Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.37; H, 5.49); 9-anthryl, 109.7–110.5° (lit.[34] 112–113°); 2-phenanthryl, 104.0–104.7° (lit.[35] 104.5–105.5°); 3-phenanthryl, 105.7–106.8° (lit.[35] 106.0–107.0°); 9-phenanthryl, 106.9–108.0° (lit.[35] 108.0–109.0); 1-pyrenyl, 143.8–144.7° (lit.[36] 146°); 7-benzanthryl, 130.9–131.6° (*Anal.* Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.41; H, 5.16). All of the esters, as well as the acids from which they were derived, showed infrared absorptions in the region 970–960 cm^{-1}, indicative of the C–H bending of a *trans*-disubstituted alkene. No absorption was observed for the C–H bending of a *cis*-disubstituted alkene (*ca.* 690 cm^{-1}).[37] The Knoevenagel synthesis appears to result in the formation of the *trans* acids only. See, for instance, the paper by Jensen, *et al.*[38]

The solvents used in the kinetic determinations were purified by literature procedures. The aqueous solvents were prepared by mixing appropriate amounts of thermostated solvent and distilled and boiled-out water. The 85% aqueous methanol (by volume before mixing) had $n^{25}D$ 1.3357 (lit.[24] $n^{25}D$ 1.3354) and 75% aqueous acetone had $n^{25}D$ 1.3436.

Kinetic Determinations.—The method was similar to that described before.[24] The hydrolyzing solutions were prepared daily as described.[24] For reasons of solubility, seven of the compounds were studied at concentrations of *ca.* 0.01 *M*, four at 0.05 *M*, and one at 0.001 *M*. The second-order rate constants were found to be independent of the concentration, as shown by the following data: 1-methyl naphthylacrylate (in aqueous acetone), 0.01028 *M*, k_2 (in l. mol^{-1} sec^{-1}) 0.0254; 0.01024 *M*, $k_2 = 0.0248$; 0.0050 *M*, $k_2 = 0.0260$; 2-methyl phenanthrylacrylate, 0.01027 *M*, $k_2 = 0.0180$; 0.01019 *M*, $k_2 = 0.0177$; 0.00113 *M*, $k_2 = 0.0175$. The reaction temperature was 24.89 ± 0.02°. Rate constants were obtained graphically from the integrated form of the second-order rate equation for equal concentrations. A least-square computer program was used for the final calculations.[39] The probable errors for rate constants in individual runs did not exceed 1.2%. Runs were conducted at least in duplicate, and reproducibility between duplicate runs was *ca.* 2%. The rate constants in Table I are average values of duplicate runs.

Acknowledgment.—This work was supported by National Science Foundation Grant GP-4986, which is gratefully acknowledged.

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[34] J. W. Cook, R. S. Ludwiczak, and R. Schoental, *J. Chem. Soc.*, 1112 (1950).

[35] W. E. Bachmann and M. C. Kloetzel, *J. Amer. Chem. Soc.*, **59**, 2207 (1937).

[36] E. Bergmann and E. Borgrachov, *ibid.*, **62**, 3016 (1940).

[37] We thank Mr. Waldemar Palaitis of the University of Pennsylvania for his assistance with some of the infrared spectral determinations.

[38] K. A. Jensen, A. Kjaer, and S. C. Linhoft, *Acta Chem. Scand.*, **6**, 180 (1952).

[39] We gratefully acknowledge the help of Dr. Ingeborg Schuster in the design of the least-square computer program.

