with H_2O and brine, and dried. Concentration and crystallization (MeCN) gave 3.2 g (33%) of **10**: mp 218–219° dec; ir 5.83 μ (C=O); NMR (DMSO-d_6) δ 7.5–7.85 (m, 5, aromatic), 8.18–8.35 (m, 3, aromatic plus exchangeable CO_2H).

Anal. Calcd for $C_{15}H_8Cl_2N_2O_2$: C, 56.45; H, 2.52; N, 8.78; Cl, 22.22. Found: C, 56.55; H, 2.77; N, 8.89; Cl, 22.41.

7-Chloro-5-(*o*-chlorophenyl)-1*H*-1,4-benzodiazepine-2,3-dione (11). A solution of 13.24 g (0.03 mol) of **4** in 60 ml of DMF was added to a mixture of 2.54 g (0.06 mol) of hexane-washed 57% NaH in 30 ml of DMF and the mixture was stirred for 1 hr at 20°. Dry O_2 was passed into the solution through a sintered tube at 20–30° for 1.5 hr, 3.8 ml (0.03 mol) of Me_3SiCl was added, and the solution was stirred for 0.25 hr. The mixture was concentrated to dryness at 40° and water and EtOAc were added. The residue was extracted twice with EtOAc. The organic layer was washed successively with H_2O and brine and dried, giving 5.73 g (mp 250° dec) of crude **11** after concentration. Crystallization (MeCN) gave 4.1 g (43%) of **11**: mp 258° dec; ir 5.77, 6.00 μ (C=O); NMR (DMSO-d_6) δ 7.18 (d, 1, J = 2 Hz, 6-CH), 7.32–7.91 (m, 7, aromatic and exchangeable NH).

Anal. Calcd for $C_{15}H_8Cl_2N_2O_2$: C, 56.45; H, 2.52; N, 8.78; Cl, 22.22. Found: C, 56.55; H, 2.62; N, 9.15; Cl, 22.53.

7-Chloro-5-(*o*-chlorophenyl)-1,3-dihydro-3-methylene-2*H*-1,4-benzodiazepin-2-one (12). A solution of 4.41 g (0.01 mol) of **4** in 75 ml of dry $(MeOCH_2)_2$ was added to a mixture of 0.85 g (0.02 mol) of hexane-washed 57% NaH in 10 ml of dry $(MeOCH_2)_2$ and the mixture was stirred at 30–40° until H_2 ceased to be evolved. Gaseous CH_2O from the pyrolysis (190°) of 1 g (0.033 mol) of paraformaldehyde was passed into the solution at 35–42° in a stream of N_2. The solution was stirred for 1 hr at room temperature, refluxed for 0.5 hr, concentrated to dryness, and, after the addition of H_2O–EtOAc, extracted three times with EtOAc. The organic layer was washed successively with H_2O and brine, dried, and concentrated, giving 3 g of crude **12**. The solid was chromatographed on 100 g of silica gel, starting with $CHCl_3$. The desired product was removed with 10% v/v Et_2O in $CHCl_3$ and was crystallized (MeCN), giving 2.0 g (63%) of **12**: mp 200–202° dec; NMR (DMSO-d_6) δ 5.18 (s, 1, C=CHH), 5.39 (s, 1, C=CHH), 6.96 (d, 1, J = 1.5 Hz, 6-CH), 7.25–7.91 (m, 6, aromatic), 11.12 (s, 1, NH).

Anal. Calcd for $C_{16}H_{10}Cl_2N_2O$: C, 60.59; H, 3.18; N, 8.81; Cl, 22.35. Found: C, 60.65; H, 3.46; N, 9.20; Cl, 22.43.

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Registry No.—**1**, 846-49-1; **3**, 54643-73-1; **4**, 54677-79-1; **5**, 54643-74-2; **6**, 54643-75-3; **7**, 54643-76-4; **8**, 54643-77-5; **9**, 54643-78-6; **10**, 54643-79-7; **11**, 54643-80-0; **12**, 54643-81-1.

