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The reaction of 2,4-di-*t*-butylphenol, **4**, with sulfur monochloride gave the trithiobisphenol **5** rather than the expected dithiobisphenol **7**. The thiol **6** was obtained by the reduction of **5** with zinc under acidic conditions. The dithiobisphenol **7** was prepared by the oxidative coupling of **6** with iodine under alkaline conditions. The dibenzo[*d,h*][1,3,6,7,2]dioxadithiasilonin **8** was prepared by the reaction of **7** with dichlorodimethylsilane using triethylamine as an acid acceptor. No change was observed in the ¹H nmr spectrum of **8** upon cooling to -55°, which suggests that the ΔG* for ring inversion is less than the corresponding eight-membered dibenzo[*d,g*][1,3,2]dioxasilocin and dibenzo[*d,g*][1,3,6,2]dioxathiasilocin **1** and **2**, respectively. The spectral data and elemental analysis are fully in accord with the nine-membered silonin structure.

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Recently, we reported the synthesis and conformational analysis of both the 2,4,8,10-tetra-*t*-butyl-6,6-dimethyl-substituted dibenzo[*d,g*][1,3,2]dioxasilocin **1** and dibenzo[*d,g*][1,3,6,2]dioxathiasilocin **2**, respectively [2,3]. The conformational analysis and free energy of activation (ΔG*) for ring inversion of these and similar systems have received renewed importance in light of recent work. In particular, Denney *et al.* provided the first examples of the inhibition of intramolecular ligand reorganization (pseudorotation) on the nmr time scale of monocyclic pentaoxyphosphoranes [4] prepared from the analogous dibenzo[*d,g*][1,3,2]dioxaphosphocins [5-7] and dibenzo[*d,f*][1,3,2]dioxaphosphpepins [8].

In contrast, much of the previous experimental work on heterocyclic nine-membered rings was centered on the question of the potential for aromatic delocalization of the lone-pair of electrons on the heteroatom into the π system, for example, the work of Quin and co-workers on the phosphonin ring system [9]. Ollis *et al.* [10] and Bindra *et al.*

[11] have reported the conformational analysis of nine-membered rings containing sulfur. More recently, Birkofer *et al.* reported the synthesis and characterization of substituted dibenzo[*f,h*][1,3,2]dioxasilonins [12]. Very limited work has been done on nine-membered rings containing a vicinal disulfide linkage. Eckhardt, for example, reported the synthesis and a ΔG* for ring inversion of 19.7 kcal/mol for **3** [13]. We report in this paper the synthesis and characterization of the first example of the dibenzo[*d,h*][1,3,6,7,2]dioxadithiasilonin ring system.

Results and Discussion.

The synthesis of the dibenzo[*d,h*][1,3,6,7,2]dioxadithiasilonin **8** required the preparation of the dithiobisphenol **7**. The trithiobisphenol **5** was obtained by the reaction of **4** with sulfur monochloride rather than the expected dithiobisphenol **7** [14]. In some instances, previous workers reported that trithiobisphenols were obtained rather than dithiobisphenols in the reactions of phenols with sulfur monochloride [15]. The factors which determine whether disulfide or trisulfide is obtained are not fully known at present and are currently under study in our laboratories.

The reduction of the trithiobisphenol **5** with zinc metal [16] under acidic conditions gave the thiol **6**. Interestingly, in the ¹H nmr spectrum of recrystallized **6** in high-purity deuteriochloroform, coupling of both the hydroxyl and thiol protons to the aromatic ring protons was observed. The calculated theoretical spectrum based upon the spectral assignments, which was obtained using the pmr program [17], was consistent with the observed ¹H nmr spectrum. Further proof of the structure of **6** was provided by ¹³C nmr, ms, ir, and elemental analysis. The dithiobisphenol **7** was prepared by the oxidative coupling of **6** with

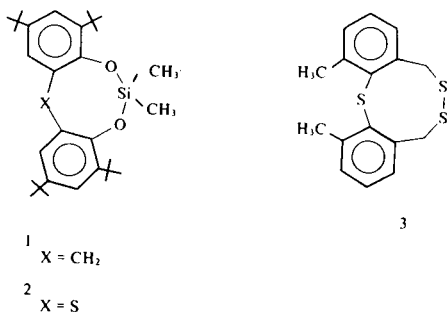
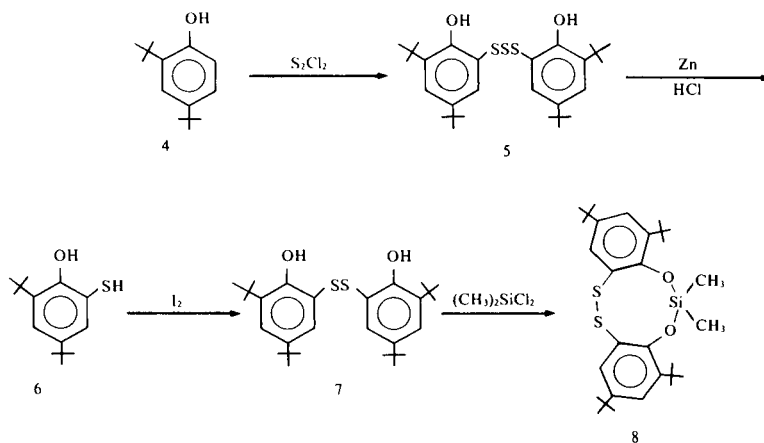


