[COMMUNICATION NO. 2111 FROM THE KODAK RESEARCH LABORATORIES]

Sulfur-Containing Large-Ring Compounds. The Preparation of 4,7,13,16-Tetraoxa-1,10-dithiacyclooctadecane and Related Compounds

J. R. DANN, P. P. CHIESA, AND J. W. GATES, JR.

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The macrocyclic thioether-containing compounds, 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane (IV), 4,7,10-trioxa-1-thiacyclododecane (XVI), 4,7,10,16,19,22-hexaoxa-1,13-dithiacyclotetracosane (XVIII), and 4,10-dioxa-1,7-dithiacyclododecane (XXI) have been prepared. Derivatives of IV include a disulfone, two disulfonium salts, and two forms each of a disulfoxide, and a disulfilimine. Derivatives of XXI include a disulfone and a disulfonium salt. Evidence of the macrocyclic structure of IV is given by elemental analysis, molecular-weight determinations, absence of end groups, increased yield on dilution of reaction mixtures, preparation of an identical compound by an independent method of synthesis, and by the isolation of apparent *cis*- and *trans*-sulfoxides and sulfilimines.

The preparation of organic sulfides by the reaction of sodium sulfide with alkyl halides is well known,[1,2] and the reaction of bishalogen compounds with sodium sulfide to form polymers is an obvious extension of this reaction.

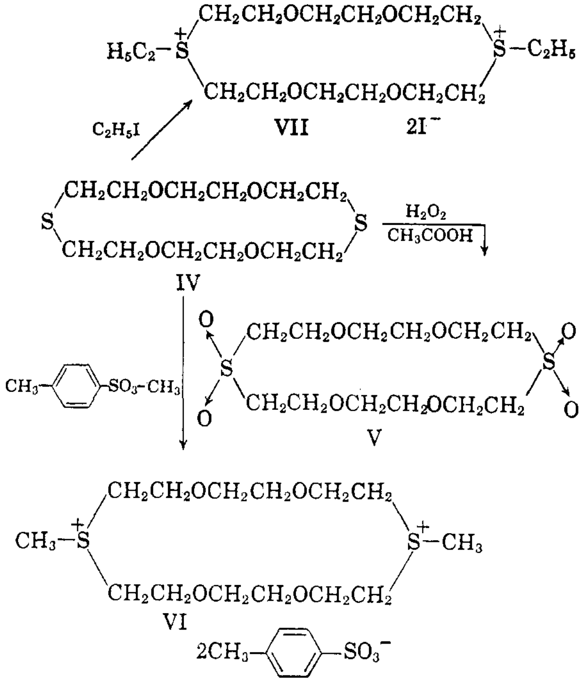
The reaction of sodium sulfide (I) and 1,2-bis(2-chloroethoxy)ethane (II) in 50% alcohol produced a crystalline material, IV, and a polymeric material, III.

$$\underset{\text{I}}{Na_2S} + \underset{\text{II}}{ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl} \longrightarrow \underset{\text{III}}{Cl(CH_2CH_2OCH_2CH_2OCH_2CH_2S)_n}$$

$$CH_2CH_2OCH_2CH_2OCH_2CH_2Cl + 2NaCl + \text{IV}$$

The crude reaction product was isolated as a sirupy oil which, on fractionation, yielded an oil, a wax, and a crystalline solid. Elemental analysis and molecular-weight determinations indicated that the crystalline material possessed the empirical formula, $C_6H_{12}SO_2$, and molecular weight, 295; the wax was a polymer, molecular weight about 5000 ($n = 30$) and the oil was a polymeric material of lower molecular weight.

