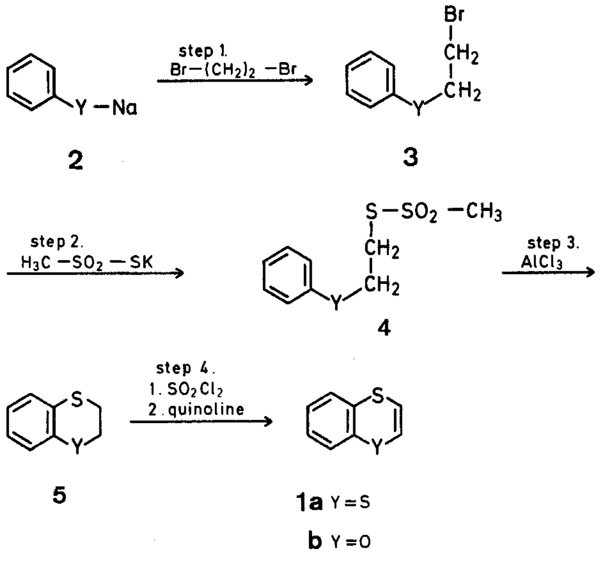
Improved Syntheses of Benzo-1,4-dithiin and of Benzo-1,4-oxathiin

J. H. Verheijen, H. Kloosterziel*

Gorlaeus Laboratories, University of Leiden, P. O. Box 75, Leiden, The Netherlands

Parham and coworkers[1,2] have synthesized benzo-1,4-dithiin (**1a**) and benzo-1,4-oxathiin (**1b**) from 1,2-dimercaptobenzene and 2-mercaptophenol, respectively, by various routes with yields never exceeding 40%. We describe here the syntheses of **1a** and **1b** starting from thiophenol (**2a**) and phenol (**2b**) with approximately 50% overall yields. The key step [step 3] is the novel synthesis of benzoannelated sulfur-heterocyclic systems by an intramolecular sulfenylation of thiosulfonates[3,4]. Reactions of the type [step 2] have repeatedly been described by Dunbar[5]. In our hands the method used for the introduction of the double band [step 4] was superior over other ones (such as by way of a sulfoxide).



2-Bromoethyl phenyl sulfide (**3a**) was obtained as described by Kochi, et al.[6]; b.p. 136–137°/15 torr; yield: 81%. 2-Bromoethyl phenyl ether (**3b**) is commercially available.

Preparation of 2-(Phenylthio)-ethyl Methanethiolsulfonate (4a):

A solution of **3a** (0.1 mol) and potassium methanethiolsulfonate[7] (0.12 mol) in ethanol (150 ml) is heated under reflux for 1.3 h. The solvent is then removed under reduced pressure. Chloroform and water are added to the residue. The organic layer is washed with water and dried over magnesium sulfate. After removal of the chloroform, 2-(phenylthio)-ethyl methanethiolsulfonate (**4a**) remains as an oil; yield: 95%; $n_D^{20} = 1.6015$ (lit.[5]: $n_D^{25} = 1.6080$). Similarly, reaction of **3b** after 66 h reflux gave 2-(phenoxy)-ethyl methanethiolsulfonate (**4b**); yield: 96%; m.p. 45–46° (lit.[5] m.p. 45–46.5°).

Preparation of Benzo-1,4-dithiene (5a):

To a stirred solution of **4a** (185.7 g, 0.75 mol) in dry nitromethane (1.5 l) is added rapidly at room temperature a concentrated solution of aluminium chloride (100 g, 0.75 mol) in nitromethane. After 20 min (N.B. this is important to optimise the yield) the reaction is stopped by addition of 3 *N* hydrochloric acid (1.5 l). Upon addition of chloroform (1.5 l) the organic layer is washed twice with 10% sodium hydrogen carbonate solution (0.75 l) and twice with water (0.75 l). The organic layer is dried with magnesium sulfate and the greater part of the solvent is removed under reduced pressure. Fractionation of the residue gave benzo-1,4-dithiene (**5a**): yield: 91.6 g (73%); b.p. 88–90°/0.05 torr (lit.[1]: 82.2 to 85°/0.18 torr); $n_D^{20} = 1.6710$ (lit.[1]: $n_D^{25} = 1.6713$).

Similarly, reaction of **4b** gave (reaction time 10 min) benzo-1,4-oxathiene (**5b**): yield: 76%: b.p. 83–85°/0.15 torr (lit.[8]: 90°/2 torr); $n_D^{20} = 1.6117$.

Preparation of Benzo-1,4-dithiin (1a):

A solution of distilled sulfuryl chloride (80.0 g, 0.59 mol) in dichloromethane (100 ml) is added to a refluxing solution of **5a** (94.0 g, 0.56 mol) in dichloromethane (1 l). After 2 h, the solvent is removed under reduced pressure, quinoline (2.8 mol) is added, and the mixture is kept at 150° for 2 h. After cooling, a solution of 3 *N* hydrochloric acid (1.1 l) and *n*-hexane (1.1 l) is added. The organic layer is washed with 3 *N* hydrochloric acid and water. The organic layer is dried with magnesium sulfate, the greater part of the solvent is removed under reduced pressure, and the residue is fractionated through a 20-inch vacuum jacketed Vigreux column; yield: 70.6 g (76%); b.p. 104–107°/0.50 torr (lit.[1] b.p. 67–70°/0.1 torr); $n_D^{20} = 1.6738$ (lit.[1] $n_D^{25} = 1.6754$).

Similarly reaction of **5b** gave benzo-1,4-oxathiin (**1b**); yield: 78%; b.p. 79–81°/0.14 torr (lit.[2]: 63–65°/0.7 torr): $n_D^{20} = 1.6152$ (lit.[2]: $n_D^{25} = 1.6168$).

Received: April 7, 1975

---

[1] W. E. Parham, T. M. Roder, W. R. Hasek, *J. Amer. Chem. Soc.* **75,** 1647 (1953).

[2] W. E. Parham, J. D. Jones, *J. Amer. Chem. Soc.* **76,** 1068 (1954).

[3] To be published.

[4] J. K. Bosscher, E. W. A. Kraak, H. Kloosterziel, *J. Chem. Soc. Chem. Commun.* **1971,** 1365.

[5] J. E. Dunbar, *U.S. Patent* 3337599 (1967) Dow Chemical Co.; *C.A.* **67,** 116719 (1967); *U.S. Patent* 3538138 (1970) Dow Chemical Co.; *C.A.* **74,** 12830 (1971).

[6] J. K. Kochi, D. M. Singleton, L. J. Andrews, *Tetrahedron* **24,** 3503 (1968).

[7] T. A. Trofimova, B. G. Boldyrev, *J. Org. Chem. USSR* **2,** 98 (1966).

[8] D. Greenwood, H. A. Stevenson, *J. Chem. Soc.* **1953,** 1514.