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Preparation of Oxathiapentadecanes[1]

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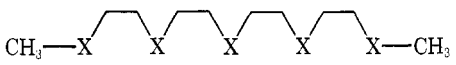
Our interest in the synthesis and complexation of cations by cyclic polyether sulfides[2–5] has led us to prepare a series of oxathiapentadecanes. These compounds are of interest because they are polydentate chelates with unique and unusual coordination properties. Such a series of related compounds may help determine how and where coordination to various cations takes place. Indeed, coordination with silver(I) and mercury(II) by these compounds appears to show definite structural features. These properties will be reported elsewhere.[5] This report deals only with the synthesis and properties of the oxathiapentadecanes.

Table I
Yield and Physical Properties of the Oxathiapentadecanes



Compd	Position of Heteroatoms 2	5	8	11	14	Yield, %	Bp, °C (0.1 mm) (mp, °C)
1	O	O	S	O	O	67	120–121 (0.1)
2	S	O	O	O	S	75	133–134 (0.1)
3	O	S	O	S	O	70	137–138 (0.1)
4	O	S	S	S	O	75	(56)
5	S	S	O	S	S	78	(36–37)[a]
6	S	S	S	S	S	89	(87–88)[b]

[a] Lit.[12] mp 37°. [b] Lit.[12] mp 88°.

The dimethyl ethers of the polyethylene glycols (often called glymes) have been prepared using the Williamson synthesis from the polyethylene glycols and alkyl halides or sulfates.[6–8] Chakhovskoy and coworkers have prepared certain glymes using alkyl tosylates which gave better yields than the halides.[9] The oxathiapentadecanes (see Table I) were prepared in a similar manner from the reaction of a mercaptan or sodium sulfide and an alkyl halide in basic media. These reactions are easier to perform than a Williamson synthesis using an alkoxide and an alkyl halide, since they require less severe conditions.[10,11] In addition, better yields are obtained. We tried to use compounds other than sulfur vesicants (blister-producing mustards) for these syntheses. Only one such compound was used (2-chloroethyl methyl sulfide in the preparation of **5**). In our synthesis of compound **1**, 1-(2-chloroethoxy)-2-methoxyethane was treated with sodium sulfide while compound **4** was prepared from bis(2-mercaptoethyl) sulfide and 2-bromoethyl methyl ether. The other compounds were prepared in a similar manner.

$$CH_3OCH_2CH_2OCH_2CH_2Cl + Na_2S \longrightarrow \mathbf{1}$$

$$HSCH_2CH_2SCH_2CH_2SH + 2BrCH_2CH_2OCH_3 \longrightarrow \mathbf{4}$$

Compounds **5** and **6** as well as other similar compounds have been prepared from the corresponding β-chloro sulfides (mustard compounds).[12–14] Meade and Moggridge[12] prepared **5** and **6** from the reaction of methyl mercaptan with 2,2′-(2-chloroethylthia)diethyl ether (**7**, X = O) and the corresponding sulfide (**7**, X = S), respectively. Williams and Woodward prepared similar compounds from **7** (X = S) using aromatic oxides and sulfides.[13] The bis(*n*-propoxyethylmercaptoethyl) ether (the di-*n*-propyl ether similar to **3**) was prepared[14] by treating the corresponding glycol with *n*-propyl alcohol in acid media.

$$X(CH_2CH_2SCH_2CH_2Cl)_2 + CH_3SH \xrightarrow{\text{base}} \mathbf{5}\ (X = O)\ \text{or}\ \mathbf{6}\ (X = S)$$

The nuclear magnetic resonance (NMR) spectra for the oxathiapentadecanes are similar to those observed for the

macrocyclic polyether sulfides.[2] The hydrogen atoms located on the ethylene groups between oxygen atoms were observed as singlets at δ 3.56 ± 0.04 while those between sulfur atoms were at δ 2.77 ± 0.00. The hydrogen atoms on methylene groups α to oxygen and β to sulfur were observed as triplets at δ 3.62 ± 0.04. The hydrogen atoms on methylene groups α to sulfur and β to oxygen were observed as triplets at δ 2.70 ± 0.02. The methyl hydrogen atoms adjacent to sulfur and oxygen were observed at δ 2.14 ± 0.01 and 3.32 ± 0.01, respectively. The physical properties of the thiatetraglymes also were similar to those of the macrocyclic polyether sulfides in that the melting point increased as the number of sulfur atoms was increased.[3,4]

Experimental Section

All infrared (ir) spectra were obtained on a Perkin-Elmer 457 spectrophotometer. A Varian A-60A spectrometer was used to record the proton nuclear magnetic resonance (NMR) spectra. Elemental analyses and molecular weight determinations were performed by M-H-W Laboratories, Garden City, Mich. Melting points were determined on a Thomas-Hoover capillary type melting point apparatus and are uncorrected.