Consideration of the empirical formula and molecular weight of the crystalline compound (IV) led to the formula, $C_{12}H_{24}S_2O_4$. An infrared absorption spectrum (Fig. 1) showed the presence of oxygen-ether linkages from the absorption near 9 μ, but the thioether absorptions, expected in the 14- to 16-μ region, were not identified because of their inherent weakness and the overlapping of skeletal vibrations. The best structure which can be written to conform to the facts just given, assuming that no rearrangement or carbon-carbon bond cleavage has taken place in the reaction, is that of the eighteen-membered ring compound, 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane (IV). Oxidation of IV with hydrogen peroxide in warm acetic acid gave the disulfone (V); treatment with methyl *p*-toluenesulfonate gave the disulfonium compound (VI) and treatment with iodoethane gave the diethiodide (VII).



VII

IV

V

VI

The compound IV was prepared by an independent synthesis, according to the method of Reid[3,4] by reaction of 1,2-bis(2-chloroethoxy)ethane (II) and 1,2-bis(2-mercaptoethoxy)ethane (VIII). Infrared absorption spectra of the crystalline material and the wax are shown in Figs. 1 and 2.

$$\underset{\text{VIII}}{HSCH_2CH_2OCH_2CH_2OCH_2CH_2SH} + \underset{\text{II}}{ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl} \longrightarrow \text{IV}$$

As further evidence of the cyclic nature of compound IV, which would be formed by an intra-

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[1] R. L. Shriner, H. C. Struck, and W. J. Jorison, *J. Am. Chem. Soc.*, 52, 2066 (1930).

[2] R. W. Bost and M. W. Conn, *Org. Syntheses*, Coll. Vol. II, 547 (1943).

[3] N. B. Tucker and E. E. Reid, *J. Am. Chem. Soc.*, 55, 775 (1933).

[4] J. R. Meadow and E. E. Reid, *J. Am. Chem. Soc.* 56, 2177 (1934).

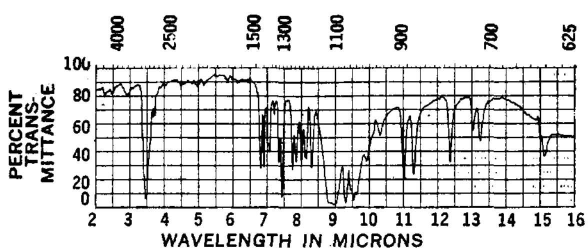


Fig. 1. Infrared absorption spectrum of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane, IV. (Upper)

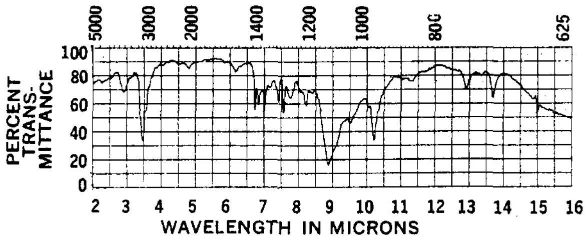


Fig. 2. Infrared absorption spectrum of the polymer, III. (Lower)

molecular reaction, it was found that increased dilution of the reaction mixture of sodium sulfide and 1,2-bis(2-chloroethoxy)ethane (II) resulted in increased yields of the crystalline material (IV), as shown in Table I. Similar effects were observed by Ziegler and co-workers[5] in the preparation of cyclic polymethylene ketones.

TABLE I

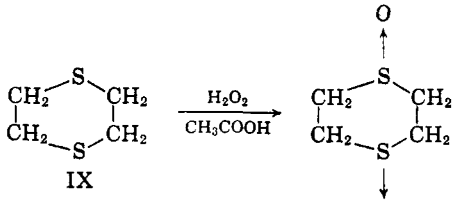
DILUTION EXPERIMENTS

Run No.	Concn. of Reactants Moles/Liter	Time (Hr.)	% Yield of IV
1	1.0	16	4.8
2	1.0	16	5.4
3	0.125	16	8.8
4	0.02	40	14.2
5	0.02	88	19.2
6	0.01	88	22.6

The yield in the reaction of II and VIII could be increased to 58.5% by a special adaptation of these high-dilution conditions where the ingredients were added dropwise over a long period of time to the dilution medium. This procedure is reported in the Experimental section.

