and tungstic acids) gave the tetroxide in 69% yield. This yield also resulted without dioxane and sulfuric acid, but the yield was 38% without tungstic acid.

The highest yield of the tetroxide, about 40%, thus was obtained from 1,2-dithiane by various means, none clearly superior. The fact that peroxide in 100% excess gave tetroxide in nearly comparable yield with or without tungstic acid suggests no marked advantage of tungstic acid in the presence of sulfuric acid and excess peroxide. The somewhat higher over-all yield by stepwise oxidation through the dioxide to the tetroxide hardly justifies this approach. Hence the most convenient route, as mentioned, seems simply to be oxidation with eight molar proportions of hydrogen peroxide and a little sulfuric acid.

Although the dithiane tetroxide was obtainable readily from the disulfide with hydrogen peroxide, the five- and seven-membered homologs could not be prepared thus. Oxidation of the dioxides of 1,2-dithiolane and 1,2-dithiepane gave the tetroxides, however, but in low yield (8–10%).

Schöberl and Gräfje ranked cyclic disulfides on a scale for which 4 represented high reactivity and 1 low reactivity.[6] 1,2-Dithiolane was ranked 4, 1,2-dithiane 1, and 1,2-dithiepane 2. Similar differences for 1,2-dithiane are conspicuous in foregoing syntheses: the dithiolane and dithiepane either were formed in lower yields or not at all in reactions quite successful for the dithiane; the dithiane could be oxidized to the dioxide in higher yields, and it alone could be oxidized directly to the tetroxide. In the oxidation of the three dioxides to tetroxides, the dithiane again gave better yields.

It is worth noting also that the uv absorption spectra of the cyclic disulfide dioxides show displacement of the absorption peak to progressively shorter wavelength as the size of the dioxide ring increases, the five-, six-, and seven-membered dioxides showing maxima at 263 mμ (ϵ 42), 244 (44),[5] and 240 (54), respectively. A similar trend in the cyclic disulfides has been ascribed to ring strain,[8] a possible factor also in this shift of wavelengths in the dioxide series.

Oxidation with ozone at 25° of 1,2-dithiolane, 1,2-dithiane, and 1,2-dithiepane in nitromethane appeared to produce the corresponding sulfonic anhydrides in yields, respectively, of 64, 33, and 65%, as measured by titration of acids produced on hydrolysis. The corresponding 1,1-dioxides simultaneously were formed in yields of 8 (7), 22 (30), and 10% (3%), respectively, as measured by titrating acid produced upon addition of thiophenol[12] and (values in parentheses) by isolating the dioxide. Ozonolysis of 1,2-dithiane in nitromethane, dioxane, and acetic acid at 25° gave presumed anhydride in yields of 33, 38, and 56%, and dioxides in yields of 22 (30), 22 (6), and 8% (26%), respectively; at 0° in nitromethane, 1,2-dithiane gave anhydride in 38% yield and dioxide in 2% (7%) yield. Results of duplicate experiments were quite variable, and the outcome fits no obvious pattern.[1b] Mechanisms have been discussed by which ozone may react with acyclic disulfides, normally giving 80–90% sulfonic anhydride and 10–20% disulfide dioxide.[21]

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(19) L. Field and R. B. Barbee, to be published.

(20) P. Allen, Jr., L. S. Karger, J. D. Haygood, Jr., and J. Shrensel, *J. Org. Chem.*, **16**, 767 (1951).

(21) D. Barnard, L. Bateman, and J. I. Cunneen in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p 229.

(22) Z. Raciszewski, *J. Amer. Chem. Soc.*, **82**, 1267 (1960).

(23) *Cf.* T. Higuchi and K.-H. Gensch, *ibid.*, **88**, 5486 (1966).

Oxidation of ethyl and *t*-butyl disulfide under conditions used with 1,2-dithiane resulted in no tetroxides, a seemingly significant difference although reasons for it are not clear. Decrease of the usual 100% excess of hydrogen peroxide to a stoichiometric amount resulted in ethyl disulfide S,S-dioxide in 23% yield (but no tetroxide). Oxidation of the dioxides of ethyl disulfide and 2-acetamidoethyl disulfide also failed to produce any tetroxide.