Preparation of 2,5,11,14-Tetraoxa-8-thiapentadecane (1). A mixture of 46.2 g (0.33 mol) of 1-(2-chloroethoxy)-2-methoxyethane (Eastman) and 350 ml of reagent ethanol were placed in a flask fitted with a stirrer, reflux condenser, and addition funnel. After the mixture was brought to reflux, an aqueous solution of 40.0 g of sodium sulfide nonahydrate, 0.5 g of sodium hydroxide, and 75 ml of water was slowly added over a 60-min period. The reaction mixture was then cooled and filtered and the ethanol was removed under vacuum. The aqueous residue was extracted three times with 150-ml portions of ether. The ether was removed and the crude product was distilled to give 26.6 g (67%) of product: bp 120–121° (0.1 mm); NMR δ 3.64 (t, 4, OCH_2CH_2S), 3.54 (s, 8, OCH_2CH_2O), 3.33 (s, 6, OCH_3), 2.72 (t, 4, SCH_2CH_2O).

Anal. Calcd for $C_{10}H_{22}O_4S$: C, 50.39; H, 9.30; S, 13.45; mol wt, 238.4. Found: C, 50.60; H, 9.05; S, 13.22; mol wt, 239.

Preparation of 5,8,11-Trioxa-2,14-dithiapentadecane (2). A mixture of 25 g of sodium hydroxide in 500 ml of reagent ethanol was cooled to −15°. Methanethiol (26.0 g, 0.54 mol, Eastman) at −15° was added to the above solution. A solid formed which dissolved when the mixture was allowed to warm to room temperature. The solution was then refluxed while 62.4 g (0.27 mol) of tetraethylene glycol dichloride[2] was slowly added. The resulting mixture was cooled and treated as in the previous example to yield 51.6 g (75%) of product: bp 133–134° (0.1 mm); NMR δ 3.68 (t, 4, OCH_2CH_2S), 3.62 (s, 8, OCH_2CH_2O) 2.68 (t, 4, SCH_2CH_2O), 2.13 (s, 6, SCH_3).

Anal. Calcd for $C_{10}H_{22}O_3S_2$: C, 47.21; H, 8.72; S, 25.21; mol wt, 254.4. Found: C, 47.20; H, 8.81; S, 25.16; mol wt, 253.

Preparation of 2,8,14-Trioxa-5,11-dithiapentadecane (3). A mixture of 12.4 g (0.09 mol) of bis(2-mercaptoethyl) ether (Aldrich) and 12 g of potassium hydroxide in 500 ml of reagent ethanol was heated to reflux. To this solution was slowly added 25.0 g (0.18 mol) of 2-bromoethyl methyl ether (Eastman) in 50 ml of reagent ethanol. The resulting mixture was refluxed for 30 min, allowed to cool, and treated as for compound 1 to give 16.1 g (70%) of product, bp 137–138° (0.1 nm); NMR δ 3.65 (t, 4, OCH_2CH_2S), 3.56 (t, 4, OCH_2CH_2S), 3.32 (s, 6, OCH_3) 2.72 (t, 8, SCH_2CH_2O).

Anal. Calcd for $C_{10}H_{22}O_3S_2$: C, 47.21; H, 8.72; S, 25.21; mol wt, 254.4. Found: C, 47.14; H, 9.01; S, 25.06; mol wt, 254.