Since disulfone (V) and disulfonium derivatives (VI and VII) of compound IV were readily obtained and easily characterized, it appeared that other derivatives might be of interest. It is known that macrocyclic compounds exhibit extreme structural flexibility in contrast to the more rigid nature of smaller rings, and it appeared interesting to determine whether geometrical isomers could be prepared with this large-ring compound, utilizing the sulfoxide and sulfilimine derivatives.

The disulfoxide (X) of dithiane (IX) has been prepared and separated into α and β forms,[6] but the configuration of these geometrical isomers was not determined until Shearer[7] carried out X-ray studies of the α modification, showing it to be in the chair form with the oxygen atoms in the *trans*-diaxial position.

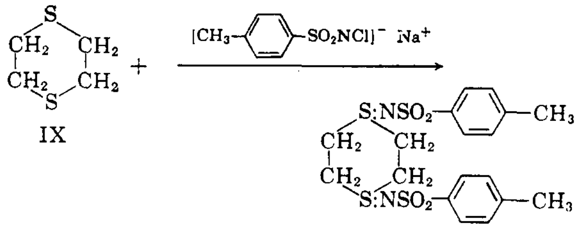


IX

X

α form; m.p. 263°
β form; m.p. 231°-250°

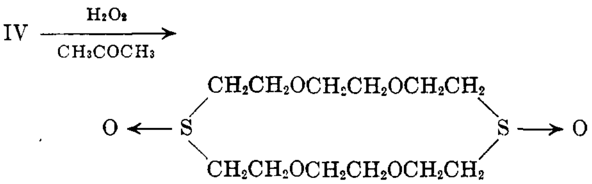
The disulfilimine derivative (XI) of dithiane (IX) has also been prepared and separated into α and β forms; the relative configuration, however, is not known.[8]



XI

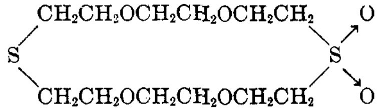
α form; m.p. 250–255° dec.
β form; m.p. 200–210° dec.

The disulfoxide (XII) of the large-ring compound (IV) was prepared, under conditions of oxidation that do not normally give rise to sulfone formation. Two forms, α and β, were isolated by careful fractionation, utilizing solubility differences. Although elemental analysis indicates that the desired compounds were obtained, the possibility of having obtained a monosulfone-sulfide (XIII) cannot be overlooked. In addition, polymorphism could exist.



XII

α form; m.p. 170–171°
β form; m.p. 153–154°



XIII

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[5] K. Ziegler, H. Eberle, and H. Ohlungen, *Ann.*, **504**, 94 (1933).

[6] E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 1798 (1927).

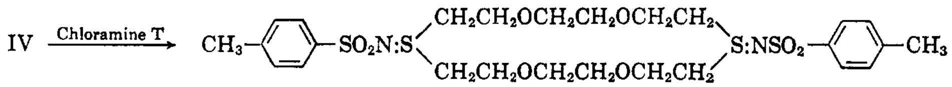
[7] H. M. M. Shearer, *J. Chem. Soc.*, 1394 (1959).

[8] E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 86 (1928).

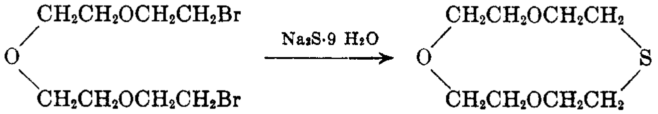
It is believed, however, that the latter may be ruled out because a mixed melting point of the α and β forms is depressed below that of either isomer. Such a behavior is not the case with polymorphism.

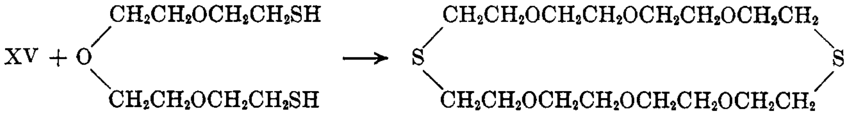
When the α and β forms of the disulfoxide of 4,7,13,16 - tetraoxa - 1,10 - dithiacyclooctadecane were oxidized with hydrogen peroxide in warm acetic acid, identical samples of the disulfone (V) were obtained from each isomer in almost quantitative yield.

