

Preparation of 12,12'-Diol 6. A mechanically stirred solution of olefin 5 (20.0 g, 26.2 mmol) in tetrahydrofuran/water (360 mL/40 mL) was adjusted to pH 6.1 (3 N HCl), and osmium tetroxide/*tert*-butyl alcohol (2.5% solution, 40 mL, 3.9 mmol) was added at room temperature. After the dark amber solution was stirred at room temperature for 1 h, sodium metaperiodate (11.2 g, 52.4 mmol) was added, and the resulting mixture was stirred at room temperature for 22 h. After this period, TLC [silica gel, CH₂Cl₂/MeOH/NH₃ (9:1:0.1)] indicated little starting 5 (ca. 10%) and essentially one, more polar material. Tetrahydrofuran (100 mL) and aqueous sodium sulfite (1 M, 220 mL) were added, and the mixture was stirred at room temperature for 15 min. The reaction mixture was then poured into a stirring mixture of methylene chloride/water (800 mL/1400 mL) and phase separated, and the aqueous phase was reextracted with methyl chloride (3 × 400 mL), dried over anhydrous sodium sulfate, and concentrated in vacuo, affording an amber solid (19.1 g). The solid was added to a stirring mixture of methylene chloride/water (100 mL/100 mL) and the pH was adjusted to 2.6. The phases were separated, the pH of the aqueous phase was readjusted to 4.8, and the aqueous phase was extracted with methylene chloride (2 × 150 mL). The phases were separated, the pH of the aqueous phase was finally adjusted to 9.5, and the aqueous phase was extracted with methylene chloride (3 × 200 mL). The methylene chloride extracts at pH 9.5 contained no starting material [TLC; silica gel, CH₂Cl₂/MeOH/NH₃ (9:1:0.1)] and upon drying over anhydrous sodium sulfate and concentration in vacuo afforded a colorless solid (14 g). The solid was dissolved in chloroform (60 mL) and allowed to stand at room temperature for 15 min, affording a thick crystalline mass. At this point, hexane (180 mL) was added with vigorous stirring, and the resulting slurry was stirred at room temperature overnight, which afforded, after filtration, colorless crystalline 6 (11 g, mp 148–151 °C): ¹H NMR (CDCl₃) δ 0.79 (t), 0.95–1.20 (m), 1.45–1.90 (m), 1.99 (s), 2.25 (s), 2.35–2.70 (m), 3.22 (s), 3.40 (br m), 3.55 (dd), 3.65 (s), 3.70 (m), 3.85 (s), 3.95 (d), 4.25 (m), 4.59 (dd), 4.91 (d), 5.05 (dd); ¹³C NMR (CDCl₃) δ 176.2 (lactone), 170.4 (acetyl), 101.5 (CH), 95.4 (CH), 83.0 (CH), 82.7 (CH), 78.3 (CH), 78.1 (CH), 77.5 (CH), 75.5 (Q), 74.6 (Q), 72.5 (Q), 70.9 (CH), 69.2 (CH), 68.1 (CH), 64.1 (CH), 63.2 (CH), 61.9 (CH₂), 49.0 (CH₃), 44.3 (CH), 41.9 (CH), 40.1 [2 (CH₃)], 36.4 (CH₂), 34.7 (CH₂), 34.3 (CH), 32.0 (CH), 29.5 (CH₂), 23.7 (CH₃), 22.1 (CH₂), 21.1 (CH₃), 21.0 (CH₃), 20.5 (CH₃), 19.4 (CH₃), 17.3 (CH₃), 15.1 (CH₃), 13.7 (CH₃), 11.0 (CH₃), 9.1 (CH₃); high-resolution mass spectrum, *m/e* 635.3554 (P - desosamine, C₃₁H₅₅O₁₃), 592.3720 (P - 4''-acetylcladinose β-cleavage, C₂₉H₅₄NO₁₁), 576.3687 (P - 4''-acetylcladinose, C₂₉H₅₄NO₁₀), 434.2814 (aglycon, C₂₁H₃₈O₉), 201.1104 (4''-acetylcladinose, C₁₀H₁₇O₄), 158.1158 (desosamine, C₈H₁₆NO₂). Anal. Calcd for C₃₉H₇₁O₁₅N: C, 58.99; H, 8.95; N, 1.76. Found: C, 58.77; H, 8.83; N, 1.72.

