# Macrocyclic Polyether Sulfide Syntheses. The Preparation of Thia-Crown-5, 6 and 7 Compounds (1,2)

*J. S. Bradshaw (3), J. Y. Hui, Y. Chan, B. L. Haymore, R. M. Izatt (4) and J. J. Christensen (5)*

Departments of Chemistry and Chemical Engineering, Contribution No. 51 from the Thermochemical Center, Brigham Young University, Provo, Utah 84602

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Macrocyclic polyether sulfides have been prepared by reacting an oligoethylene glycol dichloride with a dimercaptan or sodium sulfide as reported in a previous paper (6). The following new compounds were prepared: 1,4,7-trithia(15-crown-5) (I); 1,4,10-trithia(15-crown-5) (II); 1,4,7,10-tetrathia(15-crown-5) (III); 1-thia(18-crown-6) (IV); 1,4-dithia(18-crown-6) (V); 1,7-dithia(18-crown-6) (VI); 1,4,7-trithia(18-crown-6) (VII); 1,7-dithia(21-crown-7) (VIII); and 1,4,7-trithia(21-crown-7) (IX). The melting points of these and previously reported thia-crown compounds correlate with their structures. X-ray analyses of two thia-crown compounds indicate that the large sulfur atoms are directed away from the center of the ring.

In a previous paper (6), we reported the syntheses of thia-crown-3,4 and 5 compounds. These compounds are of interest for our continuing study of the complexation of cations by macrocyclic compounds (7,8). In this paper, we report the synthesis of selected thia derivatives of 15-crown-5, 18-crown-6 and 21-crown-7 compounds (9). We have prepared 1,4,7-trithia(15-crown-5) (I), 1,4,10-trithia(15-crown-5) (II), 1,4,7,10-tetrathia(15-crown-5) (III), 1-thia(18-crown-6) (IV), 1,4-dithia(18-crown-6) (V), 1,7-dithia(18-crown-6) (VI), 1,4,7-trithia-(18-crown-6) (VII), 1,7-dithia(21-crown-7) (VIII) and 1,4,7-trithia(21-crown-7) (IX) compounds (see Figure 1).

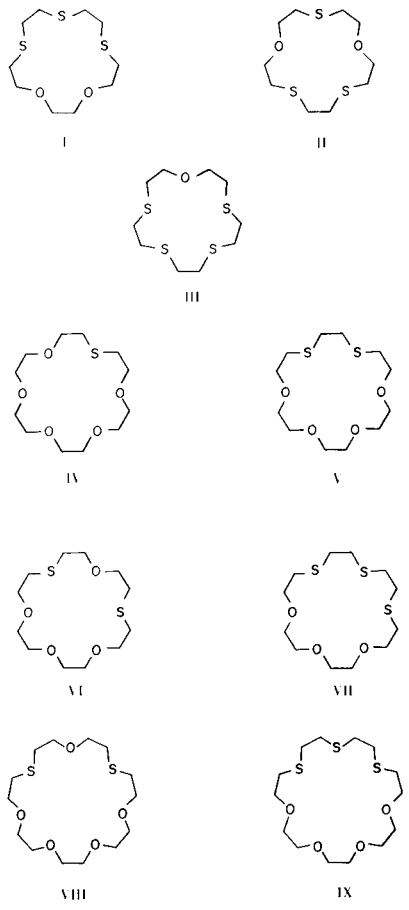



Figure 1

## Results and Discussion.

Although there are several methods which have been used to prepare thia-crown compounds, we selected the most convenient method for each synthesis. For example, three (of many) possible procedures to prepare 1-thia-(18-crown-6) (IV) are shown in Scheme 1.

In process A, the tetraethylene glycol is readily available and the dichloride could be prepared from its corresponding glycol. The dichloride, however, is a $\beta$-halosulfide (vesicant) and is very dangerous. In addition, the glycol is not reactive unless strong bases such as sodium or potassium metal or potassium *t*-butoxide are used (10). Process B can also be eliminated as a possible method to prepare IV because the alcohol portion of 2-mercaptoethanol is relatively unreactive. In process C, on the other hand, two readily available compounds of relatively high reactivity can be used to make IV. This was the method used.