Preparation of 2,14-Dioxa-5,8,11-trithiapentadecane (4). A mixture of 13.9 g (0.09 mol) of bis(2-mercaptoethyl) sulfide (Pfaltz and Bauer), 25.0 g (0.18 mol) of 2-bromoethyl methyl ether (Eastman), and 12.0 g of potassium hydroxide in 500 ml of ethanol was treated as above for compound 3. The product was distilled to give 18.3 g (75.3%): bp 154–155° (0.1 mm); NMR δ 3.56 (t, 4, OCH_2CH_2S), 3.34 (s, 6, OCH_3), 2.77 (s, 8, SCH_2CH_2S), 2.68 (t, 4, SCH_2CH_2O).

Anal. Calcd for $C_{10}H_{22}O_2S_3$: C, 44.41; H, 8.20; S, 35.56; mol wt, 270.48. Found: C, 44.62, H, 8.34; S, 35.40; mol wt, 268.

Preparation of 8-Oxa-2,5,11,14-tetrathiapentadecane (5). A mixture of 8.5 g (0.06 mol) of bis(2-mercaptoethyl) ether (Aldrich), 13.5 g (0.12 mol) of 2-chloroethyl methyl sulfide (City Chemical) (vesicant, use caution) and 5.5 g of sodium hydroxide in 300 ml of ethanol was refluxed and the product was isolated as described for 3. The product (13.6 g, 78%) was a white solid which was recrystallized from benzene–hexane: mp 36–37°; NMR δ 3.66 (t, 4, OCH_2CH_2S), 2.77 (s, 8, SCH_2CH_2S), 2.72 (t, 4, SCH_2CH_2O), 2.13 (s, 6, SCH_3).

Anal. Calcd for $C_{10}H_{22}OS_4$: C, 41.92; H, 7.74; S, 44.76; mol wt, 286.54. Found: C, 41.99; H, 7.83; S, 45.01; mol wt, 284.

Preparation of 2,5,8,11,14-Pentathiapentadecane (6). This compound was prepared from 8.4 g (0.054 mol) of bis(2-mercaptoethyl) sulfide, 12.0 g (0.108 mol) of 2-chloroethyl methyl sulfide, 5.0 g of sodium metal and 300 ml of ethanol as above for compound 3. The product (14.5 g, 89%) was a white solid which was recrystallized from benzene–hexane: mp 87–88°; NMR δ 2.77 (s, 16, SCH_2CH_2S), 2.15 (s, 6, SCH_3).

Anal. Calcd for $C_{10}H_{22}S_5$: C, 39.69; H, 7.33; S, 52.98; mol wt, 302.61. Found: C, 39.49; H, 7.22; S, 53.69; mol wt, 301.

Registry No.—**1**, 54595-64-1; **2**, 54595-65-2; **3**, 54595-66-3; **4**, 54595-67-4; **5**, 54595-68-5; **6**, 54595-69-6; 1-(2-chloroethoxy-2-methoxyethane, 52808-36-3; methanethiol, 74-93-1; tetraethylene glycol dichloride, 638-56-2; bis(2-mercaptoethyl) ether, 2150-02-9; 2-bromoethyl methyl ether, 6482-24-2; bis(2-mercaptoethyl) sulfide, 3570-55-6; 2-chloroethyl methyl sulfide, 542-81-4.

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Pyrolysis of Some Methyl- and Benzylindoles

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Under drastic pyrolytic conditions, alkylpyrroles exhibit competitive alkyl group migrations, alkyl group cleavage, and ring expansion reactions to pyridines.[1] The benzo analogs, methylindoles, likewise have been reported to undergo the ring expansion and dealkylation reactions. Thus, 2-methylindole is converted into quinoline[2] (17% yield) and 3-methylindole is converted into indole[3] when their vapors are passed through a glowing tube. The observation that allyl groups undergo competitive [3,3] and [1,5] sigmatropic shifts on the pyrolysis of allylindoles[4] prompted this investigation of the migratory behavior of alkyl groups in alkylindoles.

Results and Discussion

The pyrolysis of *N*-, 2-, and 3-methylindole and of *N*- and 3-benzylindole resulted in the formation of products arising from alkyl group migrations in addition to those arising from cleavage (dealkylation) and from ring expansion reactions (see Tables I and II). As was observed in the pyrrole series[5] and in contrast to the Claisen migrations of crotylindole,[4] the N to C isomerizations of the alkylindoles were irreversible processes. On the other hand, the 2- and