X-ray Analysis. Thionocarbonate 2 and diol 6 were converted to their corresponding 2'-benzoates, compounds 7 and 8, respectively, since these derivatives gave crystals suitable for X-ray analysis. They were prepared via exposure to an equivalent amount of either benzoic anhydride or benzoyl chloride in methylene chloride solvent.

X-ray Analysis of Benzoate 7. The structure of 7 was determined by X-ray crystallography with a crystal that measured 1.00 × 0.50 × 0.50 mm. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated diffractometer with graphite monochromated Cu K_α radiation. Preliminary indications of the unit cell based on 25 randomly selected reflections revealed orthorhombic symmetry with the following lattice parameters: *a* = 14.445 (2) Å, *b* = 17.857 (7) Å, and *c* = 27.242 (3) Å with $\alpha = \beta = \gamma = 90.0^\circ$. The space group, on the basis of the observed systematic extinctions, was determined to be *P*2₁2₁2₁ (No. 19), *Z* = 4 with one molecule of composition C₄₅H₇₁O₁₄NS forming the asymmetric unit. The calculated density was 1.67 g/cm³. There were 4896 reflections collected with $2\theta \leq 114^\circ$, of those reflections 3254 (66%) with $1 \geq 3\sigma(I)$ were adjudged observed.

The structure was solved by using MULTAN 80. After numerous runs of varying the number of Es used in Normal, MULTAN 80 was tried with six special and three general reflections. There were 421 *E* values ≥ 1.626 used. This run produced 576 sets of which set 512 was distinct from the rest and had a combined figure of merit of 2.7913. The electron-density map of that set revealed

56 of the 61 atoms comprising the molecule. Those 56 atoms were used as a phasing model in Karle recycling, which yielded 59 atoms. Two successive iterations of the WFO option in Normal produced the entire 61 non-hydrogen atom structure. The following full-matrix refinements of the non-hydrogen atoms resulted in convergence to a crystallographic unweighted residual of 0.184 and a weighted residual of 0.286.

X-ray Analysis of Benzoate 8. The structure of 8 was determined by X-ray crystallography with a crystal that measured 0.37 × 0.35 × 0.27 mm. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated diffractometer with graphite monochromated Cu K_α radiation. Preliminary indications of the unit cell based on 25 randomly selected reflections revealed orthorhombic symmetry with the following lattice parameters: *a* = 12.083 (3) Å, *b* = 19.763 (8) Å, and *c* = 20.508 (4) Å, with $\alpha = \beta = \gamma = 90.0^\circ$. The space group was *P*2₁2₁2₁ (No. 19), *Z* = 4 with one molecule of composition C₄₆H₇₅O₁₆N and one molecule of water forming the asymmetric unit. The calculated density was 1.22 g/cm³. There were 3708 reflections collected with $2\theta \leq 114^\circ$, of those reflections 2989 (81%) with $1 \geq 3\sigma(I)$ were adjudged observed.

The structure was solved by using MULTAN 80. The phasing of 386 *E* values ≥ 1.538 resulted in an electron density map that revealed 59 out of the 63 non-hydrogen atoms. The complete structure was revealed with the WFPO option in Normal. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated using SDP program HYDRO, and added to the structure calculations. The following full-matrix refinement of the non-hydrogen atoms and addition of the hydrogen atoms to the structure factor calculations, without refinement of their positions, resulted in convergence to a standard crystallographic unweighted residual of 0.046 and a weighted residual of 0.048.