Experimental Section[24]

1,2-Dithiane. A. *Via* **p-Toluenesulfonyl Chloride.**—In the preferred procedure for 1,2-dithiane, powdered *p*-toluenesulfonyl chloride (66.0 g, 346 mmol) was added (30 min) to a vigorously stirred mixture of 1,4-butanedithiol (40.0 g, 327 mmol) with 600 ml of 5% aqueous sodium hydroxide (750 mmol) at 5°. The mixture was stirred overnight and extracted with methylene chloride. The extract was washed with water, dried, and evaporated to give 36.4 g (93%) of 1,2-dithiane: mp 25–30° (lit.[8] mp 32–33°); $\lambda_{\max}^{\mathrm{AcOH}}$ 288 mμ (lit.[5] $\lambda_{\max}^{\mathrm{EtOH}}$ 288 mμ); infrared absorption (neat) at 2910 (s), 1440 (s), 1410 (s), 1230 (s), 920 (s), and 840 cm^{-1}.

Purification (a usual preliminary to subsequent oxidation) of 1,2-dithiane was best effected by recrystallizing it from hexane at −65°, decanting solvent from solid on the flask wall, and drying under reduced pressure (briefly, since 1,2-dithiane is quite volatile).

In an adaptation of a published procedure,[3] *p*-toluenesulfonyl chloride (4.25 g, 22.3 mmol) in 20 ml of ether was added (15 min) with vigorous stirring to a solution of 1,4-butanedithiol (1.82 g, 14.9 mmol) in 15 ml of ether containing powdered potassium hydroxide (2.25 g, 40.1 mmol) at 0°. The mixture was stirred at 0° for 5 hr more, washed with water, dried, and concentrated: yield of 1,2-dithiane, 1.55 g (87%); mp 27–32°.

B. *Via* **Lead 1,4-Butanedithiolate.**—A solution of lead acetate (14.0 g, 43.0 mmol) in a minimum of water (30 ml) was shaken vigorously with 1,4-butanedithiol (5.00 g, 41.0 mmol) in 5 ml of benzene. After 1 hr, orange solid which had precipitated was removed and dried: yield of lead 1,4-butanedithiolate, 12.0 g (90%). A solution of 0.86 g (26.8 mmol) of sulfur in 20 ml of carbon disulfide then was stirred overnight with a suspension of 8.0 g (24.4 mmol) of the lead dithiolate in 50 ml of benzene (immediate darkening). Solid then was removed and washed with benzene. Evaporation of the benzene left crude product, which upon sublimation (5 mm) afforded 2.8 g (95%) of 1,2-dithiane, mp 29–30°.

Anal. Calcd for $C_4H_8S_2$: S, 53.33. Found: S, 53.30.

C. Other Procedures.—Oxidation of 1,4-butanedithiol (164 mmol) with iodine in chloroform containing triethylamine (322 mmol)[5] gave 1,2-dithiane in 77% yield, mp 30–32°. With I_2–KI in water and the dithiol in pentane,[4] a yield resulted of 77%, mp 30–33°, but the product upon melting polymerized to a rubbery material, unlike others which were quite stable for many months under ambient conditions. The product with *t*-butyl hydroperoxide[6] (yield 81%) had mp 30–33°.

1,2-Dithiolane. A. *Via* **Hydrogen Peroxide.**—In the best of a number of variations,[1b] a solution of 1,3-propanedithiol (21.6 g, 200 mmol) in 400 ml of acetic acid and one of H_2O_2 (20.0 ml of 10.10 *M*, 202 mmol) in 400 ml of acetic acid were added simultaneously (6 hr) to a vessel, protected from light with metal foil, which contained 360 ml of acetic acid and potassium iodide (0.80 g, 4.8 mmol) maintained at 75°. After 1 hr more of stirring, the concentration of 1,2-dithiolane was found from the uv absorption at 330 mμ by taking ε to be 147[8] (yield of 1,2-dithiolane 84%); in five repetitions under much the same conditions, yields were 70–84%.