Biologically Oriented Organic Sulfur Chemistry. IV. Synthesis and Properties of 1,2,5-Trithiepane, a Model for Study of Sulfide and Disulfide Moieties in Proximity[1a,b]

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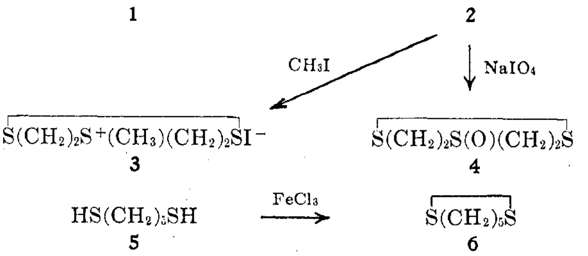
1,2,5-Trithiepane (**2**) was synthesized by oxidation of bis(2-mercaptoethyl) sulfide (**1**) with ferric chloride in 55% yield; attempted use of *p*-toluenesulfonyl chloride and dimethyl sulfoxide failed. Compound **2** was a liquid with properties quite different from any of three previously reported compounds tentatively or definitely considered to be **2**. Structural evidence for **2** included nmr, Raman, uv, and mass spectra, and molecular weight determination in solution. The trithiepane **2** formed a solid salt **3** with methyl iodide, and oxidation with 1 molar proportion of sodium metaperiodate gave a sulfoxide (**4**), showing that selective reactions of a cyclic sulfide are possible in the presence of a disulfide moiety. Comparative reactivities of **2**, **3**, **4**, and **6** (1,2-dithiepane), as adjudged by polymerization and cleavage with cyanide ion, and the uv spectra of **2**, **3**, **4**, and **6** suggest that interactions between the sulfide functions and disulfide bonds are not marked, a point which seems biochemically relevant.

1,2,5-Trithiepane, compound **2** in Scheme I, has been reported, or at least alluded to, three times in the literature. Rây assigned the name "diethylene trisulfide," presumably signifying **2**, to a solid, mp 96°, formed as a by-product of the reaction of "dithioethylene glycol" with benzylidene chloride.[2] Fromm and Jörg, seeking a synthesis of **2**, obtained a solid, mp 74–75°, from the reaction of bis(2-chloroethyl) disulfide with sodium sulfide;[3] in an effort to confirm the structure as that of **2**, they obtained a solid, also believed to be **2**, from the reaction of bis(2-chloroethyl) sulfide with sodium disulfide. Westlake and coworkers suggested that a colored liquid, $n^{20}D$ 1.5746, obtained as one product from the reaction of ethylene and sulfur might be **2**.[4]

SCHEME I



It was desirable to synthesize **2** in order to determine which, if any, of the previous reports were correct. A further objective was to provide a model for study of the chemistry of sulfide and disulfide moieties held in close proximity and thereby to afford information on the possibility of selective reactions and of interaction.

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[1] (a) Paper III: B. J. Sweetman, M. Bellas, and L. Field, *J. Med. Chem.*, **12**, 888 (1969). (b) This investigation was supported by Public Health Service Research Grant AM11685 from the National Institute of Arthritis and Metabolic Diseases. We wish to record our appreciation to Dr. Norman E. Heimer for determination of the Raman spectra, for a great deal of interpretive aid on all spectra, and for much other useful discussion. (c) J. M. Breckenridge Memorial Scholar, 1968–1969.

[2] P. C. Rây, *J. Chem. Soc.*, **125**, 1141 (1924).

[3] E. Fromm and H. Jörg, *Ber.*, **58**, 304 (1925).

[4] H. E. Westlake, Jr., M. G. Mayberry, M. H. Whitlock, J. R. West, and G. J. Haddad, *J. Amer. Chem. Soc.*, **68**, 748 (1946).

In addition to its chemical interest, such information should be biochemically relevant; for example, proteins may contain both sulfide (methionine) and disulfide (cystine) moieties,[5] sometimes close to each other in the amino acid sequence.[5b] In space-filling models, the 2 and 5 sulfur atoms of **2** nearly touch in the staggered conformation, which probably is preferred.