FIGURE 1



Scheme 1

elemental iodine under alkaline conditions [18].

The sillonin **8** was prepared by the reaction of the dithio-bisphenol **7** with dichlorodimethylsilane utilizing triethylamine as an acid acceptor (46% recrystallized). The structure of **8** rests on the following observations. In the ^1H nmr spectrum of **8**, a singlet resonance was observed at δ 0.56 that was assigned to the protons of two equivalent methyl groups bonded to silicon. Two singlet resonances were observed at δ 1.29 and δ 1.45 that were assigned to the protons of two equivalent pairs of *t*-butyl groups. In the ^{13}C nmr spectrum a singlet resonance was observed at δ 0.9 that was assigned to the two equivalent methyl group carbon atoms bonded to silicon. In the ms a molecular ion was observed at m/z 530 mass units. Both the spectral data and elemental analysis were in accord with the proposed structure **8**.

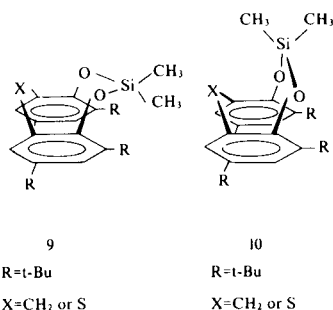


FIGURE 2

Previously, the free energy of activation (ΔG^*) for ring inversion for both **1** and **2** was determined to be 13.9 kcal/mole by variable temperature ^1H nmr [2,3]. The variable ^1H nmr spectral data of **1** or **2** in solution was consistent with either the boat-chair structure **9** or boat-boat structure **10** illustrated, respectively. In contrast, no change was observed in the ^1H nmr spectrum of **8** upon cooling to -55° . Apparently, the ΔG^* of ring inversion is significant-

ly reduced in **8** in comparison to **1** or **2**. A reasonable explanation of this observation is that the additional bridging sulfur results in increased conformational freedom of the ring. Although a planar or twisted conformation that renders the two methyl groups bonded to silicon equivalent cannot be rigorously ruled out by the nmr spectral data, the examination of a molecular model of **8** suggests that this is not the case.

EXPERIMENTAL

All melting points were determined in open-capillary tubes with a Thomas-Hoover melting point apparatus. All ir spectra (1% solution in Perkin-Elmer sodium chloride cells) were recorded on a Perkin-Elmer model 1300 spectrophotometer. The ^1H nmr spectra were obtained on a Varian (model CFT-20 or XL-200) or JEOL (FX-90Q) spectrometer. Variable temperature ^1H nmr spectra were obtained on a Varian model FT-80 equipped with a 5 mm variable-temperature broad-band probe. The ^{13}C nmr spectra were obtained on a Varian model XL-200 spectrometer with full proton decoupling. All ^1H and ^{13}C nmr chemical shifts are reported relative to tetramethylsilane, where a positive sign is downfield from the standard. Mass spectra were obtained on a Finnegan model 8200 mass spectrometer. Solvents were dried prior to use when necessary. Reagents were purchased from commercial laboratory supply houses. Reactions were carried out in flame-dried apparatus under an atmosphere of nitrogen. Elemental analysis were performed by Analytical Research Services, CIBA-GEIGY Corporation.

2,2'-Trithiobis(4,6-*t*-butylphenol) (**5**).

To a solution of 206.33 g (1 mole) of **4** and 1.98 g (10 mmoles) of titanium(IV) chloride in 700 ml of toluene at 5° was added dropwise 67.52 g (0.5 mole) of sulfur monochloride until initiation of the reaction as evidenced by the evolution of hydrogen chloride. The reaction mixture was then cooled to -5 to -10° prior to completion of the addition of sulfur monochloride. When the addition of sulfur monochloride was complete, the reaction mixture was stirred overnight at room temperature. The reaction mixture was extracted sequentially with dilute hydrochloric acid (2 x 500 ml, 1:1 concentrated hydrochloric acid:water), aqueous sodium bicarbonate, and water. The organic phase was dried over anhydrous sodium sulfate and then the solvent was removed *in vacuo*. The residue was recrystallized twice from acetonitrile to give 59.4 g of a white solid. The analytical sample was prepared by further recrystallization from both acetonitrile and acetone, mp 149 - 150° (lit [19] 142.5 - 144.5°): ^1H nmr (deuteriochloroform): δ 1.33 (s, 18 H), 1.40 (s, 18 H), 6.52 (br s, OH, 2 H), 7.43 (d, 2H), 7.52 (d, 2 H); ir (dichloromethane): 3470 cm^{-1} ; ms: 506^+ ; 474 (M-32).