B. *Via* **Depolymerization.**—The polymer of 1,2-dithiolane obtained by oxidizing dithiol in acetic acid containing potassium iodide at 25° with a one molar proportion of H_2O_2 was recrystallized twice from methylene chloride–acetone to give white solid, mp 65–70° (lit. mp 71°,[26] 73°[10]). A suspension of this material (0.71 g) in 40 ml of acetic acid in a foil-wrapped flask then was heated at 80° for 7 days. The concentration (0.15 *M*) of monomer formed (from the uv absorption) showed conversion of polymer into monomer to be 90%.

Reduction by more than 90% of the uv absorption at 330 mμ occurred when part of this solution in a quartz vessel was exposed to light for 1 day. A similar solution of 1,2-dithiolane was oxidized to the monoxide, in turn characterized as the known dioxide (*vide infra*), as follows. Hydrogen peroxide (5.94 mmol, 0.66 ml of 9.0 *M*) in acetic acid (1 ml) was added (10 min) to a solution of 1,2-dithiolane (5.94 mmol) in acetic acid (40 ml) at 75°. Stirring at 75° was continued for 1 hr and then at 25° for 2 days. Removal of solvent then gave oil, which was washed with hexane and extracted with ether. Evaporation of the ether left 0.55 g (76%) of 1,2-dithiolane monoxide as oil, which was recrystallized twice from ether at *ca.* −65° to give solid, which melted readily; the yield of 1,2-dithiolane monoxide was 0.52 g (72%): $\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ (ε 970) [lit.[8] $\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ (ε ~1025)]; strong ir absorption at 1050 cm^{-1}. At least 2 hr elapsed while the monoxide was in this isolated form, before its conversion into the solid dioxide described below; during this time it gave no indication of decomposition.

Hydrogen peroxide (8.2 mmol, 0.91 ml of 9.0 *M* hydrogen peroxide) in acetic acid (1 ml) then was added (15 min) to the 1,2-dithiolane monoxide (0.50 g, 4.1 mmol) in acetic acid (75 ml). After 24 hr, solvent was removed, and the residue was first washed with hexane and then extracted with ether. Evaporation of the ether left 0.11 g (20% from monoxide, 14% over-all from 1,2-dithiolane) of 1,2-dithiolane 1,1-dioxide, mp ~20°, which had an ir spectrum identical with that of analytically pure material described below.

C. Other Procedures.—All yields of 1,2-dithiolane were calculated as described above from the uv absorption at 330 mμ. Dropwise addition of a saturated solution of iodine in 1-butanol to 1,3-propanedithiol (5.4 g) in 50 ml of 1-butanol containing 0.1 g of ferric chloride,[6] until the iodine color persisted, resulted in a yield of 26%. When 1,3-propanedithiol (25 mmol) was added (1 hr) to a stirred solution of lead tetraacetate (13.0 g of 85% lead tetraacetate, 25 mmol) in 60 ml of acetic acid at 80° in a shielded flask, the yield was 36%, and, when added at 25° (11 hr), 40%; addition of the tetraacetate to the dithiol (25°) gave 21%.

A reaction like that used for 1,2-dithiane, in which *p*-toluenesulfonyl chloride was added to the dithiol in aqueous alkali, gave no 1,2-dithiolane. Lead acetate and 1,3-propanedithiol gave a lead dithiolate (98%), which with sulfur in acetic acid led to lead sulfide but to no absorption at 330 mμ.

1,2-Dithiepane.—Much as reported,[6] 1,5-pentanedithiol (27.2 g, 200 mmol) in ether (200 ml) was added dropwise (1.5 days) to 1500 ml of ether and 200 ml of acetic acid containing $FeCl_3 \cdot 6H_2O$ (162 g, 600 mmol) at reflux temperature. The mixture then was let stand for 1 day. Isolation as reported,[6] but without use of quartzware or exclusion of light, gave 14.6 g (54%) of 1,2-dithiepane: bp 55–60° (1.7 mm) [lit.[6] bp 41° (2 mm)]; $n^{25}\mathrm{D}$ 1.5690 (lit.[6] $n^{25}\mathrm{D}$ 1.570); $\lambda_{\max}^{\mathrm{EtOH}}$ 258 mμ (ε 444) [lit.[27] $\lambda_{\max}^{\mathrm{EtOH}}$ 259 mμ (ε 467)]; ir absorption at 2910 (s) 1450 (s), 1280, and 770 cm^{-1}.

