mixture; in many cases, duplicate experiments were performed and found to confirm the results.

Benzyl Methyl Disulfide. To a solution of benzyl trisulfide (4.17 g, 15 mmol) in 100 mL of dry THF was added trimethyl phosphite (2.11 g, 17 mmol). The mixture was refluxed (75 °C bath) under argon for 30 h, at which time GC analysis indicated complete reaction. The solution was then evaporated under reduced pressure and distilled to give four fractions of colorless liquid: (a) 2.12 g (83%), bp 56–57 °C (0.02 mm), homogeneous benzyl methyl disulfide by GC, n^{21} 1.6000 [lit.[12b] bp 64 °C (0.2 mm), n^{24}_D 1.5996]; (b) 0.37 g, 40–98 °C (0.015 mm), mixed fraction; (c) 0.97 g, bp 98–102 °C (0.015 mm), 92% *O,O*-dimethyl *S*-benzyl phosphorothioate and 8% benzyl methyl disulfide by GC; (d) 1.95 g, bp 102–107 °C (0.015 mm) [lit.[23a] bp 98 °C (0.01 mm)], homogeneous phosphorothioate by GC, n^{21} 1.5431. An overall yield of 84% (97% pure) of phosphorothioate was obtained.

Ethyl Propyl Disulfide. To a solution of di-*n*-propyl trisulfide (3.64 g, 20 mmol) in 125 mL of dry THF was added triethyl phosphite (3.65 g, 22 mmol). The mixture was refluxed (75 °C bath) under argon for 7 days, at which time GC analysis indicated essentially complete reaction. The solution was then evaporated under reduced pressure and distilled to give six fractions of colorless liquid: (a) 0.80 g, bp 47–48 °C (7 mm) [lit.[11g] bp 104–106 °C (80 mm)], ethyl propyl disulfide contaminated by a few percent of triethyl phosphite by GC; (b) 1.32 g, bp 19–20.5 °C (0.50 mm), 80% EtSSPr and 20% PrSSPr by GC; (c) 1.30 g, bp 20.5–72 °C (0.50 mm), three fractions of mixtures of EtSSPr, PrSSPr, $(EtO)_3PS$, PrSSSPr, and $(EtO)_2P(O)SPr$ by GC; (d) 3.02 g (71%), bp 72–74 °C (0.50 mm), homogeneous *O,O*-diethyl *S*-propyl phosphorothioate by GC, n^{20} 1.4589 [lit.[23b] bp 90 °C (1.2 mm), n^{20}_D 1.4581]. The overall yield of ethyl propyl disulfide was 78% (12% dipropyl disulfide) and that of the phosphorothioate was 86% (last two fractions, overall 95% pure).

Furfuryl Methyl Disulfide. To a solution of furfuryl trisulfide (3.87 g, 15 mmol) in 100 mL of dry THF was added trimethyl phosphite (2.11 g, 17 mmol). The mixture was refluxed (75 °C bath) under argon for 30 h, at which time GC analysis indicated complete reaction. The solution was then evaporated under reduced pressure and distilled to give four fractions: (a) 0.29 g of colorless liquid, bp 49–50.5 °C (0.50 mm), 75% furfuryl methyl disulfide and 25% *O,O,O*-trimethyl phosphorothioate by GC; (b) 1.66 g (69%) of colorless liquid, bp 50.5–51.5 °C (0.50 mm), homogeneous furfuryl methyl disulfide by GC, identical in all respects (odor, NMR, IR, GC/MS) with that previously prepared,[11a] n^{23} 1.5644 [lit.[11a] bp 60–61 °C (0.8 mm), n^{23}_D 1.5661]; (c) 0.33 g, bp 33–98 °C (0.015 mm), mixed fraction; (d) 2.92 g (88%) of slightly yellow liquid, bp 98–106 °C (0.015 mm), two mixed fractions, overall 94% *O,O*-dimethyl *S*-furfuryl phosphorothioate and 6% furfuryl disulfide by GC and GC/MS. The phosphorothioate was further purified by flash chromatography[24] (4:1 ethyl acetate/petroleum ether) to yield an analytical sample: n^{22} 1.5127; NMR ($CDCl_3$) δ 7.3 (m, 1 H), 6.3 (m, 2 H), 4.1 (d, 2 H, J_{HP} = 14 Hz), 3.7 (d, 6 H, J_{HP} = 13 Hz); IR(neat) 1260, 1020 cm^{-1}; MS *m/e* (rel intensity) 222 (14, M^+), 113 (14), 81 (100), 79 (8). Anal. Calcd for $C_7H_{11}O_4PS$: C, 37.84; H, 4.99; P, 13.94. Found: C, 37.63; H, 5.07; P, 13.72.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Department of Education of Quebec for financial support.