Schöberl and Gräfje synthesized 1,2-dithiepane (**6**) in good yield by adding an ethereal solution of 1,5-pentanedithiol (**5**) to a solution of ferric chloride in ether and acetic acid.[6] We used this procedure, with some modification, to convert bis(2-mercaptoethyl) sulfide (**1**) into **2** in 55% yield. The product was a colorless, viscous liquid, $n^{25}\text{D}$ 1.6424. The nmr spectrum of **2** at room temperature surprisingly showed only a sharp singlet in carbon tetrachloride, δ 3.1, and also in benzene, δ 2.7. The mass spectrum showed a parent peak at 152 (calcd: 152) and peaks at 153 and 154 having relative intensities appropriate for the molecular formula $C_4H_8S_3$.

Since **6**[7] and 1,4,5-oxadithiepane, $\overline{S(CH_2)_2O(CH_2)_2S}$,[8] as well as **2**, are liquids, the solids reported probably were polymeric. Although Westlake and coworkers did not rigorously purify their product, the refractive index indicates that it probably was not **2**.

Field and Barbee synthesized 1,2-dithiane in 93% yield and **6** in 17% yield by reaction of the corresponding dithiols with *p*-toluenesulfonyl chloride in aqueous sodium hydroxide,[7] but **2** could not be synthesized using this method. Wallace prepared 1,2-dithiane in 68% yield by oxidizing 1,4-butanedithiol with dimethyl sulfoxide,[9] but this approach also was unsuccessful for **2**. Thus **2** seems to form less readily from the corresponding dithiol than does 1,2-dithiane, and probably less so than does 1,2-dithiepane (**6**).

In an effort to determine whether the transannular sulfide and disulfide moieties could interact significantly with each other, we compared the stability of **2** with that of 1,2-dithiepane (**6**) using qualitative methods which Schöberl and Gräfje developed and applied to a number of cyclic disulfides.[6] As Table I indicates, in its cleavage by sodium cyanide **2** seemed to belong in group 1, the same stability group as 1,2-dithiane (no cleavage). On the basis of tendency toward polymerization, **2** was placed in group 2 (polymerization only with catalysis), the same group to which Schöberl and Gräfje and we assign **6**.[6] It is noteworthy that except for vigorous conditions both **2** and **6** were quite resistant to polymerization; since they were comparable in polymerization, and roughly so in cleavage by cyanide, no conspicuous transannular interaction is apparent.

The dithiepane **6** is quite stable in a glass container to ambient light,[7] a characteristic shared by **2**; indeed, **2** was not significantly changed even when irradiated strongly in a quartz vessel with uv light for *ca.* 9 hr.

Table I

The Reactivity of Cyclic Disulfides

Compd	Cleavage by NaCN[a]	Polymerization[a]	λ_{max}^{EtOH}, mμ (ϵ_{max})[b]
2	1	2	255 (441)
3	1	2?[c]	~260 (~310)
4	1	2	~255 (440)
6	2	2	260 (440)[d]

[a] All four substances were done simultaneously and (with NaCN) were simultaneously compared with *n*-butyl disulfide (group 2). The procedures used and the activity assignments of groups 1 (least reactive)–4 (most reactive) were according to Schöberl and Gräfje.[6] Details are given in the Experimental Section. [b] *Cf.* Figure 1 for details. [c] Compound **3** decomposed on addition of the acid in a rather inconclusive test. [d] Lit.[7] λ_{max}^{EtOH} 258 mμ (ϵ 444).

The effect of inserting a positively charged sulfonium salt function in close transannular proximity to a disulfide moiety likewise is both chemically interesting and biochemically relevant.[10] Synthesis of a sulfonium salt of **2** was of interest for these reasons, as well as to learn whether a cyclic sulfonium iodide could indeed be formed at all in the presence of the disulfide bond. Methyl iodide converts alkyl sulfides into methyldialkylsulfonium iodides. On the other hand, it converts alkyl disulfides (very slowly) into 2 mol of a dimethylalkylsulfonium iodide, with the liberation of free iodine.[11]