TABLE I

Yields of Thia-Crown Compounds

| Compounds | Yields, % 1-Thia | Dithia 1,4- | Dithia 1,7- | Trithia 1,4,7- | Trithia 1,4,10- | Tetrathia 1,4,7,10- |
|---|---|---|---|---|---|---|
| Thia(9-crown-3) | 5 (a) | 6 (a) | | | | |
| Thia(12-crown-4) | 14 (a) | 19 (a) | 12 (a) | 26 (a) | | |
| Thia(15-crown-5) (I, II, III) | 29 (a) | 20 (a) | 27 (a) | 41 | 5 | 13 |
| Thia(18-crown-6) (IV, V, VI, VII) | 36 | 28 | 29 | 11 | | |
| Thia(21-crown-7) (VIII, IX) | | | 25 | 11 | | |

(a) Taken from reference 6.

TABLE II

Melting Point Correlations of Thia-crown Compounds

| Thia-crown Compounds | M.p., °C |
|---|---|
| A | |
| a. 1,4,7,10-Tetrathia(12-crown-4 (a) | 215-217 |
| b. 1,4,7-Trithia(12-crown-4) (b) | 89-90 |
| c. 1,4-Dithia(12-crown-4) (b) | 20-24 |
| d. 1,7-Dithia(12-crown-4) (b) | liquid |
| e. 1-Thia(12-crown-4) (b) | liquid |
| B | |
| f. 1,4,7,10-Tetrathia(15-crown-5) (III) | 93-95 |
| g. 1,4,7-Trithia(15-crown-5) (I) | 43-44 |
| h. 1,4,10-Trithia(15-crown-5) (II) | liquid |
| i. 1,4,-Dithia(15-crown-5) (b) | 51-52 |
| j. 1,7-Dithia(15-crown-5) (b) | liquid |
| k. 1-Thia(15-crown-5) (b) | liquid |
| C | |
| l. 1,4,7,10,13,16-Hexathia(18-crown-6) (c) | 145 |
| m. 1,4,10,13-Tetrathia(18-crown-6) (b) | 125 |
| n. 1,4,7-Trithia(18-crown-6) (VII) | liquid |
| o. 1,10-Dithia(18-crown-6) (b) | 87-90 |
| p. 1,4-Dithia(18-crown-6) (V) | 54-56 |
| q. 1,7-Dithia(18-crown-6) (VI) | liquid |
| r. 1-Thia(18-crown-6) (IV) | liquid |

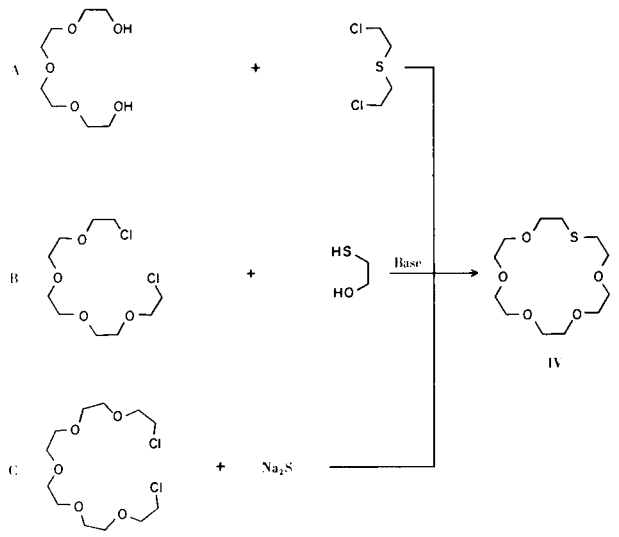
| Thia-crown Compounds | M.p., °C |
|---|---|
| D | |
| a. 1,4,7,10-Tetrathia(12-crown-4) (a) | 215-217 |
| s. 1,4,7,10-Tetrathia(13-crown-4) (a) | 134-135 |
| t. 1,4,8,11-Tetrathia(14-crown-4) (a) | 119-120 |
| u. 1,4,9,12-Tetrathia(16-crown-4) (a) | 73 |
| v. 1,5,9,13-Tetrathia(16-crown-4) (c) | 46 |
| w. 1,4,10,13-Tetrathia(18-crown-4) (a) | 89 |
| x. 1,5,10,14-Tetrathia(18-crown-4) (c) | 61 |
| y. 1,5,12,16-Tetrathia(22-crown-4) (c) | 61 |
| z. 1,4,8,11,15,18,22,25-Octathia-(28-crown-8), dimer of t. (a) | 66-67 |
| E | |
| a. 1,4,7,10-Tetrathia(12-crown-4) (a) | 215-217 |
| aa. 1,3,5,7,9-Pentathia(10-crown-5) (d) | 120-121 |
| bb. 1,4,7-Trithia(9-crown-3) (e) | 113 |
| cc. 1,5,9-Trithia(12-crown-3) (a) | 87-88 |
| dd. 1,3,5,7-Tetrathia(8-crown-4) (d) | 48-49 |