Registry No. Di-4-tolyl trisulfide, 4991-51-9; difurfuryl trisulfide, 71243-23-7; dibenzyl trisulfide, 6493-73-8; di-*n*-propyl trisulfide, 6028-61-1; di-2-octyl trisulfide, 71243-24-8; trimethyl phosphite, 121-45-9; triethyl phosphite, 122-52-1; triisopropyl phosphite, 116-17-6; tri-*n*-butyl phosphite, 102-85-2; methyl 4-tolyl disulfide, 57266-34-9; ethyl 4-tolyl disulfide, 61565-48-8; isopropyl 4-tolyl disulfide, 29627-31-4; furfuryl methyl disulfide, 57500-00-2; benzyl methyl disulfide, 699-10-5; benzyl ethyl disulfide, 21230-16-0; benzyl butyl disulfide, 16601-16-4; benzyl isopropyl disulfide, 57413-29-3; methyl propyl disulfide, 2179-60-4; ethyl propyl disulfide, 30453-31-7; methyl 2-octyl disulfide, 71243-25-9; ethyl 2-octyl disulfide, 71243-26-0; 4-tolyl disulfide, 103-19-5; furfuryl disulfide, 4437-20-1; benzyl disulfide, 150-60-7; propyl disulfide, 629-19-6; 2-octyl disulfide, 1574-31-8; sulfur dichloride, 10545-99-0; furfuryl mercaptan, 98-02-2; (±)-2-octyl mercaptan, 10435-81-1; *O,O*-dimethyl *S*-benzyl phosphorothioate, 7205-16-5; *O,O*-diethyl *S*-propyl phosphorothioate, 20195-06-6; *O,O,O*-trimethyl phosphorothioate, 152-18-1; *O,O*-dimethyl *S*-furfuryl phosphorothioate, 71243-27-1.

(23) (a) Reference 8, p 711; (b) Reference 8, p 699.

(24) W. C. Still, M. Kahn, and A. Mitra, *J. Org. Chem.*, **43**, 2923 (1978).

Cyclic Trisulfides by Alkoxide Decomposition of Bis(sulfenyl) Thiocarbonates[1]

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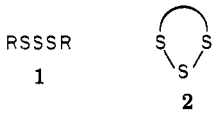
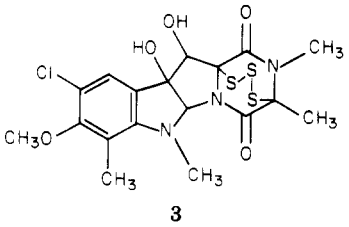
A series of bis(sulfenylated) thiocarbonates ($CH_3O_2SS(CH_2)_nSSCO_2CH_3$) was prepared and treated with potassium *tert*-butoxide in an effort to synthesize monocyclic trisulfides. In all cases (n = 2–10), polymeric material was obtained, and no target compounds were isolated. For n = 6, 7, 8, 10, cyclic bis(trisulfides) (dimers) were formed in moderate yield. Structural evidence for these macrocycles derives largely from MS, ^{13}C NMR, and osmometric molecular weight determinations.

While organic trisulfides **1** are a well-known class of



1 **2**

compounds, having such diversity as to have a role in marine[2] and insect life,[3] their cyclic versions **2** are much less common; only a few are naturally occurring. Representative among the several sulfur-containing metabolites from the fungus *Pitomyces chartarum* is the bicyclic trisulfide sporidesmin E (**3**).[4] Two others (**4** and **5**) have



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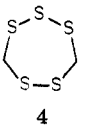

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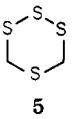

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(1) Organic Sulfur Chemistry, Part 36. For Part 35, see D. N. Harpp, and R. A. Smith, *J. Org. Chem.*, companion paper in this issue.

(2) R. E. Moore, *Chem. Commun.*, 1168 (1971).

(3) G. Casnati, A. Ricca, and M. Pavan, *Chem. Ind. (Milan)* **49**, 57 (1967).

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Table I. Spectral Properties of Bis(sulfenyl) Thiocarbonates (7)
$HS(CH_2)_nSH + 2\ ClSCO_2CH_3 \rightarrow CH_3O_2CSS(CH_2)_nSSCO_2CH_3$

no.	n	yield, %	n^{25}_D or mp, °C[a]	^{1}H NMR, δ	IR (CO), cm^{-1}
7a	2	82	92-94[b]	3.85 (s, 6 H), 3.00 (s, 4 H)	1740, 1695
7b	3	97	1.5688[b]	3.85 (s, 6 H), 2.95 (t, 4 H), 2.10 (m, 2 H)	1725, 1700
7c	4	93	1.5552	3.90 (s, 6 H), 2.85 (t, 4 H), 1.85 (m, 4 H)	1735, 1705
7d	5	98	1.5521	3.85 (s, 6 H), 2.75 (t, 4 H), 1.60 (m, 6 H)	1735, 1705
7e	6	97	1.5500[c]	3.85 (s, 6 H), 2.80 (t, 4 H), 1.50 (m, 8 H)	1730, 1700
7f	7	99	1.5410[b]	3.85 (s, 6 H), 2.75 (t, 4 H), 1.40 (m, 10 H)	1735, 1708
7g	8	99	1.5364[b]	3.80 (s, 6 H), 2.75 (t, 4 H), 1.35 (m, 12 H)	1735, 1710
7h	9	97	1.5361[d]	3.85 (s, 6 H), 2.80 (t, 4 H), 1.30 (m, 14 H)	1735, 1708
7i	10	99	1.5306[b]	3.85 (s, 6 H), 2.80 (t, 4 H), 1.30 (m, 16 H)	1740, 1710

[a] All compounds were pure by TLC. [b] These compounds gave correct high resolutions MS. [c] Correct elemental analysis. [d] Correct low-resolution MS.

been isolated from the mushroom *Lentinus edodes*.[5] While several cyclic trisulfides have been reported,[6,7] no generally useful synthetic approach has yet been advanced for this class. We wish to report our efforts on this problem.