In procedures like those used for 1,2-dithiane, *p*-toluenesulfonyl chloride (152 mmol) was added (20 min) to a stirred mixture of 1,5-pentanedithiol (147 mmol) with 260 ml of 5% aqueous NaOH (320 mmol) at *ca.* 10°; distillation gave 3.35 g (17%) of 1,2-dithiepane, $n^{25}\mathrm{D}$ 1.5710. Reaction of lead acetate and 1,5-pentanedithiol resulted in lead 1,5-pentanedithiolate (80%),

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[24] Melting points are corrected. Elemental analyses and molecular weights (unless otherwise stated) were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Molecular weights were determined with a Mechrolab Model 301A osmometer. Ir spectra were done using a Beckman Model IR-10 with films of liquids and potassium bromide pellets or Nujol mulls of solids; absorptions are given in cm^{-1}, s signifying strong (others reported were medium). Uv spectra were obtained with a Cary Model 14 and nmr spectra with a Varian Model A-60 (tetramethylsilane as an internal standard; we thank the National Science Foundation for Departmental Grant GP-1683 toward purchase of the instrument). Unless otherwise stated, reactions were carried out at room temperature. Moist extracts were dried using anhydrous $MgSO_4$. Solvents were evaporated under reduced pressure with a rotary evaporator. When isolation of known products is mentioned, identity was established invariably by ir or uv spectra, and usually also by mixture melting point. 1,3-Propanedithiol, 1,4-butanedithiol, and 1,5-pentanedithiol were obtained from the Wateree Chemical Co., Lugoff, S. C., and were used directly. Hydrogen peroxide was standardized with 0.1 *N* potassium permanganate;[25] the molarity of "30% solution" ranged from 7.60 to 10.10 and such material was used as "H_2O_2" unless otherwise stated.

[25] W. W. Scott, "Standard Methods of Chemical Analysis," Vol. 2, N. H. Furman, Ed., 5th ed, D. Van Nostrand Co., New York, N. Y., 1939, p 2181.

[26] L. Hagelberg, *Ber.*, **23**, 1083 (1890).

[27] E. E. Smissman and J. R. J. Sorenson, *J. Org. Chem.*, **30**, 4008 (1965).

which (23.5 mmol), after suspension in 50 ml of benzene, was treated with sulfur (26.8 mmol); distillation gave 0.20 g (6%) of 1,2-dithiepane, n^{25}_{D} 1.5692. In a procedure like that for 1,2-dithiolane, 1,5-pentanedithiol (100 mmol) in acetic acid (200 ml) and H_2O_2 (106 mmol) in acetic acid (200 ml) were added simultaneously (3 hr) to 160 ml of acetic acid containing KI (0.50 g, 3.0 mmol) at 75°; distillation gave 1.0 g (7%) of 1,2-dithiepane, n^{25}_{D} 1.5698.

1,2-Dithiane 1,1-Dioxide.—1,2-Dithiane (0.50 g, 4.2 mmol) in acetone (5 ml) was added to a stirred solution of **potassium metaperiodate** (4.0 g, 17.4 mmol) in water (50 ml). After 4 days, the product was extracted with chloroform, which then was washed with water, dried, and evaporated to leave 0.43 g (68%) of 1,2-dithiane 1,1-dioxide, mp 53–55°. Similarly prepared material upon recrystallization from carbon tetrachloride, ethyl ether, and benzene–pentane gave 1,2-dithiane 1,1-dioxide with mp 54.5–55° (lit.[5] mp 56–57°); ir absorption (Nujol) somewhat different from that described,[5] perhaps because of a different medium, occurred at 1325, 1282, 1162, 1125 (s), 1100 (s), 1025, 913, 800, and 715 (s) cm^{-1}; positive disulfide dioxide test.[12]

Anal. Calcd for $C_4H_8O_2S_2$: C, 31.56; H, 5.29; S, 42.12. Found: C, 31.82; H, 5.24; S, 41.98.

Use of **sodium metaperiodate** resulted only in a yield of 16%, mp 45–50°, although there were some differences in procedure. **Hydrogen peroxide**, used much as described (26.6 ml of 9.5 *M* H_2O_2 in 25 ml of glacial acetic acid added to 0.1 mol of dithiane in 75 ml of acetic acid over 35 min at *ca.* 22–62°),[5] oxidized 1,2-dithiane to 1,2-dithiane 1,1-dioxide (66%), mp 54–55°.