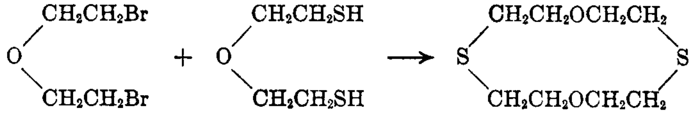
The disulfilimine derivative (XIV) of the large-ring compound (IV) was also prepared and separated into α and β forms. With this type of derivative, the mixed form, such as that of compound XIII, is not possible; polymorphism is again eliminated by the fact that the mixed melting point of the α and β forms is depressed below that of either separately.

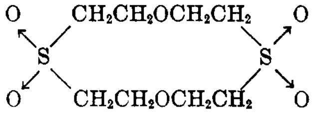

XIV

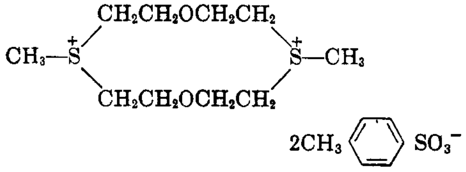
α form; m.p. 175–177°
β form; m.p. 143–144°


XV XVI


XVII XVIII


XIX XX XXI


XXII


XXIII

Infrared absorption-spectra determinations were carried out on the two forms of the two types of derivatives of IV, both on the crystals as potassium bromide pressings and in solution, in an effort to elucidate the structures. The spectra of the crystals were quite different, as is the case with *cis-trans* isomers, but the spectra in solution were only slightly different. The interpretation of these data is difficult since little is known about the behavior of *cis-trans* isomers in macrocyclic compounds. Infrared absorption spectra of the isomeric sulfoxides, when compared with the absorption spectrum of the disulfone, indicated that they are disulfoxides[9] and not the monosulfone-sulfide since the disulfone shows greater absorption in the 7.4- to 7.7-μ region than does either of the isomers. A sulfoxide would be expected to absorb near 9.4 to 9.8 μ, while a sulfone would absorb near 8.8 to 8.9 μ and 7.4 to 7.7 μ. During the preparation of the solution spectra of the sulfoxide isomers, added confirmation for the existence of geometrical isomers instead of polymorphism was obtained, in that no interconversion had occurred when the materials were recovered from solution.

Infrared absorption spectra of the sulfoxides and the sulfilimine derivatives of dithiane (IX) prepared according to the procedure of Bell and Bennett[6,8] were also obtained, both as potassium bromide pressings and in solution. The two forms (α and β) of both derivatives were again quite different both as crystal pressings and in solution, a fact that rules out polymorphism.

Additional examples of macrocyclic compounds were obtained by the two methods of preparation outlined. The reaction of bis-2-(2-bromoethoxy) ethyl ether (XV) with sodium sulfide in 50% alcohol at high dilution gave 4,7,10-trioxa-1-thiacyclododecane (XVI), along with polymeric materials; and the reaction of this ether (XV) with bis-2-(2-mercaptoethoxy)ethyl ether (XVII) under the same conditions gave 4,7,10,16,19,22-hexaoxa-1,13-

dithiacyclotetracosane (XVIII), along with polymeric materials. These compounds were constant-boiling oils and attempts to prepare crystalline sulfone or methyl *p*-toluenesulfonate derivatives yielded only oils. The reaction of bis(2-bromoethyl)-ether (XIX) with bis(2-mercaptoethyl)ether (XX)[9] in 50% alcohol at high dilution gave 4,10-dioxa-1,7-dithiacyclododecane (XXI), as outlined. This compound was obtained in solid form, and the sulfone (XXII) and methyl-*p*-toluenesulfonate (XXIII) were also crystalline. Elemental analyses and molecular-weight determinations confirmed the structure; tests for the absence of halogen and free thiol added further confirmation.