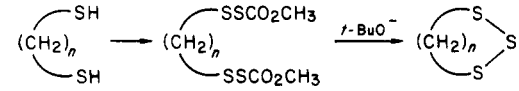
We previously reported a series of sulfenyl thiocarbonates **6** according to the method developed by Zumach and Kühle.[8] These compounds have been shown to be useful in preparing unsymmetrical disulfides.[9] We

$$\underset{\mathbf{6}}{RSSC(=O)OCH_3} + t\text{-}BuO^- \rightarrow RSS^- + t\text{-}BuOC(=O)OCH_3$$

$$RSS^- + RSSC(=O)OCH_3 \rightarrow \underset{\mathbf{1}}{RSSSR} + {}^-SC(=O)OCH_3$$

found that sulfenyl thiocarbonates decomposed cleanly in the presence of a molar amount of *tert*-butoxide to give trisulfides **1**.[10]

We have investigated the possibility of preparing cyclic trisulfides starting with bis(sulfenyl) thiocarbonates **7** according to the following scheme.



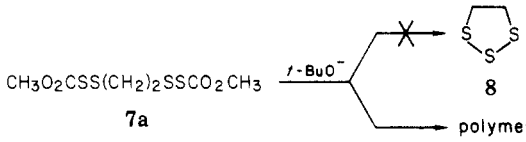
n = 2-10

7a, n = 2
b, n = 3
c, n = 4
d, n = 5
e, n = 6
f, n = 7
g, n = 8
h, n = 9
i, n = 10

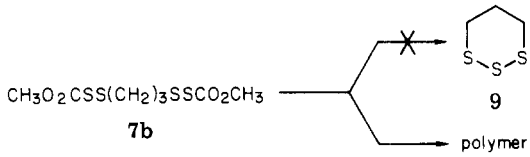
Results and Discussion

It was possible to prepare a series of bis(sulfenyl) thiocarbonates **7** under very mild conditions. The products were obtained in almost quantitative yield and high purity by reacting a dithiol with 2 mol of chlorosulfenyl carbonyl methoxide[8] (Table I).

Treatment of bis(sulfenyl) thiocarbonates **7** (n = 2–10) with *tert*-butoxide yielded reproducible but variable results. With compound **7a** (n = 2) reaction with *tert*-butoxide did not yield 1,2,3-trithiolane (**8**) but rather a grey-white insoluble solid with a wide melting point range.



Reaction of **7b** (n = 3) with t-BuO$^-$ gave rise to a solid with



mp 60–65 °C. Milligan and Swan report 44 °C as the melting point for 1,2,3-trithiane **9**. The material we obtained was slightly soluble in CS_2 and gave a ^{1}H NMR spectrum comparable to that reported by Lüttringhaus and co-workers.[6a] The mass spectrum showed a parent ion at m/e 138 and peaks at m/e 106 and 73. The infrared spectrum revealed the absence of any C=O peak. Unfortunately, attempts to purify this product by sublimation according to the method of Milligan and Swan[6b] led only to an intractable resin. It seems reasonable to assume that the reaction afforded mostly polymer. The CS_2 soluble portion may have contained monomer, but it polymerized in such a short time it was not possible to determine its molecular weight.

(4) R. Rahman, S. Safe, and A. Taylor, *J. Chem. Soc. C*, 1665 (1969); D. Brewer, R. Rahman, S. Safe, and A. Taylor, *Chem. Commun.*, 1571 (1968).

(5) K. Morita and S. Kobayashi, *Chem. Pharm. Bull.*, **15**, 988 (1967); K. Morita and S. Kobayashi, *Tetrahedron Lett.*, 573 (1966); a polysulfide with antibiotic activity has been isolated from the red alga *Chondria californica*; the structure has been proposed as either a symmetrical tetrakis(disulfide) or a symmetrical bis(trisulfide)–bis(sulfide); S. J. Wratten and D. J. Faulkner, *J. Org. Chem.*, **41**, 2465 (1976).