(a) See K. Travis and D. H. Busch, *Chem. Commun.*, 1041 (1970) and previous publications. (b) Reference 6. (c) J. R. Meadow and E. E. Reid, *J. Am. Chem. Soc.*, **56**, 2177 (1934). (d) L. Mortillaro, M. Russo, L. Credali, and C. Dechecchi, *J. Chem. Soc., C*, 428 (1966). (e) P. C. Ray, *J. Chem. Soc.*, 1090 (1920).

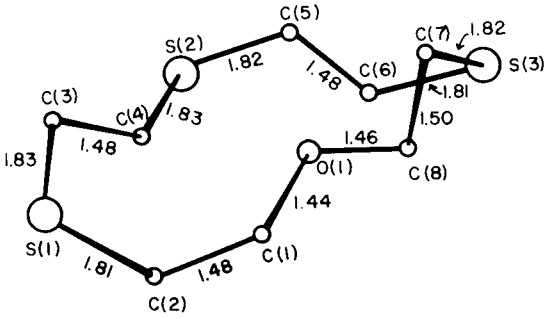
The synthetic routes to the other thia-crown compounds shown in Figure 1 were chosen by a similar consideration of safety, availability of starting materials, and reaction conditions. In all cases, a dimercaptan or sodium sulfide was reacted with an oligoethylene glycol dichloride in base. This method was first used by Dann and co-workers to prepare 1,10-dithia(18-crown-6) (11). The mercaptans are more acidic so that the reactions were generally carried out in sodium hydroxide. In general, good yields were obtained in all reactions except for the thia(9-crown-3) preparations (see Table I).

The structures of all products were consistent with those derived from the nmr spectra as well as combustion analysis and in most cases molecular weight determinations. The nmr spectra were particular instructive. The methylene hydrogens next to sulfur but $\beta$ to oxygen gave a triplet peak at 2.5-2.6 $\delta$ while those next to oxygen but $\beta$ to sulfur gave a triplet peak at 3.7-3.8 $\delta$. Singlet nmr peaks

SCHEME I




were observed for ethylenes between two sulfur atoms (at 2.8-2.9 δ) and between two oxygen atoms at (3.5-3.6 δ) (12).




(a) See reference 18.

Figure 2. Crystal Structure of 1,4,7-Trithia(12-crown-4) (a).

It is interesting to note that the relative yields of our reactions (Table I) were similar to those obtained in other ring closure reactions. In the formation of cycloaliphatic compounds by the acyloin condensation, the pyrolysis of thorium salts of dicarboxylic acids or by the Ziegler nitrile condensation, relatively low (or zero) yields were obtained for nine-membered rings and increasing yields were obtained for twelve and higher membered rings (13). In fact, medium-sized hydrocarbon rings (8-11-membered) were not available until the acyloin synthesis was developed (14).

