Eight-Membered Organosulfur Heterocycles. Synthesis of Dibenzo[*d*,*g*][1,3,6,2]dioxathiaphosphocin and Dibenzo[*d*,*g*][1,3,6,2]dioxathiasilocin Ring Systems

Stephen D. Pastor* [1], John D. Spivack and Leander P. Steinhuebel

Research and Development Laboratories, Plastics and Additives Division,
CIBA-GEIGY Corporation, Ardsley, New York, 10502

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The reaction of 2,2′-thiobisphenols with either phenylphosphonous dichloride or phosphorus trichloride followed by an alcohol gave derivatives of the dibenzo[*d*,*g*][1,3,6,2]dioxathiaphosphocin ring system. The analogous reaction of 2,2′-thiobisphenols with alkyl and aryl dichlorosilanes gave the heretofore unreported dibenzo[*d*,*g*][1,3,6,2]dioxathiasilocin ring system. The analytical and spectral data are reported.

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Introduction.

Although the dibenzo[*d*,*g*][1,3,6,2]dioxathiaphosphocin ring system has been claimed in the patent literature, neither a detailed account of its synthesis nor spectral characterization has been reported in the chemical literature [2]. The analogous dibenzo[*d*,*g*][1,3,6,2]dioxathiasilocin ring system was unknown prior to this report. Our interest in the synthesis of new organosulfur heterocycles [3] led us to investigate the preparation and characterization of these novel ring systems.

Results and Discussion.

Reports on the preparation of alkylated thiobisphenols are largely confined to the patent literature [4], although investigations on the antioxidant stabilization mechanisms of **2a** by Pospisil *et al.* have appeared [5]. However, no synthetic procedure was reported for the preparation of **2a**. The preparation of 2,2′-thiobisphenols from sulfur dichloride and 4-alkylated phenols has been described [6].

The reaction of **1a** with sulfur chloride using anhydrous zinc chloride as a mild Lewis acid catalyst gave **2a** in 59% recrystallized yield. The tlc of the crude reaction product prior to workup showed that **2a** was the major product. Either petroleum ether or chloroform was found to be a satisfactory reaction solvent. No difficulty was encountered due to the effect of the electron withdrawing carbomethoxy substituent in the analogous conversion of **1b** [7] to **2b**.

The chloridite **3a** was prepared by the reaction of **2a** with phosphorus trichloride utilizing triethylamine as an acid acceptor and was used without further purification. The reaction of **3a** with methyl alcohol using pyridine as a base gave **4a** in 63% recrystallized yield.

Similarly the reaction of **2b** with phosphorus trichloride gave **3b**. Attempts to hydrolyze **3b** to the cyclic secondary phosphite derivative **4b** with an equivalent of water using pyridine as a base were unsuccessful. The ir and nmr spectra of the hydrolysis product showed a complex mixture of which the predominant products appeared to be the result of ring opening. The transesterification of 4,4′-thiobisphenols with diphenyl phosphite has been reported to give a cyclic secondary phosphite derivative [2d].

The 6-aryl substituted derivative **5** was prepared by the reaction of **2c** [8] with phenylphosphonous dichloride using triethylamine as an acid acceptor. Interestingly, tlc of **4a** on silica gel plates (Merck # 5767) was possible, whereas decomposition of **5** was evident. Whether this observed decomposition was due to air oxidation or silica gel catalyzed decomposition of **5** was not determined.

Table 1

Analytical and Spectral Data

Compound	Mp (°C)	Recrystallization Solvent	Percent Yield	Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S
2a	98-101	Acetonitrile	59	76.0	9.6	—	75.7	9.5	—
2b	132-132.5	Heptane	54	64.6	6.8	7.2	64.3	7.0	7.3
4a	163-165	Acetonitrile	63	69.3	8.6	—	69.4	8.8	—
5	181-183	Hexane:Benzene	67	72.4	7.2	—	72.5	7.5	—
7a	178-180	Acetone	56	71.9	9.2	—	71.7	9.2	—
7b	175-177	Acetone	41	74.7	8.5	—	74.9	8.6	—