(6) The Bunte salt method has been used for simple five-, six-, and seven-membered ring trisulfides; (a) S. Kabuss, A. Lüttringhaus, H. Friebolen, and R. Mecke, *Z. Naturforsch. B*, **21**, 320 (1966); (b) B. Milligan and J. M. Swan, *J. Chem. Soc.*, 2901 (1965); (c) B. Milligan, B. Saville, and J. M. Swan, *J. Chem. Soc.*, 3608 (1963); (d) *ibid.*, 4850 (1961); (e) the coupling of dithiols via SCl_2 has been effective for simple five-, six-, and seven-membered rings; G. Goor and M. Anteunis, *Synthesis*, 329 (1975); these authors also reacted Na_2S_4 with a dimesylate to afford cyclic trisulfides; (f) F. Fehér and B. Degen, *Angew. Chem., Int. Ed. Engl.*, **6**, 703 (1967); (g) a bis(trisulfide) (ten-membered ring) was prepared with SCl_2 and the appropriate dithiol; F. Fehér, M. Langer, and R. Volkert, *Z. Naturforsch. B*, **27**, 1006 (1972); (h) a seven-membered ring trisulfide was claimed, by reaction with acetonylacetone and H_2S under pressure; T. L. Cairns, G. L. Evans, A. W. Larcher, and B. C. McKusick, *J. Am. Chem. Soc.*, **74**, 3982 (1952); (i) a five-ring bicyclic trisulfide was prepared using a bicyclic olefin, sulfur, and light; S. Inoue, T. Tezuka, and S. Oae, *Phosphorus Sulfur*, **4**, 219 (1978); (j) a bis(bicyclic) trisulfide was reported prepared by employing olefin, sulfur, and ammonia; J. Emsley, D. W. Griffiths, and R. Osborn, *Chem. Commun.*, 658 (1978); this compound is the first cyclic trisulfide for which a crystal structure has been reported; an extension of this work has appeared; J. Emsley, D. W. Griffiths, and G. J. J. Jayne, *J. Chem. Soc., Perkin Trans. 1*, 228 (1979); (k) a nine-membered trisulfide diene (cycloheptatriene, S_8, NH_3) has been reported; H. Fritz and C. D. Weis, *Tetrahedron Lett.*, 1659 (1974); (l) other bicyclic five-ring trisulfides are known; T. C. Shields and A. N. Kurtz, *J. Am. Chem. Soc.*, **91**, 5415 (1969).

(7) In a careful study it has been shown that in cyclizations using SCl_2 and Na_2S_4,[6e] mono- and disulfides are present in the reaction mixture; G. Goor and M. Anteunis, *Chromatographia*, **8**, 41 (1975).

(8) G. Zumach and E. Kühle, *Angew. Chem., Int. Ed. Engl.*, **9**, 54 (1970).

(9) K. Nokihara and H. Berndt, *J. Org. Chem.*, **43**, 4893 (1978); R. G. Hiskey, M. Muthukumaraswamy, and R. Vunnam, *J. Org. Chem.*, **40**, 950 (1975); S. J. Brois, J. F. Pilot, and M. W. Barnum, *J. Am. Chem. Soc.*, **92**, 7629 (1970).

(10) D. N. Harpp and A. Granata, *Tetrahedron Lett.*, 3001 (1976).

Table II. Preparation of Cyclic Bis(trisulfides)

n	no.	yield %	mp, °C	^{1}H NMR[a]	^{13}C NMR[b]	mol wt, theory	mol wt,[c] found
6	12	5-16[f]	75-77	2.9 (t, 4 H) 1.2-2 (m, 8 H)	40.29, 29.03 27.80	360	360
7	13	22	58-59	2.8 (t, 4 H) 1.2-2 (m, 10 H)	40.41, 28.33 27.77	388	384[d]
8	14	38	65-66	2.8 (t, 4 H) 1.2-2 (m, 12 H)	39.98, 28.85 28.03	416	423[e]
10	16	85	75-77	2.8 (t, 4 H) 1.2-2 (m, 16 H)		472	470

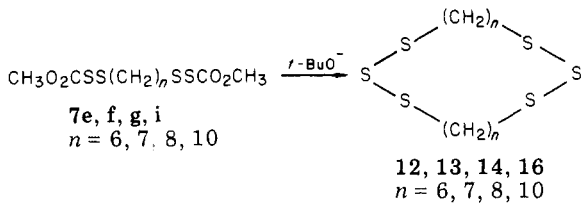
[a] All absorptions are expressed in δ units. NMR of the polymeric products were similar to those of the crystalline products given here. [b] Absorptions are expressed in ppm units. $CHCl_3$ was used as solvent and Me_4Si as internal reference. [c] Osmometric molecular weight. [d] Average of two determinations (380, 388). [e] Average of two determinations (416, 429). [f] The purification of this compound was particularly difficult because of the large amount of polymer formed; nevertheless the experiment is reproducible.

The reaction to give 1,2,3-trithiepane **10** (reported by Lüttringhaus[6a] in a yield of less than 5%) gave an oil (90%) with a ^{1}H NMR spectrum which compared well to that in the literature.[6a] The infrared spectrum was free from carbonyl absorption. The MS showed a correct exact mass for $C_4H_8S_3$, a strong parent, as well as m/e peaks at 120 and 87. No large m/e value was found above 152. Attempted purification of compound **10** [Kugelrohr, 50 °C (2 mm)] led to the formation of crystals which decomposed in a few minutes. Further, the unpurified product became very viscous and gummy after a few hours. It is our hypothesis that the monomer was formed but polymerized. This type of polymerization is not unknown in cyclic disulfide chemistry and applies to compounds of the type **11**.[11] The results in the case of **7d** were also not definitive

11a, $n = 6$
b, $n = 7$
c, $n = 8$

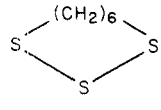
as to formation of a monomer. Here, a yellow oil was obtained in high yield (correct CHS); however, on standing, an insoluble, rubbery material was formed.