EXPERIMENTAL

The reaction of sodium sulfide (I) *and 1,2-bis(2-chloroethoxy)ethane* (II). 1,2-Bis(2-chloroethoxy)ethane 93.5 g. (0.5 mole) was mixed with 120 g. (0.5 mole) of sodium sulfide nonahydrate in 250 ml. of ethyl alcohol and 250 ml. of water. The reaction mixture was refluxed on the steam bath for 16 hr. and, upon cooling, 70 g. of yellow oil separated.

Anal. Calcd. for $Cl(CH_2CH_2OCH_2CH_2OCH_2CH_2S)_{10}$-$CH_2CH_2OCH_2CH_2OCH_2CH_2Cl$, $C_{66}H_{132}S_{10}O_{22}Cl_2$: C, 47.5; H, 7.9; S, 19.2; Cl, 4.2; mol. wt., 1666. Found: C, 50.2; H, 8.7; S, 21.3; Cl, 1.4; mol. wt., 1580 (b.p. elevation in benzene).

This oil was fractionated by dissolving it in 400 ml. of hot ethyl acetate and adding 470 ml. of ethyl alcohol and then cooling the mixture to 7°. A white wax (III) separated and was filtered cold and washed with cold alcohol. The alcohol-ethyl acetate mother liquor was evaporated to a small volume and, on standing at room temperature, 1.67 g. of white crystals (IV) were formed, m.p. 90–91°. The mother liquor from the original reaction mixture was allowed to evaporate slowly at room temperature and 2.4 g. more of crystals (IV) identical with those just described were recovered.

Anal. Calcd. for 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane, $C_{12}H_{24}S_2O_4$: C, 48.6; H, 8.1; S, 21.6; mole. wt., 296. Found: C, 48.7; H, 8.5; S, 21.8; mol. wt., 295 (average of six determinations by boiling-point elevation in ethyl alcohol).

The wax (III) described in the preceding paragraph was reprecipitated three times from ethyl alcohol–ethyl acetate by dissolving it in hot ethyl acetate, adding ethyl alcohol to the "cloud point" and chilling, and then dried to give 23 g. of purified product.

Anal. Calcd. for $C_{186}H_{372}S_{30}O_{62}Cl_2$: C, 48.1; H, 8.4; S, 20.7; Cl, 1.5; mol. wt., 4646. Found: C, 48.9; H, 8.4; S, 21.4; Cl, 2.7; mol. wt., 4800.

Evaporation of the solvent mixtures left a residual oil.

Anal. Found: C, 49.0; H, 9.1; S, 10.8; Cl, 1.1.

Preparation of 1,2-bis(2-mercaptoethoxy)ethane (VIII). This material was prepared from 1,2-bis(2-chloroethoxy)-ethane and thiourea by the procedure of Speziale[10] used for the preparation of ethanedithiol, b.p. 125–131°/5mm.

Anal. Calcd. for $C_6H_{14}O_2S_2$: C, 39.6; H, 7.7; S, 35.2. Found: C, 39.9; H, 8.0; S, 34.9.

Reaction of 1,2-bis(2-mercaptoethoxy) ethane with 1,2-bis-(2-chloroethoxy)ethane. Method A. 1,2-Bis(2-chloroethoxy) ethane, 4.7 g. (0.025 mole), and 1,2-bis(2-mercaptoethoxy)-ethane, 4.6 g. (0.025 mole), were dissolved in a solution of 2.6 g. (0.025 mole) of sodium carbonate in 1 l. of 50% aqueous ethyl alcohol. The reaction mixture was refluxed for 64 hr. and the solvent removed in a vacuum. The residue was extracted with three 50-ml. portions of boiling ethyl acetate. An equal volume of ethyl alcohol was added to the combined extracts and, on slow evaporation, 2.5 g. (34%) of white crystals, m.p. 90–91°, were obtained. No depression in melting point was observed when these crystals were mixed with those obtained from sodium sulfide and 1,2-bis(2-chloroethoxy)ethane. The crystals obtained by both methods of preparation gave identical infrared absorption spectra.