The substitution of hetero atoms for methylene groups greatly facilitates ring formation. In the cyclization of dinitriles, for example, the substitution of oxygen for a methylene in the center of 1,9-dicyanononane increased the yield of the resulting 10-membered ring from less than 0.5 to over 5% (15). Thus it is not surprising that in our preparation of thia(9-crown-3) compounds (6), the yields were relatively high (5 and 6%) as compared with those for medium-sized cycloalkanes (13).

Structures based on X-ray data have been reported for the metal complexes of various crown compounds (16,17). However, no structure of an uncomplexed crown compound had been reported until Dalley and coworkers determined the crystal structure of 1,4,7-trithia(12-crown-4) (18). As shown in Figure 2, only the oxygen is directed toward the center of the ring with the sulfur atoms directed outward. Preliminary X-ray data for 1,10-dithia(18-crown-6) (Compound I in reference 6) also indicate that the two sulfur atoms are directed outward and the oxygens toward the center of the ring (18). The larger Van der Waals radius of the sulfur atom probably is the dominating factor in these structures.

The fact that the sulfur atoms are outside the ring cavity may make these compounds important for some applications. For example, the cavity of 1-thia(18-crown-6) (IV) probably is larger than the macrocyclic polyether 15-crown-5 but smaller than the peroxa-18-crown-6. On the other hand, transition state ions which bind more strongly to sulfur than oxygen will not be found in the cavity. This is evident by the fact that binding in the thia(15-crown-5) compounds involves a 2:1 ligand metal complex (19).

Dale has pointed out that melting points of macrocyclic compounds are related to their conformations (20). The melting point can be expressed as $T_m = \Delta H_m/\Delta S_m$. Since the heat of fusion will probably be constant (or nearly so) for all compounds of a particular series, a large entropy of fusion will mean a low melting point or vice versa (20). If a compound has a unique conformation which persists in the liquid state, it will have a low entropy change and therefore a high melting point. Large flexible rings have many equivalent conformations in the liquid state and therefore have a high entropy of fusion and thus a low melting point (20).

We have arranged various related thia-crown compounds with their melting points in Table II, and have observed a number of interesting correlations. In general, the melting point increases as the number of sulfur atoms is increased for each similar series A, B, and C. The larger sulfur atoms cause these rings to become less flexible and reduces the number of possible conformations in the liquid state. The perthia(15-crown-5) compound has not been reported. When prepared, it should have a melting point in excess of 100°.

Also in series A, B, and C, the more symmetrical compounds have higher melting points. 1,10-Dithia(18-crown-

6) (o) is the most symmetrical of the eighteen-membered rings containing two sulfur atoms, while the 1,7-dithia compound (q) is probably the least symmetrical. Also in the twelve and fifteen-membered rings, the 1,4-dithia compounds (c and i) have higher melting points than the less symmetrical 1,7-dithia compounds (d and j).

The series D compounds have the same number of sulfur atoms but a differing ring size. The smallest ring (compound a) should have the most rigid conformation and the highest melting point. As the ring size becomes larger, it becomes more flexible and the melting point decreases. In fact, very large rings (over 20 atoms) resemble two parallel chains connected by methylene bridges or heteroatoms on each end. Compound z, (see Table II), which is a dimer of compound t has a much lower melting point probably because it does resemble two alkyl sulfide chains.

Macrocyclic thia compounds where the sulfur atoms are separated by ethylene moieties seem to have a favorable conformation. Both compounds u and w which are isomeric to v and x respectively, have higher melting points. In u and w, the sulfur atoms are separated by ethylene groups. This is also shown in series E where the symmetrical 12-crown-4 compound (sulfur atoms are separated by ethylenes) has a much higher melting point than either compound aa (methylene groups separate the sulfur atoms) or cc (propylene groups separate the sulfur atoms).