In the case of the attempted cyclization of sulfenyl thiocarbonates **7e**, **7f**, **7g**, and **7i**, a variable yield of polymer was obtained in each case along with a crystalline derivative. Separations were achieved by chromatography on silica gel. The early fractions afforded stable, crystalline compounds, while later elutions gave intractable polymeric material. The data regarding the crystalline products **12**, **13**, **14**, and **16** are summarized in Table II. It is instructive to summarize the data concerning bis(trisulfide) **12** (n = 6) as a typical example. The crystalline material isolated was sharp melting (75–77 °C), gave a correct elemental analysis, and had infrared and ^{1}H NMR spectra which were consistent with a monomeric trisulfide[12] structure.



7e, f, g, i
n = 6, 7, 8, 10

12, 13, 14, 16
n = 6, 7, 8, 10



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Further, the mass spectrum at 70 eV showed its highest peak at m/e 180. The ^{13}C spectrum displayed three sharp single lines consistent with structures **12** or **17**. Evidence for the dimeric structure **12** was obtained from the osmometric molecular weight which was 360. A low-voltage mass spectrum[13] (15 eV, 100 °C) revealed the 360 peak. Similar experiments indicated bis(trisulfide) structures for the crystalline products **13**, **14**, and **16**.[14] Such macrocycles are of current interest as sulfur analogues of crown ethers.[15] In addition, certain polysulfides of similar structure have been proposed to have antibacterial activity. The crystal structure of one interesting 16-membered tetrakis(disulfide) was recently reported.[16]

In sum, the bis(sulfenyl) thiocarbonate method appears to be ineffective as a technique for the synthesis of monomeric cyclic trisulfides[17] but does provide access to novel bis(trisulfide) macrocycles.

Experimental Section

Dithiols were obtained from commercial sources and were used directly; 1,7-dithiol was prepared according to the method of Urquhart.[19] Melting points were obtained on a Gallenkamp melting point apparatus in open capillaries and are uncorrected. A Carl Zeiss Model 28241 refractometer was employed in the determination of the refractive indices. Infrared spectra were recorded on a Perkin-Elmer Model 257 grating spectrophotometer. Spectra were calibrated by means of the 1601 cm^{-1} band of polystyrene film. Nuclear magnetic resonance spectra were taken

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

(12) The structure of **12** was initially proposed as a monomeric cycle (ref 10) based on combustion analysis, ^{1}H NMR, ^{13}C NMR, and MS information. It should be cautioned that MS at 70 eV did not reveal the dimeric structure **12**. Further, Rast molecular weight determinations (camphor) gave misleading values (196, 213).

(13) We are grateful to Dr. D. J. H. Smith (Leicester, England) for this measurement.

(14) In the case of **7h** (n = 9) the results were less clear-cut. After treatment with *tert*-butoxide, followed by chromatography, a semisolid was obtained which could not be induced to crystallize. It gave a correct elemental analysis for $C_9H_{18}S_3$. An osmometric molecular weight gave a value of 823 (tetramer calcd 890). Whether this is, in fact, impure tetramer (48-membered ring) or a mixture of cyclic oligomers giving an average molecular weight of 823 is not clear.

(15) R. E. DeSimone and M. D. Glick, *J. Am. Chem. Soc.*, **98**, 762 (1976); R. E. DeSimone and M. D. Glick, *J. Am. Chem. Soc.*, **97**, 942 (1975); J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974); L. A. Ochrymowycz, C. P. Mak, and J. D. Michna, *J. Org. Chem.*, **39**, 2079 (1974); W. Rosen and D. H. Busch, *Inorg. Chem.*, **9**, 262 (1970); W. Rosen and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4694 (1969).

(16) M. Braid, G. T. Kokotailo, P. S. Landis, S. L. Lawton, and A. O. M. Okorodudu, *J. Am. Chem. Soc.*, **100**, 6160 (1978).

(17) At present it would appear that no widely useful, reproducible method exists for the construction of monomeric cyclic trisulfides. Other experience in our laboratory[18] using a different synthetic approach confirms the necessity of using reliable molecular weight techniques for structure determination.

(18) K. Steliou and R. A. Smith, unpublished results.

(19) G. Urquhart, J. W. Gates, Jr., and R. Connor, "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1955, p 363.

on a Varian Associates T-60 spectrometer, while ^{13}C decoupled spectra were taken on a Bruker WH-90 equipped with Fourier transform. Low- and high-resolution mass spectra were taken on a AEI-MS-902 mass spectrometer. Elemental analyses of new compounds were performed by Microanalysis Laboratories, Montreal, Canada, and by Scandinavian Microanalytical Laboratories, Herlev, Denmark. Molecular weight determinations were kindly carried out by Dr. Hector Séguin of the National Research Council.