Method B. 1,2-Bis(2-chloroethoxy)ethane, 23.5 g. (0.125 mole), and 1,2-bis(2-mercaptoethoxy)ethane, 23.0 g. (0.125 mole), were mixed together and added dropwise over a period of 1 hr. to a stirred and refluxing solution of 0.125 mole of sodium carbonate in 4 l. of 50% aqueous ethyl alcohol. The reaction mixture was refluxed for 48 hr. and the solvent was then removed in a vacuum. The residue was extracted with three 50-ml. portions of boiling ethyl acetate from which 21.6 g. (58.5%) of crystals, m.p. 90–91°, were obtained.

Preparation of the disulfone (V) *of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane.* Three-tenths of a gram of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane was dissolved in 10 ml. of glacial acetic acid containing 2 ml. of 30% hydrogen peroxide. The reaction mixture was warmed on the steam bath for 1 hr. and left overnight at room temperature. The crystals (0.308 g.) which formed were filtered off and washed with ether, m.p. 237–238°.

Anal. Calcd. for $C_{12}H_{24}S_2O_8$: C, 40.0; H, 6.7; S, 17.8. Found: C, 39.9; H, 6.4; S, 17.4.

Preparation of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane-1,10-bis(metho-p-toluenesulfonate) (VI). Three-tenths of a gram of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane and 3 ml. of methyl *p*-toluenesulfonate were heated for 16 hr. on a steam bath. The cooled reaction mixture was washed with three 25-ml. portions of diethyl ether and then recrystallized from a mixture of 5 ml. of ethyl alcohol and 20 ml. of ethyl acetate to give 0.3155 g. of crystals, m.p. 146.5–147.5°.

Anal. Calcd. for $C_{28}H_{44}S_4O_{10}$: C, 50.2; H, 6.6; S, 19.2. Found: C, 50.3; H, 6.6; S, 18.9.

Preparation of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane-1,10-diethiodide (VII). One gram of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane and 10 ml. of iodoethane were heated together on a steam bath for 48 hr., the excess iodoethane was removed in a vacuum and the residue washed with ethyl acetate. The residue was then taken up in 20 ml. of boiling absolute ethyl alcohol. The crystals which formed upon cooling were light yellow, m.p. 158–160°.

Anal. Calcd. for $C_{16}H_{34}S_2O_4I_2$: C, 31.6; H, 5.6; S, 10.5; I, 41.7. Found: C, 31.5; H, 5.6; S, 10.1; I, 41.5.

Preparation of the sulfoxides (XII) *of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane* (IV). Compound IV, 2.96 g. (0.01 mole), was dissolved in 150 ml. of acetone and 2.2 ml. (0.02 mole) of 30% hydrogen peroxide was added. The mixture was left at room temperature for 14 days. Two types of crystals were formed and separated: A, large blocks, m.p. 153–154°, 1.05 g.; and B, needles, m.p. 170–171°, 0.4 g.

Anal. Calcd. for $C_{12}H_{24}S_2O_6$: C, 43.8; H, 7.3; S, 19.5. Found (A): C, 43.3; H, 7.0; S, 19.3. Found (B): C, 44.2; H, 7.1; S, 19.1. A mixed melting point of A and B was 148–155°.

Preparation of the sulfilimines (XIV) *of, 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane* (IV). Compound IV, 1.48 g. (0.005 mole), in 50 ml. of acetone was mixed with a solution of 2.82 g. (0.01 mole) of Chloramine T in 50 ml. of water and left at room temperature for 24 hr. Chilling gave 1.5 g. of crystals, m.p. 120–140°, which were separated into a water-insoluble fraction, A, 0.8 g., recrystallized from ethyl alcohol, m.p. 175–177°; and a water-soluble fraction, B, 0.7 g., recrystallized from ethyl alcohol, m.p. 143–144°.