In an adaptation of a procedure of Fierce and Weichman,[15] excess **nitrogen dioxide** was bubbled (20 min) through a solution of 1,2-dithiane (4.2 mmol) in chloroform (5 ml). The chloroform then was washed with water, dried, and evaporated to leave 0.27 g (42%) of 1,2-dithiane 1,1-dioxide, mp 47–49°. Dropwise addition of liquid nitrogen dioxide (0.5 ml, 10 min) to 1,2-dithiane (4.2 mmol) in chloroform at 5°, followed by stirring (16 hr, 25°), separation of water-soluble solid, and evaporation of the chloroform, resulted in yellow oil; trituration under pentane gave 0.08 g (13%) of the dioxide, mp 50–54°.

Chromium trioxide (10.0 mmol) in *ca.* 9 *N* H_2SO_4 was added to 1,2-dithiane (4.2 mmol) in 25 ml of acetone. The mixture was stirred overnight and diluted with methylene chloride, and solid was removed. The methylene chloride was washed with water, dried, and evaporated, leaving 0.20 g (31%) of the dioxide, mp 49–52°.

***t*-Butyl hydroperoxide** (20 mmol) was added (20 min) to 1,2-dithiane (4.2 mmol) in 75 ml of benzene containing 0.08 g of vanadium pentoxide, at 50°. After 25 hr at 25°, removal of solvent left oil, which was washed with hexane and then extracted with ether. Evaporation of ether gave 0.15 g (23%) of 1,2-dithiane 1,1-dioxide, mp 43–46°.

Aqueous peroximonosulfuric acid (18.5 mmol)[28] was added to 1,2-dithiane (4.2 mmol) in 25 ml of acetic acid. The mixture was stirred for 2 days, then extracted with methylene chloride, which was washed with water, dried, and evaporated: yield, 0.12 g (19%); mp 54–56°.

Aqueous potassium permanganate (11 mmol, 45 ml of 4% solution) was added to 1,2-dithiane (4.2 mmol) in 50 ml of acetic acid. Evaporation of solvent and extraction of the residue with methylene chloride gave 0.04 g (6%) of the dioxide: mp 53–56°; mol wt,[12] 150 (calcd 152).

The sample of 1,4-butanedisulfinic acid[29] (4.8 g), which had decomposed during 3 years, was extracted with methylene chloride: content of 1,2-dithiane 1,1-dioxide, 0.35 g (7%); mp 52–54°.

1,2-Dithiolane 1,1-Dioxide.—In the best of several variations,[1b] H_2O_2 (185 mmol, 18.3 ml of 10.10 *M*) in 20 ml of acetic acid was added dropwise (30 min) to 1,2-dithiolane (37 mmol) in 290 ml of acetic acid at 65° containing tungstic acid (2.4 mmol), shielded from light with foil. The mixture then was stirred at 25° for 2 days, solid was removed, and the solvent was evaporated. Residual oil was dissolved in 50 ml of methylene chloride, which was washed with water, dried, and evaporated to give 1.67 g (33%) of 1,2-dithiolane 1,1-dioxide, mp 15–20°. Recrystallization from benzene–hexane and from carbon tetrachloride gave the dioxide with mp 22–22.5°; strong ir absorption at 1300 and 1120 cm^{-1}; λ_{max}^{EtOH} 263 mμ (ϵ 42); nmr ($CDCl_3$) τ 6.25 (2 H, triplet), 6.55 (2 H, triplet), 7.10–7.64 (2 H, multiplet); disulfide dioxide test,[12] positive. The melting point of similarly prepared dioxide remained unchanged for more than 1 month.

Anal. Calcd for $C_3H_6O_2S$: C, 26.07; H, 4.38; S, 46.40; mol wt, 138. Found: C, 25.98; H, 4.31; S, 46.50; mol wt, 144 (Barbee), 140.