Compound	IR (cm^{-1})	^1H NMR (deuteriochloroform)	MS
2a	3400 (OH)	δ 1.19 (s, $C(CH_3)_3$, 18H), 1.40 (s, $C(CH_3)_3$, 18H), 6.49 (br exchangeable s, OH, 2H), 7.23 (c, ArH, 4H)	—
2c [a]	3520 (OH) 1720 (C=O)	δ 1.38 (s, $C(CH_3)_3$, 18H), 3.86 (s, OCH_3, 6H), 6.22(br s, OH, 2H), 7.90 (c, ArH, 4H)	—
4a	1050 (aliphatic POC)	δ 1.06 (s, $C(CH_3)_3$, 18H), 1.31 (s, $C(CH_3)_3$, 18H), 3.93 (d, OCH_3, 3H), 7.38 (c, ArH, 4H)	—
5	—	δ 1.19 (s, $C(CH_3)_3$, 18H), 2.06 (s, CH_3, 6H), 7.12-7.88 (c, ArH, 9H)	—
7a	2200 (SiH)	δ 0.66 (s, $SiCH_3$, 3H), 1.30 (s, $C(CH_3)_3$, 18H), 1.44 (s, $C(CH_3)_3$, 18H), 7.29 (d, ArH, 2H), 7.54 (d, ArH, 2H)	m/z 484 (M^+), 483 (M—1), 369 (M—15), 57 ($C_4H_9^+$)
7b	2200 (SiH)	δ 1.20 (s, $C(CH_3)_3$, 18H), 1.44 (s, $C(CH_3)_3$, 18H), 7.18 (c, ArH, 3H), 7.40 (d, ArH, 2H), 7.75 (d, ArH, 2H), 7.96 (c, ArH, 2H)	m/z 546 (M^+), 545 (M—1), 469 (M—77)

[a] Compound was prepared using chloroform as the reaction medium.

The analogous reaction of the corresponding dichlorosilane **6a-b** with **2a** using triethylamine as an acid acceptor gave **7a** and **7b** respectively. This constitutes the first reported synthesis and characterization of the dibenzo-[*d*,*g*][1,3,6,2]dioxathiasilocin ring system.

EXPERIMENTAL

All melting points were determined in open capillary tubes on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The ir spectra (1% solution in carbon tetrachloride; sodium chloride cells) were recorded on a Perkin-Elmer 710 spectrometer. Mass spectra were obtained on an AEI (KRATOS) MS 902. The ^1H nmr spectra were taken on a Varian model XL-100, T-60, or CFT-20 spectrometer. The ^{13}C nmr spectra were taken on a Varian model FT-80 spectrometer equipped with a broad band probe. All ^{13}C and ^1H chemical shifts are reported in ppm relative to tetramethylsilane. The ^{13}C nmr spectra were obtained using a 30° flip angle, a 2-s repetition rate with no pulse delay and with full proton decoupling. Unless otherwise indicated, all reagents were purchased from Aldrich Chemical Company. All solvents were dried prior to use. Reactions were carried out in flame-dried apparatus under a dry nitrogen atmosphere. All spectral data were obtained on analytical samples. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY Corporation. The syntheses of **2a**, **4a**, and **6a** are illustrative of the methods employed for compound preparation. Analytical and spectral data are collected in Table 1.

2,2'-Thiobis(2,4-di-*t*-butylphenol) (**2a**).

To a solution of 206.3 g (1 mole) of 2,4-di-*t*-butylphenol and 1.02 g (7.5 mmoles) of anhydrous zinc chloride in 250 ml of petroleum ether (bp 30-60°) at 0° was added dropwise over a one-hour duration a solution of 51.5 g (0.5 mole) of sulfur dichloride in 100 ml of petroleum ether. The reaction mixture was stirred for 15 hours at room temperature with a slow nitrogen sweep to remove evolved hydrogen chloride gas. The solvent was removed *in vacuo* and the residue was crystallized from acetonitrile to give 130 g (59%) of a white solid, mp 98-101°; ^{13}C nmr (deuteriochloroform): δ 30.0 (s, $C(CH_3)_3$), 31.9 (s, $C(CH_3)_3$), 34.8 (s, $C(CH_3)_3$), 35.7 (s, $C(CH_3)_3$), 119.5 (s), 125.6 (s), 128.3 (s), 136.5 (s), 143.5 (s), 152.3 (s).

2,4,8,10-Tetra-*t*-butyl-6-methoxydibenzo[*d*,*g*][1,3,6,2]dioxathiaphosphocin (**4a**).

To a solution of 6.87 g (50 mmoles) of phosphorus trichloride and 10.12 g (100 mmoles) of triethylamine in 100 ml of dry toluene at 5° was added dropwise a solution of 22.15 g (50 mmoles) of **2a** in 80 ml of toluene. The reaction mixture was stirred for 10 hours at room temperature. The reaction mixture was cooled to 5° and then to it was added a solution of 1.60 g (50 mmoles) of methyl alcohol and 3.96 g (50 mmoles) of pyridine in 25 ml of toluene. The reaction mixture was stirred 15 hours at room temperature. The suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized from acetonitrile to give 15.73 g (63%) of a white solid, mp 163-165°.

2,4,8,10-Tetra-*t*-butyl-6-methyldibenzo[*d*,*g*][1,3,6,2]dioxathiasilocin (**7a**).

To a solution of 5.75 g (50 mmoles) of dichloromethylsilane in 50 ml of dry toluene at 5-10° was added dropwise a solution of 22.15 g (50 mmoles) of **2a** and 10.12 g (100 mmoles) of triethylamine in 100 ml of toluene. The reaction mixture was stirred at room temperature for 15 hours and then the suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized from acetone to give 13.63 g (56%) of a white solid, mp 178-180°.

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[1] Author to whom all correspondence should be addressed.

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