Preparation of Bis(sulfenyl) Thiocarbonates (7). Bis(sulfenyl) thiocarbonates were obtained in almost quantitative yields and high purity by reaction of a dithiol with 2 mol of carbomethoxysulfenyl chloride in methanol solution. This procedure was used for the synthesis of all bis(sulfenyl) thiocarbonates, hence only the preparation of dimethyl 2,3,6,7-tetrathiaoctane-1,8-dioate will be given. Spectral properties of the bis(sulfenyl) thiocarbonates (7) are summarized in Table I.

Dimethyl 2,3,6,7-Tetrathiaoctane-1,8-dioate (7a). 1,2-Ethanedithiol (3.0 g, 32.0 mmol) was dissolved in methanol (10 mL) and added dropwise to a solution of carbomethoxysulfenyl chloride (8.1 g, 64.0 mmol) in methanol (10 mL). During the addition, the reaction was cooled in an ice bath. It was then allowed to reach room temperature and stirred for 4 h. The volatiles were evaporated to leave a white solid, which was recrystallized from benzene/hexane (7.2 g, 82%); mp 92–94 °C; mass spectrum, parent peak at m/e 273.9452 (calcd for $C_6H_{10}O_4S_4$, 273.9462). Compounds **7** were purified by column chromatography [silica gel/chloroform–hexane (1:3)], or were homogeneous (TLC) after evaporation of solvent. Compounds **7b–7e** employed chloroform/hexane (1:3) for TLC, while **7g** was clean with hexane/benzene (1:1). Carbon tetrachloride was used for **7h–7i**.

Reaction of Bis(sulfenyl) Thiocarbonates (7) with Potassium *tert*-Butoxide. These reactions were performed under similar conditions, but the products obtained differed considerably, hence the details of each preparation will be given when considered necessary.

Attempted Preparation of 1,2,3-Trithiolane (8). Dimethyl 2,3,6,7-tetrathiaoctane-1,8-dioate (**7a**) (5.0 g, 18.2 mmol) was dissolved in methanol (10 mL). Potassium *tert*-butoxide (4.12 g, 3.7 mmol) was dissolved in methanol and added dropwise to the previous solution. During the addition the reaction was cooled in an ice bath. It was then allowed to reach room temperature and stirred for 3 h. A grey-white solid precipitated and was collected by filtration, giving 3.0 g: mp >103 °C (not sharp); IR (KBr) 2900, 1410, 1190, 1108, 1000, 730, 675 cm^{-1}. This compound was found to be insoluble in chloroform, water, ethanol, methanol, dimethyl sulfoxide, and benzene.

Attempted Preparation of 1,2,3-Trithiane (9). The reaction was performed as the previous one. Starting materials were **7b** (2.0 g, 6.9 mmol), potassium *tert*-butoxide (1.55 g, 13.8 mmol) and methanol (20 mL). A white precipitate formed which was separated by filtration giving 0.95 g: mp 60–65 °C; ^1H NMR (CS_2) δ 3.1 (t, 4 H), 2.5 (m, 2 H); IR (KBr) 2900, 1409, 1255, 870, 800 cm^{-1}; mass spectrum, peaks at m/e 138, 107, 76, 65. All attempts at crystallization of the product failed because of its lack of solubility in most organic solvents. Attempted sublimation according to the method of Milligan and co-workers[6b] led only to a resin.

Attempted Preparation of 1,2,3-Trithiepane (10). Dimethyl 2,3,8,9-tetrathiadeca-1,10-dioate (**7c**) (1.79 g, 5.88 mmol) was stirred in methanol and cooled to −10 °C. Potassium *tert*-butoxide (1.32 g, 12 mmol) was dissolved in methanol (10 mL) and added dropwise to the previous solution. The reaction was allowed to reach room temperature and stirred for 14 h. The methanol was evaporated under vacuum and the residue dissolved in chloroform. The chloroform was washed with water, dried over magnesium sulfate, and evaporated under vacuum. A yellow oil was obtained (0.80 g, 90%); ^1H NMR ($CDCl_3$) δ 2.93 (m, 4 H), 1.95 (m, 4 H). The ^1H NMR spectrum showed the presence of about 5% of impurities; IR (neat) 2900, 2815, 1428, 1295, 1220, 910, 870, 830, 770 cm^{-1}; mass spectrum, parent peak at m/e 151.9788 (calcd for $C_4H_8S_3$, 151.9795). A fraction of the yellow oil was distilled with a Kugelrohr apparatus at 53 °C (0.2 mm). Some white needle-like crystals formed in the receiver, but decomposed in a few minutes. The fraction of the oil which was not distilled became very viscous and gummy after a few hours.

Attempted Preparation of 1,2,3-Trithiocane. Potassium *tert*-butoxide (3.55 g, 3.2 mmol) was dissolved in methanol and added dropwise to compound **7d** (5.0 g, 1.6 mmol) previously dissolved in methanol (10 mL). During the addition, the reaction was cooled in an ice bath. The reaction was allowed to reach room temperature and stirred for 3 h. An oil separated. The methanol was evaporated and the residue dissolved in chloroform, washed with water, and dried over magnesium sulfate, and the chloroform was evaporated. A yellow oil was obtained (2.35 g). The oil was chromatographed [silica gel, benzene/hexane (1:1)], and two fractions were collected. The first was a colorless oil (2.2 g, 86%); ^1H NMR ($CDCl_3$) δ 2.90 (m, 4 H), 1.88 (m, 6 H); IR (neat) 2930, 1460, 1420, 1305, 805 cm^{-1}; mass spectrum, parent peak at m/e 166. The oil became a transparent rubber-like compound on standing.