1,2-Dithiepane 1,1-Dioxide.—Hydrogen peroxide (272 mmol, 35.8 ml of 7.6 *M*) in 50 ml of acetic acid was added dropwise (40 min) to 1,2-dithiepane (14.6 g, 109 mmol) in 200 ml of acetic acid. After the mixture had been stirred for 2 days, solvent was evaporated. Oily residue was dissolved in methylene chloride which was washed to neutrality with water, dried, and evaporated: yield of the dioxide as viscous oil, 3.1 g (17%); mp *ca.* 25°, unchanged by several recrystallizations from ether at −65°; ir bands at 1310 (s) and 1120 cm^{-1} (s); λ_{max}^{EtOH} 240 mμ (ϵ 54); disulfide dioxide test[12] positive.

Anal. Calcd for $C_5H_{10}O_2S_2$: C, 36.12; H, 6.06; S, 38.57. Found: C, 36.37; H, 6.20; S, 38.82.

1,2-Dithiane 1,1,2,2-Tetroxide. A. By Oxidation of 1,2-Dithiane Using Hydrogen Peroxide.—The preferred preparation was the result of numerous variations[1b] of an earlier procedure.[18] 1,2-Dithiane (0.50 g, 4.2 mmol) was dissolved in a mixture of 25 ml of acetic acid, 50 ml of dioxane, and 2 ml of concentrated H_2SO_4 at 25°. Hydrogen peroxide (33 mmol, 3.8 ml of 8.8 *M*) was added during 15 min and the mixture was stirred for 2 days. Solvent then was evaporated, and residue was washed with cold water, then dried: yield of 1,2-dithiane 1,1,2,2-tetroxide, 0.27 g (35%); mp 239° dec. Recrystallization of similarly prepared material from acetonitrile, dioxane, and nitromethane–carbon tetrachloride gave product with mp 240–240.5° dec; strong ir absorption at 1350, 1330, 1320, 1290, 1170, 1140, and 1100 cm^{-1}; nmr (DMSO) τ 5.90–6.16 (4 H, multiplet), 7.78–8.04 (4 H, multiplet).

Anal. Calcd for $C_4H_8O_4S_2$: C, 26.08; H, 4.38; S, 34.81; mol wt, 184. Found: C, 25.90; H, 4.33; S, 34.66; mol wt, 190.

Use of formic acid in much the same way gave the tetroxide in 30% yield, mp 239–242° dec. Hydrogen peroxide (32 mmol, 3.5 ml of 9.0 *M*) also was added to 1,2-dithiane (0.50 g, 4.2 mmol) in 50 ml of acetone containing tungstic acid (0.06 g), the solution was stirred for 2 days, solid and then solvent were removed, and the residue was washed with cold water and dried: yield, 0.21 g (27%); mp 240° dec.

When hydrochloric acid[13] was used instead of sulfuric acid, 1,4-butanedisulfonyl chloride resulted. Thus H_2O_2 (90 mmol) was added dropwise (30 min) to 1,2-dithiane (13 mmol) and 0.18 g of tungstic acid in 150 ml of dioxane, 75 ml of acetic acid, and 30 ml of 12 *N* HCl. After 3 days, solid was separated, solvent was evaporated, and residue was taken up in ether, washed with water, and dried. Evaporation of the ether gave 1.7 g (51%) of 1,4-butanedisulfonyl chloride; after recrystallization the melting point was 82–84° (lit.[30] mp 83–84.5°), and the sulfonyl chloride was identical with material prepared from the thiuronium halide by a standard method.[31]

Anal. Calcd for $C_4H_8Cl_2O_4S_2$: C, 18.83; H, 3.16. Found: C, 18.90; H, 3.09.

A 3:1 molar ratio of H_2O_2–1,2-dithiane resulted in formation of the sulfonyl chloride in only 36% yield, mp 65–75°. Potassium permanganate in acetic acid containing HCl converted 1,2-dithiane into the sulfonyl chloride in 49% yield, mp 79–82°.

B. Use of Other Oxidants.—**Peracetic acid** was prepared by adding acetic anhydride (47 mmol) to 5 ml of acetic acid containing 36.0 mmol of 90% H_2O_2 and 0.06 g of H_2SO_4 at 0°, and stirring for 15 min at 0°, then for 30 min more with the ice bath removed. The solution was added to the disulfide as described with H_2O_2 under A: yield of the tetroxide, 0.30 g (39%), mp 238° dec. The **peroxytrifluoroacetic acid**[32] from 17 mmol of 90% H_2O_2 was added (15 min) to 1,2-dithiane (0.50 g, 4.2 mmol) in 10 ml of methylene chloride at 0°; the ice bath then was removed and stirring continued for 24 hr; solvent was evaporated, and residue washed with cold water to give 0.22 g (29%) of the tetroxide, mp 239° dec.