## EXPERIMENTAL

All infrared (ir) spectra were obtained on a Perkin-Elmer 457 spectrometer. A Varian A-60A spectrometer was used to obtain the nuclear magnetic resonance (nmr) spectra. Elemental analyses and molecular weights were performed by MHW Laboratories, Garden City, Michigan. Melting points were obtained on a Thomas-Hoover capillary type melting point apparatus and are uncorrected.

### General Synthesis.

All macrocyclic polyether sulfides were prepared by reacting oligoethylene glycol dichlorides with the appropriate dimercaptan or sodium sulfide in base as previously reported (6). The starting materials were used as purchased. The dihalides were prepared from the corresponding glycols: 1,11-dichloro-3,6,9-trioxaundecane, 1,14-dichloro-3,6,9,12-tetraoxatetradecane and 1,17-dichloro-3,6,9,12,15-pentaoxaheptadecane from tetraethylene glycol (Aldrich), pentaethylene glycol (Baker) and hexaethylene glycol (21) respectively. Specific details are given for each compound prepared in the preparation of thia-crown compound section.

### Preparation of Starting Thia Compounds.

1,10-Dioxa-4,7-dithiadecane was prepared by slowly adding 161 g. (2.0 moles) of 2-chloroethanol (Baker) in 500 ml. of ethanol to a refluxing mixture of 46 g. (2.0 moles) of sodium and 94.2 g. (1.0 mole) of 1,2-ethanedithiol (Aldrich) in 1500 ml. of ethanol. After heating for an additional 30 minutes, the mixture was cooled and filtered. The ethanol was removed from the filtrate under vacuum leaving 188 g. (90%) of crude product. The 1,10-dioxa-4,7-dithiadecane was recrystallized from methyl acetate to yield large platelets, m.p. 63-64° (lit. value, 64°) (22).

*Anal.* Calcd. for $C_6H_{14}O_2S_2$: C, 39.53; H, 7.74; S, 35.18. Found: C, 39.45; H, 7.64; S, 35.36.

### 1,4,7,10-Tetrathiadecane.

This compound was prepared by refluxing 164 g. (0.9 mole) of 1,10-dioxa-4,7-dithiadecane, 141 g. (1.85 moles) of thiourea (Baker) and 180 ml. of concentrated hydrochloric acid for 3 hours. The mixture was cooled and 92 g. of sodium hydroxide in 400 ml. of water was cautiously added with stirring in a nitrogen atmosphere. This mixture was refluxed for one hour and allowed to cool. The organic product was separated and the aqueous layer was made slightly acidic and extracted twice with ether. The combined organic layer and ether extracts were dried over anhydrous magnesium sulfate. After filtration, the ether was removed under vacuum leaving 98 g. (51%) of a low melting solid. The solid was recrystallized from benzene-hexane, m.p. 44-45°.

*Anal.* Calcd. for $C_6H_{14}S_4$: C, 33.61; H, 6.58; S, 59.81. Found: C, 33.38; H, 6.76; S, 59.60.

### Preparation of Thia-Crown Compounds.

#### 1,4,7-Trithia(15-crown-5) (I) (10,13-Dioxa-1,4,7-trithiacyclopentadecane).

1,2-Bis-(2-chloroethoxy)ethane (Eastman, 93.6 g., 0.5 mole) and 77.2 g. (0.5 mole) of bis-(2-mercaptoethyl)sulfide (Pfaltz and Bauer) were added to 23 g. (1.0 mole) of sodium in ethanol. The product, 55 g. (41%) was a solid, m.p. 43-44.5°; nmr (δ): 2.73 (t, 4, $SCH_2CH_2O$), 2.88 (s, 8, $SCH_2CH_2S$), 3.63 (s, 4, $OCH_2CH_2O$) and 3.78 (t, 4, $OCH_2CH_2S$).

*Anal.* Calcd. for $C_{10}H_{20}O_2S_3$: C, 44.74; H, 7.51; S, 35.83. Found: C, 44.99; H, 7.52; S, 36.09.

