Transesterification of Orthothiocarbonates (1)

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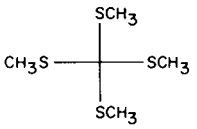
The first spiro-bicyclic orthothiocarbonate was described in 1962 by Johnston and co-workers (2) who isolated and characterized compound **3** as a product from the reaction of diethanolamine with 1,3-dithiane-2-thione. It can be shown, however (3), that compound **3** is present as an impurity (*ca.* 15%) in crude 1,3-dithiane-2-thione prepared by the method of Mills and Saunders (4), and that it is not formed when pure 1,3-dithiane-2-thione is heated with diethanolamine.

A second route to this class of spiro-compounds was described by D'Amico and Campbell (5). This method, which involves condensation of alkanedithiols with 2-cyanoimino-1,3-dithiolane and -dithiane has the advantage of making unsymmetrical spiro-compounds accessible.



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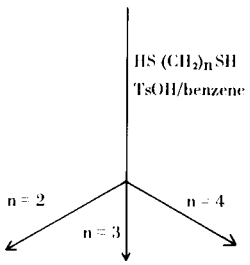

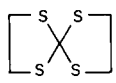

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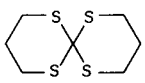

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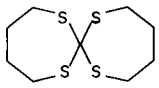

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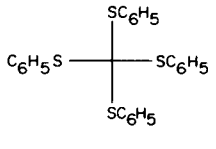

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An investigation of the electronic absorption spectra of spirobicyclic orthothiocarbonates (3) entailed the preparation of various members of this class of compounds. It was found that they are easily prepared by acid-catalyzed transesterification of tetramethyl orthothiocarbonate (**1**) with alkanedithiols. By this procedure, the readily available orthothiocarbonate **1** (6) has been transformed into compounds **2**, **3**, and **4**.

By virtue of its simplicity and improved yields, this method is probably the most convenient route to compounds of this class. Moreover the transesterification of orthothiocarbonates appears to be general. Thiophenol reacted with compound **1**, using the same conditions as for the spiro compounds, to give a modest yield of tetraphenyl orthothiocarbonate (**5**). Although these reactions are probably reversible, the equilibrium is shifted to favor the products by allowing the volatile methyl mercaptan to escape.

EXPERIMENTAL

Melting points are uncorrected. Nmr spectra were recorded on a Varian A-60A instrument using deuteriochloroform as solvent and tetramethylsilane as internal standard. The analysis was carried out by Galbraith Laboratories Inc., Knoxville, Tennessee.

General Procedure

A solution of tetramethyl orthothiocarbonate (6) (2 g., 10 mmoles), 20 mmoles of the appropriate alkanedithiol, and 50 mg. of *p*-toluenesulfonic acid in benzene (50 ml.) was heated under reflux for 24 hours. Benzene was evaporated from the solutions and the residues were triturated with ethanol. The crude products were filtered, washed with ethanol, and recrystallized.

1,4,6,9-Tetrathiaspiro[4.4]nonane (**2**).

The crude product (1.61 g.) was recrystallized from methylene chloride/ethanol giving 1.56 g. (80%) of colorless crystals, m.p. 141° and nmr singlet at 3.46 ppm. (Lit. (5) m.p. 139-141° and nmr singlet at 3.43 ppm.)

1,5,7,11-Tetrathiaspiro[5.5]undecane (**3**).

The crude product (2.34 g.) was recrystallized from methylene chloride/ethanol giving 2.10 g. (94%) of colorless crystals, m.p. 116° (Lit. (2,5) m.p. 116° and 119-

120°). The nmr spectrum and tlc behavior were identical with those of a sample isolated from crude 1,3-dithiane-2-thione by preparative layer chromatography.

1,6,8,13-Tetrathiaspiro[6.6]tridecane (**4**).

The crude product (2.33 g.) was recrystallized from benzene/ethanol giving 0.78 g. (31%) of colorless crystals, m.p. 165°. The nmr spectrum exhibited two narrow multiplets (1:1) at 2.05 and 2.90 ppm. Mol. wt. 252 (mass spectrum).

Anal. Calcd. for $C_9H_{16}S_4$: C, 42.81; H, 6.39; S, 50.80. Found: C, 43.07; H, 6.34; S, 50.95.

Tetraphenyl Orthothiocarbonate (**5**).

A solution of tetramethyl orthothiocarbonate (1 g., 5 mmoles), thiophenol (2.2 g., 20 mmoles) and *p*-toluenesulfonic acid (25 mg.) in benzene (25 ml.) was heated under reflux for 20 hours. The solvent was evaporated and the residue recrystallized twice from ethanol to give 485 mg. (22%) of colorless crystals, m.p. 155-158° (Lit. (7) m.p. 159°).

The nmr spectrum consisted of two multiplets at 7.30 and 7.68 ppm. The 70 eV mass spectrum does not show a molecular ion; the most prominent peak appears at m/e 339, the mass of $(C_6H_5S)_3C^+$.

REFERENCES

(1) Research supported by the National Science Foundation (GP-10950).

(2) T. P. Johnston, C. R. Strongfellow, and A. Gallagher, *J. Org. Chem.*, 27, 4068 (1962).

(3) D. R. Williams, D. L. Coffen, P. E. Garrett, and R. N. Schwartz, *J. Chem. Soc.* (B), 1132 (1968).

(4) W. H. Mills and B. C. Saunders, *ibid.*, 537 (1931).

(5) J. J. D'Amico and R. H. Campbell, *J. Org. Chem.*, 32, 2567, (1967).

(6) Compound **1** is obtained from thiourea by a simple two-step procedure, H. J. Backer and P. L. Stedehouder, *Rec. Trav. Chim.*, 52, 923 (1933); *Organic Syntheses*, Coll. Vol. II, John Wiley and Sons, Inc., New York, 1943, p. 411.

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