***m*-Chloroperbenzoic acid** (23.7 mmol) in 50 ml of ether was added (15 min) to 1,2-dithiane (0.50 g) in 50 ml of ether. After 3 days, solvent was evaporated, and the residue was washed with

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(28) A. Baeyer and V. Villiger, *Ber.*, **32**, 3625 (1899).

(29) M. T. Beachem, J. T. Shaw, G. D. Sargent, R. B. Fortenbaugh, and J. M. Salsbury, *J. Amer. Chem. Soc.*, **81**, 5430 (1959).

(30) J. W. Griffin and D. H. Hey, *J. Chem. Soc.*, 3334 (1952).

(31) T. B. Johnson and I. B. Douglass, *J. Amer. Chem. Soc.*, **61**, 2548 (1939).

(32) W. D. Emmons, *ibid.*, **76**, 3470 (1954).

ether and water, then dried: yield, 0.32 g (42%), mp 235° dec.

C. **From 1,2-Dithiane 1,1-Dioxide.**—Hydrogen peroxide (20 mmol, 2.0 ml of 10.0 *M*) was added to 1,2-dithiane 1,1-dioxide (0.50 g, 3.3 mmol) in 25 ml of acetic acid containing 0.06 g of tungstic acid. After 24 hr, solid was separated, solvent was evaporated, and residue was washed with water to give 0.42 g (69%) of the tetroxide, mp 240° dec.

D. **From 1,4-Butanedisulfinic Acid as Evidence of Structure.**—Oxidation of 1,4-butanedisulfinic acid[29] in acetic acid with aqueous potassium permanganate by the procedure of Allen, *et al.*,[20] gave 1,2-dithiane tetroxide: yield, 1%; mp 246° dec. This product was identical (ir spectra and mmp 244° dec) with tetroxide prepared from 1,2-dithiane with H_2O_2. Oxidation of the diacid with H_2O_2 or manganese dioxide gave the tetroxide in 2 and 6% yields, respectively.

E. **Attempted Preparations.**—Presumed 1,4-butanedisulfonyl iodide, prepared from the sulfinate salt with I_2–KI by appropriate modification of a reported procedure,[33] showed ir absorption as expected (SO_2) at 1120 and 1300 cm^{-1}, but decomposed without showing a meaningful melting point; treatment with zinc dust in dioxane (70°, 2 days) or irradiation in carbon tetrachloride gave no tetroxide. Presumed lead 1,4-butanedisulfinate (from mixture of aqueous solution of the diacid and lead acetate in 90% yield) was not cyclized to the tetroxide by treating it with sulfur in carbon disulfide or refluxing benzene, only starting material being recovered; addition of 0.1 *N* I_2–KI solution to a suspension of lead 1,4-butanedisulfinate resulted in precipitation of the presumed 1,4-butanedisulfonyl iodide (100% yield).

1,2-Dithiolane 1,1,2,2-Tetroxide.—In the best of several variations,[1b] H_2O_2 (15 mmol, 1.7 ml of 8.8 *M*) was added (5 min) to 1,2-dithiolane 1,1-dioxide (0.50 g, 3.6 mmol) and 0.06 g of tungstic acid in 50 ml of dioxane and 25 ml of acetic acid at 5°. The solution then was stirred at *ca.* 25° for 2 days. After removal of tungstic acid, then solvent, the residue was washed with cold water and dried to give 0.05 g (8%) of 1,2-dithiolane 1,1,2,2-tetroxide: mp 149–152° (after four recrystallizations from methylene chloride, this was 168–169°); strong ir absorption at 1350, 1160, and 1110 cm^{-1}; nmr (DMSO) τ 6.13 (4 H, triplet), 7.36–7.80 (2 H, multiplet). The tetroxide seems quite stable, having a mp of 166–167° after 9 months.