1,2,5-Trithiepane (**2**) was allowed to react with a fivefold excess of methyl iodide to give 1,2,5-trithiepane-5-methylsulfonium iodide (**3**) in 72% yield. The reaction itself is a clean one at room temperature, although the salt **3** is not particularly stable to heat. Thus, in an attempt to recrystallize **3** from boiling 95% ethanol, an insoluble, yellow solid, mp 113.5–115.5°, formed, which was not identified but appeared to be polymeric. The conclusion that salt formation involved the sulfide moiety, leading to **3**, rather than the disulfide moiety is based on the elemental analysis (inconsistent with a bis- or trissulfonium salt), on the failure to observe iodine formation, and on the mass spectrum. Interestingly, the dithiepane **6** became quite dark in 12 hr with methyl iodide; the failure of the salt **3** to react readily with methyl iodide may be due to its positive charge. In the mass spectrum, although no parent ion of **3** was clearly seen, thermal decomposition resulted in peaks characteristic of methyl iodide and of **2**, and a peak at *m/e* 75 was seen, consistent with the fragment $CH_3SCH_2CH_2$ from undissociated **3**.

Another interesting facet of the chemistry of **2** lay in whether oxidation would occur at the sulfide or disulfide bond and in whether proximity effects could be seen in the products. Hiskey and Harpold reported selective oxidation of a sulfide to a sulfoxide in an acyclic molecule containing a disulfide bond.[12] Their procedure, slightly modified, gave 1,2,5-trithiepane 5-oxide (**4**) in 66% yield. The nmr spectrum of **4** has multiplets at δ 2.5–3.4 and 3.4–4.3. Although the integration of these two multiplets is difficult to interpret because of overlap,[13a] the ratio appears to be *ca.* 2.3:1.7. The mass spectrum was more helpful structurally. It had peaks corresponding to SS and SO fragments at *m/e* 92 ($C_2H_4S_2$), 77 (C_2H_5SO), 76 (C_2H_4SO), and 64 (S_2);

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(5) (a) H. R. Mahler and E. H. Cordes, "Biological Chemistry," Harper and Row, New York, N. Y., 1966, pp 37, 659; (b) pp 82, 290.

(6) A. Schöberl and H. Gräfje, *Justus Liebigs Ann. Chem.*, **614**, 66 (1958).

(7) L. Field and R. B. Barbee, *J. Org. Chem.*, **34**, 36 (1969).

(8) F. O. Davis and E. M. Fettes, *J. Amer. Chem. Soc.*, **70**, 2611 (1948).

(9) T. J. Wallace, *ibid.*, **86**, 2018 (1964).

(10) *Cf.*, for example, the highly important sulfonium salt S-adenosylmethionine (ref 5, pp 698–700).

(11) (a) M. L. Selker and A. R. Kemp, *Ind. Eng. Chem.*, **36**, 16 (1944); (b) *cf.* G. K. Helmkamp, H. N. Cassey, B. A. Olsen, and D. J. Pettitt, *J. Org. Chem.*, **30**, 933 (1965).

(12) R. G. Hiskey and M. A. Harpold, *ibid.*, **32**, 3191 (1967).

(13) (a) Chemical shifts of less than τ 0.2 have been observed for R^1R^2-CHS(O)– compared with R^1R^2CHS–;[13b] (b) C. Y. Meyers and A. M. Malte, *J. Amer. Chem. Soc.*, **91**, 2123 (1969).

since the disulfide bond ordinarily does not seem to undergo fragmentation readily,[14] the mass spectrum thus supports the conclusion that oxidation occurred at the sulfide moiety, leading to **4**, rather than at the disulfide moiety. The ir spectrum of **4** also supports this conclusion, since it is very similar to that of **3** (except for the expected strong SO absorption of **4** at 1025 and 1005 cm^{-1}), as would be expected because of the presumably similar symmetries of **3** and **4**.