#### 1,4,10-Trithia(15-crown-5) (II) (7,13-Dioxa-1,4,10-trithiacyclopentadecane).

1,11-Dichloro-6-thia-3,9-dioxaundecane (23) [13.6 g., 0.055 mole, b.p. 123°/0.25 mm (lit. value 145°/1 mm) (23)] and 5.2 g. (0.055 mole) of ethanedithiol were added to 3.03 g. (0.13 mole) of sodium in 500 ml. of ethanol. The product, 0.5 g. (5%) was a high boiling liquid, b.p. 180°/1 mm.; nmr (δ): 2.86 (t, 8, $SCH_2CH_2O$), 2.90 (s, 4, $SCH_2CH_2S$) and 3.75 (t, 8, $OCH_2CH_2S$).

*Anal.* Calcd. for $C_{10}H_{20}O_2S_3$: C, 44.74; H, 7.51; S, 35.83. Found: C, 44.65; H, 7.32; S, 35.67.

#### 1,4,7,10-Tetrathia(15-crown-5) (III) (13-Oxa-1,4,7,10-tetrathiacyclopentadecane).

Bis-(2-chloroethyl) ether (Aldrich, 46.6 g., 0.33 mole) and 69.9 g. (0.33 mole) of 1,4,7,10-tetrathiadecane were added to 15 g. of sodium in 1.5 l. of ethanol. The product, (12 g., 13%) was recrystallized from ether-petroleum ether and purified by passing it through alumina using petroleum ether and benzene as eluants, m.p. 93-95°; nmr (δ): 2.77 (t, 4, $SCH_2CH_2O$), 2.91 (s, 12, $SCH_2CH_2S$) and 3.81 (t, 4, $OCH_2CH_2S$).

*Anal.* Calcd. for $C_{10}H_{20}OS_4$: C, 42.21; H, 7.08; S, 45.07. Found: C, 42.39; H, 7.19; S, 44.90.

#### 1-Thia(18-crown-6) (IV) (4,7,10,13,16-Pentaoxa-1-thiacyclooctadecane).

1,17-Dichloro-3,6,9,12,15-pentaoxaheptadecane (14 g., 0.044 mole) was added to 24 g. (0.1 mole) of sodium sulfide nonahydrate in ethanol. The product (4.5 g., 36%) was a colorless liquid, b.p. 164-170°/0.1 mm; $n_D^{30}$ = 1.4935; nmr (δ): 2.68 (t, 4H,

$SCH_2CH_2O$), 3.57 (s, 16H, $OCH_2CH_2O$) and 3.64 (t, 4H, $OCH_2CH_2S$).

*Anal.* Calcd. for $C_{12}H_{24}O_5S$: C, 51.50; H, 8.55; S, 11.43; mol. wt. 280.3. Found: C, 51.61; H, 8.44; S, 11.21; mol. wt. 291.

1,4-Dithia(18-crown-6) (V) (7,10,13,16-Tetraoxa-1,4-dithiacyclooctadecane).

1,14-Dichloro-3,6,9,12-tetraoxatetradecane (20 g., 0.073 mole) and 6.85 g. (0.073 mole) of 1,2-ethanedithiol were added to 6 g. of sodium hydroxide in ethanol. The solid product, 6.1 g. (28%) was recrystallized from chloroform-hexane, m.p. 54-56°; nmr ($\delta$): 2.66 (t, 4H, $SCH_2CH_2O$), 2.79 (s, 4H, $SCH_2CH_2S$), 3.60 (s, 12H, $OCH_2CH_2O$), and 3.76 (t, 4H, $OCH_2CH_2S$).

*Anal.* Calcd. for $C_{12}H_{24}O_4S_2$: C, 48.62; H, 8.16; S, 21.63; mol. wt., 296.5. Found: C, 48.79; H, 8.06; S, 21.78; mol. wt., 280.

1,7-Dithia(18-crown-6) (VI) (4,10,13,16-Tetraoxa-1,7-dithiacyclooctadecane).