Anal. Calcd. for $C_{26}H_{38}N_2S_4O_8$: C, 49.2; H, 6.0; N, 4.4; S, 20.2. Found (A): C, 48.9; H, 6.0; N, 4.5. Found (B): C, 48.9; H, 6.2; N, 4.4; S, 20.1.

Oxidation of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane-1,10-dioxide. The high-melting isomer, 0.3 g. (0.091 mole) was dissolved in 10 ml. of glacial acetic acid and 2 ml. (0.018 mole) of 30% hydrogen peroxide was added. After the

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[9] J. R. Meadow and E. E. Reid, *J. Am. Chem. Soc.*, **56**, 2177 (1934).

[10] A. J. Speziale, *Org. Syntheses*, **30**, 35 (1950).

reaction mixture had been heated for 30 min. on the steam bath, it was left at room temperature overnight. The small, white needles which formed were filtered off and washed with ether and then with boiling ethyl alcohol to give 0.27 g. of product (82%), m.p. 233.5–237°.

When the lower-melting isomer was oxidized in the same manner, crystals of identical melting point were obtained (0.31 g., 94%). The melting point of a mixture of the two products was not depressed.

Preparation of bis-2-(2-bromoethoxy)ethyl ether (XV). A mixture of 582 g. (3.0 moles) of tetraethylene glycol and 80 ml. of pyridine was stirred and cooled in a Dry Ice–isopropyl alcohol bath to −10°. Addition of 596 g. (2.2 moles) of phosphorus tribromide was carried out dropwise at a rate which allowed the reaction temperature to be maintained between −5° and +5°. After the addition, the mixture was stirred while the temperature rose gradually to room temperature and, after standing overnight, was poured into 500 ml. of water. The heavy oil which separated was drawn off, and the aqueous layer was extracted with three 250-ml. portions of ether. The combined oil and extracts were washed twice with 10% sodium bicarbonate solution, 10% sulfuric acid, and water. The mixture was dried over calcium chloride, the ether was removed, and the residue distilled in a vacuum to yield 413 g. of product boiling at 161–165° at 7 mm.

Anal. Calcd. for $C_8H_{16}O_3Br_2$: C, 30.0; H, 5.0; Br, 50.0. Found: C, 30.0; H, 4.6; Br, 50.5.

Preparation of bis-2-(2-mercaptoethoxy)ethyl ether (XVII). This material was prepared from bis-2-(2-bromoethoxy)-ethyl ether and thiourea by the method just given for 1,2-bis(2-mercaptoethoxy)ethane, b.p. 168–169°/7 mm.

Anal. Calcd. for $C_8H_{18}O_3S_2$: C, 42.5; H, 8.0; S, 28.3. Found: C, 43.0; H, 7.8; S, 28.0.

Preparation of 4,7,10-trioxa-1-thiacyclododecane (XVI). Thirty-two grams (0.1 mole) of 2,2′-bis(2-bromoethoxy)-ethyl ether dissolved in 2000 ml. of ethyl alcohol was mixed with a solution of 24 g. (0.1 mole) of sodium sulfide nonahydrate in 2000 ml. of water. The reaction mixture was refluxed on a steam bath for 41 hr., after which the solvent was removed in a vacuum. The residue was extracted with three 100-ml. portions of ethyl acetate. Removal of the solvent and vacuum distillation of the residual oil gave 7.7 g. of colorless oil, boiling at 90–95°/1 mm.

Anal. Calcd. for $C_8H_{16}O_3S$: C, 50.0; H, 8.3; S, 16.7; mol. wt., 192. Found: C, 50.4; H, 8.1; S, 16.3, mol. wt., 224.