It is worth adding, although models were not available for comparison, that occurrence of a strong Raman frequency at about the same point for the sulfoxide **4** (517 cm^{-1}), the salt **3** (510 cm^{-1}), **2** (516 cm^{-1}), and **6** (518 cm^{-1}) confirms the presence of an unmodified disulfide bond in each substance; a Raman frequency at *ca.* 500 cm^{-1} is expected for disulfides.[15]

The stability of **4**, reflected in Table I and in the failure of the ir spectrum or melting point to change appreciably during more than 2 months, also seems inconsistent with formulation of the product with an -S(O)S- moiety, since thiolsulfinates often decompose rapidly.[16] The similarity of **4** to **6** in resisting polymerization and cleavage by cyanide ion (Table I) extends the conclusion of Hiskey and Harpold that intramolecular interactions between acyclic sulfoxide and disulfide species are probably insignificant.[12]

The uv spectra of cyclic disulfides show a displacement of the absorption peak to progressively longer wavelengths with diminishing ring size.[17] Barltrop, Hayes, and Calvin ascribed this red shift to ring strain.[17a] In a further effort to discover whether or not there is significant interaction between the disulfide and sulfide-type moieties, the uv spectra of **2**, **3**, **4**, and **6** were compared (*cf.* Table I and Figure 1). Since the absorption spectrum of **2** is much like that of **6**, no marked effect of the sulfide moiety on the disulfide seems indicated. In compounds **3** and **4** the sulfur atom in the 5 position bears a positive charge. Although absorption near 240 mμ is enhanced in the spectra of **3** and **4** (presumably by the sulfonium and sulfoxide moieties), the absorption maxima attributable to the disulfide bond in **3** and **4** seem too similar to those of the trithiepane (**2**) and dithiepane (**6**) to imply marked transannular interactions of the sulfonium or sulfoxide functions with the disulfide bond (at least in the absence of definitive models which unequivocally afford information on what is to be expected from such interactions). Such differences as exist may well be of conformational origin.

The tendencies of the salt **3** and the sulfoxide **4** toward polymerization and cleavage by cyanide seem much the same as for the disulfides **2** and **6** (*cf.* Table I). Thus the sulfide, sulfonium, or sulfoxide moieties, in this respect also, seem to have little transannular effect on the chemistry in solution of the disulfide bond. It might be added that the salt **3** seems less stable in being handled than do **2**, **4**, or **6**; such an effect might be attributable to polymerization induced by attack of I$^-$ on the disulfide bond, or to dissociation of **3** to **2** and methyl iodide followed (at higher temperatures) by a usual disulfide-type reaction.[11]

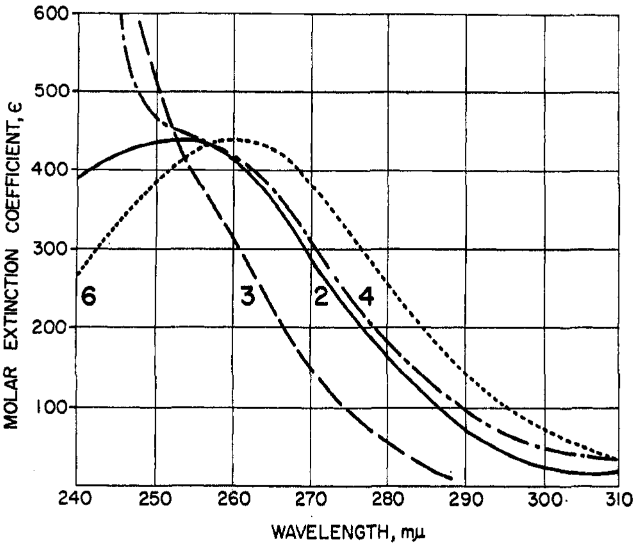

Figure 1.—Uv absorption spectra in EtOH: 1,2,5-trithiepane (**2**), ——; 1,2,5-trithiepane-5-methylsulfonium iodide (**3**), - - -; 1,2,5-trithiepane 5-oxide (**4**), —·—.; 1,2-dithiepane (**6**),· · ·.