1,2,3,10,11,12-Hexathiacyclooctadecane (12). Potassium *tert*-butoxide (1.32 g, 11.8 mmol) was dissolved in methanol (10 mL) and added dropwise to a solution of (**7e**) (2.0 g, 5.9 mmol) in methanol (10 mL). During the addition, the temperature of the reaction was kept between 0 and 10 °C. The reaction was then allowed to reach room temperature and stirred overnight. The methanol was evaporated and the residue was dissolved in chloroform. The chloroform was washed with water; a milky mixture formed which took several hours to separate into two layers. The organic layer was dried over magnesium sulfate and the chloroform was evaporated. The residue was purified by chromatography [silica, chloroform/hexane (1:3)]. Attempts to purify the residue by crystallization resulted in lower yields. The earlier fractions gave a solid which was thoroughly leached with hot ethanol. On cooling, white crystals formed from the ethanol (0.175 g, 16%): mp 75–77 °C; IR (KBr) 2920, 1468, 1273, 1215, 765, 718 cm^{-1}; osmometric molecular weight, found 360 (calcd 360). Anal. Calcd: C, 39.95; H, 6.71; S, 53.34. Found: C, 40.20; H, 7.09; S, 52.97. The later fractions from the chromatography provided 0.73 g (70%) of an oil which became very viscous in time, but which gave a ^1H NMR spectrum similar to that of the solid.

1,2,3,11,12,13-Hexathiocycloeicosane (13). Starting materials were **7f** (4.0 g, 12.0 mmol), potassium *tert*-butoxide (3.0 g, 26.0 mmol), and methanol (20 mL). A yellow oil was obtained (2.25 g, 100%). The oil was purified by chromatography [silica, chloroform/hexane (1:4)]. The earlier fractions gave a colorless liquid which solidified (0.50 g, 22%): mp 58–59 °C; IR (KBr) 2919, 1465, 1300, 1210, 730 cm^{-1}; osmometric molecular weight, found 380 (calcd 388). Anal. Calcd for $C_{14}H_{28}S_6$: C, 43.25; H, 7.26; S, 49.49. Found: C, 43.40; H, 7.41; S, 49.29. The later fractions provided 1.70 g (68%) of an oil which became viscous in time. The ^1H NMR spectrum of this oil was similar to that of the solid.

1,2,3,12,13,14-Hexathiacyclodocosane (14). Starting materials were **7g** (5.0 g, 14.0 mmol), potassium *tert*-butoxide (3.13 g, 28.0 mmol), and methanol (20 mL). A yellow oil was obtained which was purified by chromatography [silica, benzene/hexane (1:1)]. The earlier fractions consisted of a colorless oil which solidified on standing (1.50 g, 50%), mp 46–50 °C. Recrystallization from benzene/hexane gave white crystals (1.15 g, 38%); osmometric weight determination, found 416 (calcd 416). Anal. Calcd for $C_{16}H_{32}S_6$: C, 46.10; H, 7.70; S, 46.23. Found: C, 45.95; H, 7.67; S, 46.12.

1,2,3,14,15,16-Hexathiacyclohexacosane (16). Starting materials were **7i** (5.0 g, 13.0 mmol), potassium *tert*-butoxide (2.9 g, 26.0 mmol), and methanol (20 mL). A yellow oil was obtained which was purified by chromatography [silica, benzene/hexane (1:1)]. The earlier fractions gave a colorless oil which solidified on standing (3.0 g, 98%). This was recrystallized from benzene (2.6 g, 86%); mp 75–77 °C; osmometric molecular weight, found 470 (calcd 472). Anal. Calcd for $C_{20}H_{40}S_6$: C, 50.79; H, 8.53; S, 40.68. Found: C, 50.65; H, 8.62; S, 40.82.

Attempted Preparation of 1,2,3,13,14,15-Hexathiacyclotetracosane (15). This reaction was performed as the previous one. Starting materials were dimethyl 2,3,13,14-tetrathiapentadeca-1,15-dioate (**7h**) (4.0 g, 0.0107 mol), potassium *tert*-butoxide (2.4 g, 0.0214 mol), and methanol (15 mL). The residue, a brownish oil, was purified by chromatography (silica, carbon tetrachloride). After the chromatography, a colorless oil was obtained which became a white semisolid compound; yield was 0.27 g: ^1H NMR ($CDCl_3$) δ 2.9 (t, 16 H), 1.2–2.0 (m, 56 H); IR (neat) 2920, 1470, 1410, 1300, 1260, 800, 725 cm^{-1}; ^{13}C ($CDCl_3$,

ppm from Me_4Si) 40.028, 29.087, 28.850, 28.613, 28.052; osmometric molecular weight, found 823 (calcd 890). Anal. Calcd: C, 48.60; H, 8.15; S, 42.25. Found: C, 48.61; H, 7.52; S, 41.93.