Preparation of 4,7,10,16,19,22-hexaoxa-1,13-dithiacyclotetracosane (XVIII). A mixture of 71.2 g. (0.222 mole) of 2,2′-bis(2-bromoethoxy)ethyl ether, 50.2 g. (0.222 mole) of 2,2′-bis(2-mercaptoethoxy)ethyl ether, and 23.6 g. (0.222 mole) of sodium carbonate in 10 l. of 50% aqueous ethyl alcohol was refluxed on a steam bath for 72 hr. The solvent was removed in a vacuum, and the residue was extracted with three 150-ml. portions of ethyl acetate. The extracts were dried over anhydrous sodium sulfate, the ethyl acetate was removed, and the residue was vacuum-distilled in a molecular still, using a cottonseed carrier oil. Two similar fractions were collected, 14 g. at 200°, and 3.3 g. at 220°.

Anal. Calcd. for $C_{16}H_{32}O_6S_2$: C, 50.0, H, 8.3; S, 16.7; mol. wt., 384. Found (fraction distilling at 200°): C, 50.2; H, 8.7; S, 16.3; mol. wt., 352.

Preparation of 4,10-dioxa-1,7-dithiacyclododecane (XXI). *Method A.* A solution of 46.4 g. (0.2 mole) of bis-2-bromoethyl ether and 27.6 g. (0.2 mole) of bis-2-mercaptoethyl ether in 1300 ml. of 60% ethyl alcohol was added dropwise over a period of 24 hr. to a refluxing solution of 24.8 g. (0.2 mole) of sodium carbonate monohydrate in 8 l. of 50% ethyl alcohol. Refluxing was then continued for 72 hr., after which most of the solvent was removed in a vacuum, until a volume of about 500 ml. remained. This cloudy residue, after standing for a time, deposited a heavy oil layer which was drawn off, and the aqueous layer was extracted with four portions of ethyl acetate totaling 200 ml. These were combined with the oil and dried over anhydrous sodium sulfate, after which removal of the solvent and distillation in a vacuum gave 16.0 g. of colorless oil, b.p. 133–142°, at 0.17 mm. Some solidification occurred in the apparatus during distillation, and the entire product fraction slowly crystallized upon standing at room temperature; f.p. 22.5–23°.

Anal. Calcd. for $C_8H_{16}O_2S_2$: C, 46.1; H, 7.7; S, 30.8; mol. wt., 208. Found: C, 46.5; H, 7.6; S, 30.7; mol. wt., 219.

Method B. The same general procedure was used as that of Method A, except that 76.8 g. (0.2 mole) of diethyl ether bisisothiouronium bromide, an intermediate in the preparation of bis-2-mercaptoethyl ether by the procedure of Speziale,[10] was used in place of the bismercaptan; and instead of sodium carbonate, 90 g. (1.6 moles) of potassium hydroxide was used to accomplish hydrolysis of the isothiouronium salt and reaction with the halide, without prior isolation of the free mercaptan. There was obtained 14.4 g. of colorless oil which solidified at room temperature, b.p. 120–136° at 0.12–0.17 mm. The products from both Method A and Method B yielded the same disulfone derivative.

Preparation of the disulfone (XXII) *of 4,10-dioxa-1,7-dithiacyclododecane.* Following the same procedure given for V, there was obtained 1.25 g. of crystalline product from 1.3 g. of XXI; m.p. 241.5–243°.

Anal. Calcd. for $C_8H_{16}O_6S_2$: C, 35.3; H, 5.9; S, 23.5. Found: C, 35.5; H, 5.9; S, 23.2.

Preparation of 4,10-dioxa-1,7-dithiacyclododecane-1,7-bis-(metho-p-toluenesulfonate) (XXIII). Following the same procedure given for VI, there was obtained 1.8 g. of crystalline product from 1.2 g. of XXI, recrystallized from ethyl alcohol–acetone; m.p. 155–156.5°.

Anal. Calcd. for $C_{24}H_{36}O_8S_4$: C, 49.6; H, 6.2; S, 22.1. Found: C, 49.4; H, 6.3; S, 21.9.

Starting Materials: The sodium sulfide nonahydrate was obtained from Baker and Adamson and the tetraethylene glycol from Union Carbide Chemicals Co. Unless otherwise specified, all other chemicals were obtained from Eastman Kodak Company.

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