Experimental Section[18]

Materials.—1,5-Pentanedithiol (**5**) and bis(2-mercaptoethyl) sulfide (**1**, *ca.* 90% pure by titration with I_2–KI) were used as obtained from the Wateree Chemical Co., Lugoff, S. C. 1,2-Dithiepane (**6**) was obtained from **5** essentially by a reported modification[7] of the procedure of Schöberl and Gräfje[6] in 49% yield, n^{25}D 1.5700 (lit.[7] n^{25}D 1.5690); the ir and uv spectra agreed with reported values.[7] Use of the simple but effective high-dilution mixer of Allen and VanAllan,[19] with addition of **5** during 14 hr, increased the yield to 60%; extension of the time to 8 days also gave **6** in 60% yield.

1,2,5-Trithiepane (**2**). A. **Preparation.**—Bis(2-mercaptoethyl) sulfide (**1**, 30.8 g, 0.20 mol) in ether (400 ml) was added (24 hr) through a high-dilution mixer[19,20] to a solution of $FeCl_3 \cdot 6H_2O$ (162 g, 0.60 mol) in ether (1500 ml) and acetic acid (200 ml) under reflux. The mixture then was kept under reflux for 2 days, after which ether was distilled until the volume was 1200 ml. The mixture then was washed with 700-ml portions of water until the aqueous layer was neutral. The first two washes were back-extracted twice with 100-ml portions of ether. The ether layers were combined, and an aqueous solution of I_2–KI was added dropwise with vigorous stirring until a faint iodine color remained (to remove unchanged **1**). An aqueous solution of sodium thiosulfate then was added dropwise until the iodine color disappeared. The resulting organic layer was washed with water, dried, filtered, and evaporated to give **2** as a brown liquid, yield 25.45 g (84%), n^{25}D 1.6288. Distillation of the crude **2**

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[14] *Cf.* J. H. Bowie, S.-O. Lawesson, J. Ø. Madsen, C. Nolde, G. Schroll, and D. H. Williams, *J. Chem. Soc.*, *B*, 946 (1966).

[15] N. B. Colthup, L. H. Daly, and S. H. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press Inc., New York, N. Y., 1964, p 306.

[16] D. Barnard, *J. Chem. Soc.*, 4675 (1957).

[17] (a) J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Amer. Chem. Soc.*, **76**, 4348 (1954); (b) for related comment, *cf.* ref 7.

[18] Melting points are corrected and boiling points are uncorrected. Elemental analyses and osmometric molecular weights were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Ir spectra were done using a Beckman Model IR-10 with films of liquids, and KBr pellets of solids, s signifying strong (others reported were medium). Uv spectra were obtained with a Cary Model 14, nmr spectra with a Varian Model A-60 (TMS as an internal standard), and Raman spectra with a Cary Model 81 instrument; we thank the National Science Foundation for Departmental Grants GP-1683 and GP-6932, respectively, toward purchase of the latter two instruments. Mass spectral analyses were kindly determined by C. T. Wetter using an LKB Model 9000 instrument, at 70-eV electron energy with a direct inlet system or (**2**) gc inlet, obtained through Science Development Program Grant GU-2057 from the National Science Foundation; only parent peaks and those exceeding 5% in relative intensity at *m/e* >44 are reported. Unless otherwise stated, reactions were carried out at room temperature. Moist extracts were dried with anhydrous $MgSO_4$, and solvents were then evaporated under reduced pressure using a rotary evaporator.

[19] C. F. H. Allen and J. A. VanAllan, *J. Org. Chem.*, **14**, 754 (1949).