1,11-Dichloro-3,6,9-trioxaundecane (23.1 g., 0.1 mole) and 13.8 g. (0.1 mole) of bis(2-mercaptoethyl) ether (Aldrich) were added to 9 g. of sodium hydroxide in ethanol. The product was a colorless liquid, 8.6 g. (29%), b.p. 174-179°/1 mm. $n_D^{22} = 1.5260$; nmr ($\delta$): 2.72 (t, 8H, $SCH_2CH_2O$), 3.55 (s, 8H, $OCH_2CH_2O$) and 3.65 (t, 8H, $OCH_2CH_2S$).

*Anal.* Calcd. for $C_{12}H_{24}O_4S_2$: C, 48.62; H, 8.16; S, 21.63; mol. wt., 296.5. Found: C, 48.61; H, 8.01; S, 21.50; mol. wt., 289.

1,4,7-Trithia(18-crown-6) (VII) (10,13,16-Trioxa-1,4,7-trithiacyclooctadecane).

1,11-Dichloro-3,6,9-trioxaundecane (42.6 g., 0.19 mole) and 28.5 g. (0.19 mole) of bis(2-mercaptoethyl) sulfide were added to 9 g. of sodium hydroxide in ethanol. The product was a light colored liquid, 6.5 g. (11%), b.p. 200-206°/2 mm. This was purified by eluting through silica gel using a 1:4 mixture of chloroform-hexane as eluant. The nmr spectrum exhibited peaks at ($\delta$): 2.68 (t, 4H, $SCH_2CH_2O$), 2.76 (s, 8H, $SCH_2CH_2S$), 3.55 (s, 8H, $OCH_2CH_2O$) and 3.66 (t, 4H, $OCH_2CH_2S$).

*Anal.* Calcd. for $C_{12}H_{24}O_3S_3$: C, 44.69; H, 7.50. Found: C, 44.33; H, 7.77.

1,7-Dithia(21-crown-7) (VIII) (4,10,13,16,19-Pentaoxa-1,7-dithiacycloheneicosane).

1,14-Dichloro-3,6,9,12-tetraoxatetradecane (27.5 g., 0.1 mole) and 13.8 g. (0.1 mole) of bis(2-mercaptoethyl) ether were added to 10 g. of sodium hydroxide in ethanol. The product was a light colored liquid, 8.5 g., (25%), b.p. 180°/1 mm., $n_D^{25} = 1.5165$; nmr ($\delta$): 2.72 (t, 8H, $SCH_2CH_2O$), 3.58 (s, 12H, $OCH_2CH_2O$) and 3.65 (t, 8H, $OCH_2CH_2S$).

*Anal.* Calcd. for $C_{14}H_{28}O_5S_2$: C, 49.53; H, 8.82; S, 18.84; mol. wt., 322.5. Found: C, 49.53; H, 8.05; S, 18.98; mol. wt., 290.

1,4,7-Trithia(21-crown-7) (IX) (10,13,16,19-Tetraoxa-1,4,7-trithiacycloheneicosane).

1,14-Dichloro-3,6,9,12-tetraoxatetradecane (27.5 g., 0.1 mole) and 15.4 g. (0.1 mole) of bis(2-mercaptoethyl) sulfide were added to 9.5 g. of sodium hydroxide in ethanol. A viscous liquid (4.0 g., 11%) was isolated by repeated extraction and purification by silica gel chromatography using a 1:4 mixture of chloroform-hexane as eluant. This material exhibited an nmr spectrum as follows ($\delta$): 2.75 (t, 4H, $SCH_2CH_2O$), 2.84 (s, 8H, $SCH_2CH_2S$), 3.66 (s, 12H, $OCH_2CH_2O$), and 3.74 (t, 4H, $OCH_2CH_2S$).

*Anal.* Calcd. for $C_{14}H_{28}O_4S_3$: C, 47.16; H, 7.91; S, 26.98; mol. wt., 356. Found: C, 46.98; H, 8.17; S, 26.73; mol. wt., 365.

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(4) Department of Chemistry.

(5) Department of Chemical Engineering.

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