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Registry No. 7a, 71370-11-1; **7b**, 71370-12-2; **7c**, 71370-13-3; **7d**, 71370-14-4; **7e**, 61775-37-9; **7f**, 71370-15-5; **7g**, 71370-16-6; **7h**, 71370-17-7; **7i**, 71370-18-8; **12**, 71370-19-9; **13**, 71370-20-2; **14**, 71370-21-3; **16**, 71370-22-4; 1,2-ethanedithiol, 540-63-6; 1,3-propanedithiol, 109-80-8; 1,4-butanedithiol, 1191-08-8; 1,5-pentanedithiol, 928-98-3; 1,6-hexanedithiol, 1191-43-1; 1,7-heptanedithiol, 62224-02-6; 1,8-octanedithiol, 1191-62-4; 1,9-nonanedithiol, 3489-28-9; 1,10-decanedithiol, 1191-67-9; carbomethoxysulfenyl chloride, 26555-40-8.

Structure of the Dimethyl Sulfoxide–Oxalyl Chloride Reaction Product. Oxidations of Heteroaromatic and Diverse Alcohols to Carbonyl Compounds[1a]

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"Activation" of dimethyl sulfoxide (Me_2SO) by oxalyl chloride (OC) at low temperatures in methylene chloride yields an unstable intermediate that instantaneously loses CO_2 and CO. Low-temperature ^{13}C NMR and IR coupled with chemical evidence show that the product after loss of gas is identical with that obtained from the low-temperature reaction of dimethyl sulfide with chlorine. Reaction of this product with about 30 diverse alcohols (heteroaromatic, heterocyclic, small ring and allylic alcohols, carbohydrate ketals, diols, and ketols) followed by basification gives high to quantitative yields of carbonyl compounds in most cases without overoxidation or interference by other functional groups. Methyl chloroglyoxylate is also a useful "activator" for Me_2SO but offers no advantage over OC. The oxidation of allenic alcohols and most acetylenic alcohols fails with the Me_2SO–OC reagent.

Oxalyl Chloride–Me_2SO Reaction Product. Oxalyl chloride (OC) reacts explosively with dimethyl sulfoxide (Me_2SO) at room temperature; therefore, successful "activation" of Me_2SO by OC and survival and use of the requisite intermediate **1** in synthetic applications require low temperatures (eq 1). Intermediate **1** reacts rapidly with primary and secondary alcohols to form the alkoxysulfonium salts **2** that are convertible to carbonyl compounds in high to quantitative yields upon addition of triethylamine (TEA) (eq 2).[2,3]

$$Me_2SO + (COCl)_2 \xrightarrow[-60\ ^\circ C]{CH_2Cl_2} [\underset{\mathbf{1a}}{Me_2\overset{+}{S}OC(O)C(O)Cl}\ Cl^-] \xrightarrow[-CO]{-CO_2} [\underset{\mathbf{1b}}{Me_2\overset{+}{S}Cl}\ Cl^-] \quad (1)$$

$$\mathbf{1} + R^1R^2CHOH \rightarrow [\underset{\mathbf{2}}{Me_2\overset{+}{S}OCHR^1R^2}\ Cl^-] \xrightarrow{TEA} R^1R^2C{=}O + Me_2S \quad (2)$$

Of the numerous Me_2SO "activators" we and others have studied,[2-5] OC is the most efficient and generally useful one. With only a few exceptions, use of Me_2SO–OC permits the high-yield, selective oxidation of primary and secondary alcohols to the corresponding carbonyl compounds without overoxidation in the presence of other potentially oxidizable functional groups.

In the first part of this paper we discuss the structure of **1** and provide evidence that, of the two possibilities (**1a** or **1b**), it is best written as **1b** derived from **1a** by virtually instantaneous loss of CO_2 and CO at −60 or −140 °C. Intermediate **1b** is the same as that obtained by Corey and Kim from chlorine and dimethyl sulfide at low temperature.[6,7] In the second part we report expansion of the range of oxidations possible with Me_2SO–OC to include heteroaromatic and other diverse alcohols.

The initial clue that the "activated" intermediate is not **1a** was the observation that only one of the acyl halide functions of OC is displaceable by Me_2SO at −60 °C, whereas both (if present) would be expected to react. Also, with a molar ratio of OC–Me_2SO–2-octanol of 1:2:2, the yield of 2-octanone is only 50%, and 50% of the starting alcohol is recovered. With a molar ratio of reactants of 1:2:1 or 1:1:1, the yield of 2-octanone is >95%. The conclusion that only one chlorine is displaced is consistent with the observation that the exothermic reaction between OC and Me_2SO ceases after 1 mol of Me_2SO has been added to OC.

Low-temperature IR (−140°C) and ^{13}C NMR (−60 °C) examination of the intermediate show no carbonyl group absorptions or ^{13}C-carbonyl carbon signals, respectively, thus excluding **1a**. (In the absence of Me_2SO, the ^{13}C NMR signal of OC in CD_2Cl_2 is observed at ca. 160 ppm

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