[20] During the addition, a white solid, presumed to be polymeric, formed in the dropping funnel. Performing the addition in the dark under N_2 in peroxide-free ether did not inhibit formation of the solid.

using a 20-cm Vigreux column gave 16.63 g (55%) of colorless **2**, bp 61–63° (0.2 mm), $n^{25}\text{D}$ 1.6415–1.6424. A sample, $n^{25}\text{D}$ 1.6424, was analyzed: ir 2900 (s), 1410 (s), 1280 (s), and 830 (s) cm^{-1}; nmr δ 3.1 (s, CCl_4) or 2.7 (s, benzene); mass spectrum *m/e* (rel intensity) 154 (15), 153 (7), 152 (100, $C_4H_8S_3$), 124 (32, $C_2H_4S_3$), 106 (18), 105 (7), 96 (10), 92 (17), 87 (30), 78 (25), 73 (5), 64 (30), 61 (15), 60 (66), 59 (56, C_2H_3S), 58 (20), 57 (5), 47 (9), 46 (16), and 45 (52, CHS).

Anal. Calcd for $C_4H_8S_3$: C, 31.54; H, 5.31; S, 63.16; mol wt, 152. Found: C, 31.80; H, 5.29; S, 63.38; mol wt, 165 (Mechrolab osmometer), 152 (mass spectrum).

In a procedure with DMSO similar to one used by Wallace,[9] 40 mmol of **1** was added (30 min) to DMSO (80 mmol) at 140–160°. After 3 hr, the gum which resulted was washed with ether. The ether was washed with water, dried, and evaporated to give 0.12 g (2% assuming it to be **2**) of liquid which had an ir spectrum like **2** except for an additional weak band at 1480 cm^{-1}.

B. Stability of 2 Neat.—A sample sealed in a glass ampoule was stored next to a window. In 3 months the sample became cloudy, and its refractive index increased by 0.0011. Other samples were stored in ambient light, in the dark, and refrigerated in the dark. These samples did not become cloudy over a period of 7 months, and the refractive indices decreased by 0.0018, 0.0012, and 0.0014, respectively. The osmometric molecular weight of the sample stored in ambient light was found to be 140.

C. Stability of 2 in Ultraviolet Light.—*Ca.* 1.5 ml of **2**, was placed in a 1-cm quartz cell under N_2, which was exposed to ultraviolet light from a 100-W Hanovia lamp 15 cm from the cell. Aliquots were taken at regular time intervals, and the refractive indices were taken. After 32 min the refractive index had decreased by 0.0032, but after 532 min the index had increased again to its starting value. Some coating was observed on the face of the cell. The molecular weight of the remaining sample was found to be 178, and the appearance of the liquid was unchanged. Refractive index seems to be of little help in following the polymerization, probably because of very sparing solubility of polymer in the monomer.

1,2,5-Trithiepane-5-methylsulfonium Iodide (3).—Methyl iodide (9.35 g, 65.8 mmol) was added to **2** (2.00 g, 13.15 mmol), and the mixture was allowed to stand in a tightly closed flask for 30 hr. Crystals began to form within a few minutes. The resulting mass of friable yellow crystals was rubbed with ether to give 2.80 g (72%) of the sparingly water-soluble salt **3**, mp 131–134° dec. Recrystallization of 0.5 g of the crude **3** from 50 ml of warm, anhydrous ethanol by addition of ether gave white crystals: yield 0.30 g (43% overall); constant mp 131–132° dec; ir 1420, 1390, and 840 cm^{-1}; nmr (DMSO-d_6) δ 3.1 (s) and 2.8–4.2 (br m); mass spectrum *m/e* (rel intensity) 154 (10), 153 (5), 152 (75, $C_4H_8S_3$), 142 (100, CH_3I), 141 (15), 140 (5), 139 (6), 128 (10), 127 (67, I), 124 (30), 106 (14), 105 (5), 96 (9), 92 (14), 87 (30), 79 (6), 78 (20), 75 (50, C_3H_7S), 64 (30), 60 (58, C_2H_4S), 59 (58, C_2H_3S), 58 (23), 57 (6), 47 (19), 46 (18), and 45 (58, CHS).

Anal. Calcd for $C_5H_{11}IS_3$: C, 20.41; H, 3.78; I, 43.13. Found: C, 20.51; H, 3.85; I, 43.38.