Anal. Calcd for $C_3H_6O_4S_2$: C, 21.16; H, 3.55; S, 37.68. Found: C, 21.36; H, 3.52; S, 37.83.

1,2-Dithiepane 1,1,2,2-Tetroxide.—Hydrogen peroxide (15.2 mmol, 2.00 ml of 7.6 *M*) in 10 ml of acetic acid was added dropwise (10 min) to 1,2-dithiepane 1,1-dioxide (0.50 g, 3.0 mmol) in 75 ml of acetic acid containing 0.06 g of tungstic acid at *ca.* 25°. After the reaction mixture had been stirred for 2 days, removal of solid and evaporation of solvent left solid, which was washed with cold water. Residual material amounted to 0.06 g (10%) of 1,2-dithiepane 1,1,2,2-tetroxide, mp 157–158.5°. Similarly prepared material was analyzed after three recrystallizations from methylene chloride–ether: mp 159–160°; ir absorption at 1330, 1160 and 1120 cm^{-1}; nmr ($CDCl_3$), τ 6.25–6.60 (4 H, multiplet), 7.75–8.00 (6 H, multiplet).

Anal. Calcd for $C_5H_{10}O_4S_2$: C, 30.29; H, 5.08; S, 32.35. Found: C, 30.40; H, 5.28; S, 32.17.

An attempt to oxidize 1,2-dithiepane directly to the tetroxide by the procedure used with 1,2-dithiane failed. Use of a 6:1 ratio of peroxide to the dithiepane dioxide resulted in a yield of 4%. The tetroxide appears quite stable, having mp 157–158° after 5 months.

Ozonization.—Typically, ozone was passed for 90 min into a solution of cyclic disulfide (8 mmol) in 50 ml of acetic acid, dioxane, or nitromethane, at 25° or cooled to 0°. The content of sulfonic anhydride was determined by titration of the acid produced on hydrolysis of 0.150 g of product (after removal of solvent under vacuum) when stirred with 10 ml of water for 5 min. The content of disulfide dioxide next was established by titration of the acid produced upon addition of thiophenol (0.1 g),[12] and also when possible by isolation of the disulfide dioxide product. That the disulfide dioxide does not interfere with the initial titration of hydrolysis products was confirmed by the addition of a small amount of base to a solution of disulfide dioxide in ethanol containing phenolphthalein and observing the intensity of the color of the indicator which did not diminish, even after 15 min. Since no sulfonic anhydride actually could be isolated and identified, however, the titration results must be interpreted cautiously.

Oxidation of Alkyl Disulfides.—Very poor yields (2–23%) of ethyl disulfide S,S-dioxide and no tetroxide resulted upon oxidation of ethyl disulfide under conditions successfully used in converting 1,2-dithiane into the tetroxide.[1b] An approach similar to that of Allen and Brook[34] with 20 molar proportions of H_2O_2 also produced the dioxide (8%) but no tetroxide. *m*-Chloroperbenzoic acid and benzoyl peroxide were unsuccessful oxidants, giving no product which had the characteristic ir spectrum of either the dioxide or tetroxide.

Attempts also failed to oxidize ethyl disulfide S,S-dioxide and 2-acetamidoethyl disulfide S,S-dioxide to the corresponding tetroxides in the manner which gave an excellent yield of 1,2-dithiane tetroxide from the dioxide. In each case, only starting material could be recovered in poor yield.

Registry No.—1,2-Dithiane, 505-20-4; 1,2-dithiolane, 557-22-2; 1,2-dithiepane, 6008-51-1; 1,2-dithiane 1,1-dioxide, 18321-15-8; 1,2-dithiolane 1,1-dioxide, 18321-16-9; 1,2-dithiepane 1,1-dioxide, 18321-17-0; 1,2-dithiane 1,1,2,2-tetroxide, 18321-18-1; 1,2-dithiolane 1,1,2,2-tetroxide, 18321-19-2; 1,2-dithiepane 1,1,2,2-tetroxide, 18321-20-5.

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(33) L. Field, T. F. Parsons, and R. R. Crenshaw, *J. Org. Chem.*, **29**, 918 (1964).

(34) P. Allen, Jr., and J. W. Brook, *ibid.*, **27**, 1019 (1962).