Anal. Calcd. for $C_{28}H_{42}O_2S_3$: C, 66.4; H, 8.4; S, 19.0. Found: C, 66.3; H, 8.6; S, 18.7.

3,5-Di-*t*-butyl-2-hydroxybenzenethiol (**6**).

To a mixture of 22.20 g (43 mmoles) of **5**, 2 l of 3M hydrochloric acid, 500 ml of toluene, and 250 ml of ethanol was added portionwise over a 2 day period 156.9 g (2.4 moles) of zinc metal powder. The organic phase was separated and was washed with water. The organic phase was dried over anhydrous sodium sulfate and then the solvent was removed *in vacuo* to give 19.8 g (97%) of crude product as a white solid. The analytical sample was prepared by recrystallization from acetonitrile, mp 70-73° (lit [20] 64-65°); 1H nmr (deuteriochloroform): δ 1.25 (s, 9 H), 1.38 (s, 9 H), 2.79 (dd, SH, $^4J = ^6J = 1$ Hz, 1 H), 6.46 (d, OH, $J = 0.4$ Hz, 1H), 7.25 (ddd, ArH, 1 H), 7.33 (dd, ArH, 1 H); ^{13}C nmr (deuteriochloroform): δ 31.5, 33.4, 36.6, 37.5, 113.2, 128.2, 133.2, 138.2, 145.1, 155.8; ms: *m/z* 238 (M^+); ir (dichloromethane): 3440 (OH), 2540 (SH) cm^{-1} .

Anal. Calcd. for $C_{24}H_{32}OS$: C, 70.5; H, 9.3. Found: C, 70.8; H, 9.4.

2,2'-Dithiobis(4,6-di-*t*-butylphenol) (**7**).

To a stirred solution of 8.8 g (22 mmoles) of sodium hydroxide in 50 ml of water was added 4.77 g (20 mmoles) of **6**. After the addition was complete, 5.80 g (50 mmoles) of elemental iodine was added using a powder-addition funnel. The solid that separated from the reaction mixture was separated from the liquid phase by decantation and the solid was dissolved in dichloromethane. The dichloromethane solution was extracted sequentially with saturated sodium thiosulfate and saturated sodium chloride. The organic phase was dried over anhydrous sodium sulfate and then the solvent was removed *in vacuo*. The residue was recrystallized from nitromethane to give 3.11 g (65%) of a light yellow solid, mp 111-114° (lit [19] 111.5-113°); 1H nmr (deuteriochloroform): δ 1.27 (s, 18 H), 1.46 (s, 18 H), 6.65 (s, OH, 2 H), 7.27 (d, 2 H), 7.43 (s, 2 H); ir (dichloromethane): 3455 (OH) cm^{-1} .

Anal. Calcd. for $C_{28}H_{42}O_2S_2$: C, 70.8; H, 8.9; S, 13.5. Found: C, 70.8; H, 8.9; S, 13.1.

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

To a solution of 1.87 g (15 mmoles) of dimethyldichlorosilane in 50 ml of toluene cooled with an ice bath was added dropwise a solution of 7.12 g (15 mmoles) of **7** and 3.04 g (30 mmoles) of triethylamine in 25 ml of toluene. The reaction mixture was stirred overnight at room temperature and then it was heated at 55° for 24 hours. The cooled reaction mixture was filtered to remove the suspension of triethylamine hydrochloride and the solvent was removed *in vacuo*. The residue was recrystallized from 2-butanone to give 3.66 g (46%) of a light yellow solid, mp 214-215°; 1H nmr (deuteriochloroform): δ 0.59 (s, CH_3Si , 6 H) 1.29 (s, 18 H), 1.45 (s, 18 H), 7.37 (d, 2 H), 7.43 (d, 2 H); ^{13}C nmr (deuteriochloroform): δ 0.9 (H_3C-Si), 29.3, 30.5, 33.7, 34.9, 122.1, 126.9, 130.9, 140.1, 143.7, 152.5; ms: *m/z* 530 $^+$.

Anal. Calcd. for $C_{30}H_{46}O_2S_2Si$: C, 67.9; H, 8.7; S, 12.1. Found: C, 67.8; H, 8.6; S, 11.8.

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