When the procedure was repeated using 1 molar proportion of methyl iodide, the yield decreased to 55%, mp 127–130°.

1,2,5-Trithiepane 5-Oxide (4).—In a procedure like that of Hiskey and Harpold,[12] a solution of $NaIO_4$ (2.81 g; 13.15 mmol) in water (55 ml) was added to a stirred solution of **2** (2.00 g, 13.15 mmol) in tetrahydrofuran (150 ml). The temperature of the mixture was maintained at 0–9° throughout the 30-min addition and for 3 hr thereafter. Tetrahydrofuran (50 ml) then was added, and stirring was continued for 5 hr without cooling. The mixture was cooled to 0° and filtered, and the residue was washed with tetrahydrofuran. Evaporation of the combined filtrate gave a yellow oil suspended in an aqueous layer. The oil was extracted with chloroform. Evaporation of the extract left 1.45 g (66%) of yellow solid, mp 84–89°. Recrystallization of 0.30 g from CCl_4 gave white crystals: yield 0.18 g (40% overall); constant mp 95–96°; ir 1025 (s) and 1005 (s) (all other ir bands were quite like those of **3**); ir spectrum and melting point essentially unchanged after more than 2 months, showing good stability for **4**; nmr ($CDCl_3$) δ 2.5–3.4 (m) and 3.4–4.3 (m); mass spectrum *m/e* (rel intensity) 168 (14, $C_4H_8S_3O$), 126 (12), 125 (5), 124 (97, $C_2H_4S_3$), 112 (27), 109 (14), 92 (13, $C_2H_4S_2$), 81 (9), 79 (6), 78 (10), 77 (100, C_2H_5SO), 76 (45, C_2H_4SO), 75 (6), 66 (6), 64 (58, S_2), 61 (9), 60 (81, C_2H_4S), 59 (58, C_2H_3S), 58 (21), 57 (6), 48 (12), 47 (16), 46 (16) and 45 (45, CHS).

Anal. Calcd for $C_4H_8OS_3$: C, 28.54; H, 4.80; S, 57.15. Found: C, 28.63; H, 4.82; S, 57.48.

Relative Reactivity of 2, 3, 4, and 6. A. NaCN Cleavage.—According to the procedure of Schöberl and Gräfje,[6] each disulfide (*ca.* 50 mg) was dissolved in MeOH (2 ml) and 2% methanolic sodium nitroprusside solution (1 ml). Then a saturated methanolic sodium cyanide solution (1 ml) and a 5% methanolic ammonia solution (0.1 ml) were added. For **2**, **3**, and **4**, no color appeared, but after 1 hr the solution became cloudy. This behavior was identical with that reported for 1,2-dithiane (group 1).[6] Both **6** and *n*-butyl disulfide (group 2) produced a violet color after several minutes. In the Schöberl–Gräfje definition,[6] group 3 soon gives a strong color, group 2 is slower and gives a less intense color, and group 1 gives no color.

B. Polymerization.—In accordance with the procedure of Schöberl and Gräfje,[6] the disulfide (*ca.* 0.2 g), which had been standing for at least 7 days (group 3 polymerizes)[6] without change in refractive index (**2**, **6**) or melting point (**3**, **4**), was mixed with a solution of concentrated HCl in glacial acetic acid (3 ml each). The mixture was shaken vigorously. With **2**, **4**, and **6**, obvious changes occurred and a white precipitate formed in less than 1 hr (group 2,[6] since up to 24 hr is allowed, but not group 1, which must remain nearly unchanged for 24 hr); these precipitates, unlike **2**, **4**, and **6**, were virtually insoluble in $CHCl_3$. Compound **3** turned brown (I_2?) and seemed to change markedly immediately upon addition of the acid, but the test seemed rather inconclusive for group classification.

Registry No.—**2**, 6576-93-8; **3**, 22809-85-4; **4**, 22809-86-5; **6**, 6008-51-1.