Acknowledgment. We thank R. Ware and D. Sweet for assistance in obtaining spectra and A. Grodski and D. Watrous for synthesizing preparative quantities of all intermediates.

Supplementary Material Available: Tables containing fractional coordinates, temperature factors, bond distances, torsional angles, and anisotropic temperature factors for Figures 1 and 3 (21 pages). Ordering information is given on any current masthead page.

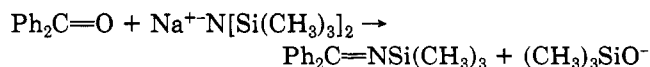
Synthesis of Symmetrical Bis(aryl)sulfur Diimides

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The Peterson reaction involves the addition of an α -silyl carbanion to the carbonyl group of a ketone or aldehyde to yield a β -silyl alkoxide, which decomposes to an alkene and a silanoate.¹ Similarly, the reaction of the sodium salt of hexamethyldisilazane with nonenolizable ketones yields *N*-(trimethylsilyl)imines.²

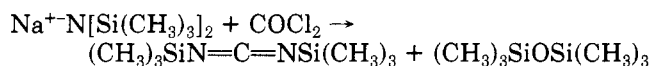


Bis(trimethylsilyl)carbodiimide has been prepared by the reaction of sodium bis(trimethylsilyl)amide with phosgene,³ while reaction of lithium (trimethylsilyl)amides

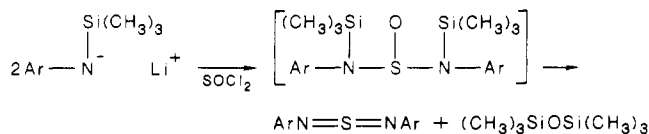
(1) For a recent review, see: Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; pp 58–76.

(2) Kruger, C.; Rochow, E. G.; Wannagat, U. *Chem. Ber.* 1963, 96, 2132.

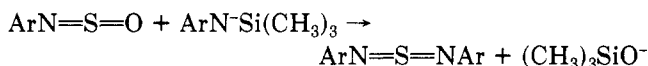
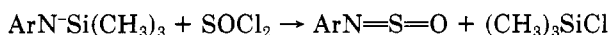
with sulfur dioxide gives *N*-sulfinylamines.⁴



We now report that symmetrical diarylsulfur diimides^{5,6} can be prepared by reaction of lithium (trimethylsilyl)anilides with thionyl chloride. This reaction may involve intermediate formation of bis[*N*-aryl-*N*-(trimethylsilyl)amino] sulfoxides, which spontaneously decompose to yield the diarylsulfur diimides and hexamethyldisiloxane.



Alternatively, this reaction may occur by initial formation of *N*-sulfinylaniline, which reacts with a second equivalent of lithium (trimethylsilyl)anilide to give the bis(aryl)sulfur diimide.^{7,8} In this latter case, hexamethyldisiloxane is formed by the reaction of trimethylchlorosilane with lithium trimethylsilanoate.



Consistent with this possibility, the reaction of *N*-sulfinylanilines with lithium (trimethylsilyl)anilides does indeed yield bis(aryl)sulfur diimides. However, this approach is not, in general, suitable for the preparation of unsymmetrical bis(aryl)sulfur diimides, since mixtures consisting of the desired product as well as the symmetrical bis(aryl)sulfur diimide derived from the *N*-sulfinylaniline are often formed. The symmetrical product probably results from the base (trimethylsilanoate)-catalyzed condensation of two molecules of *N*-sulfinylaniline with loss of sulfur dioxide.⁹

Experimental Section

¹H NMR spectra were obtained at 270 MHz on an IBM WP-270-SY spectrometer operating in the FT mode with 5% solutions in CDCl₃ with CHCl₃ and TMS as internal standards. ¹³C NMR spectra were obtained at 67.925 MHz with 10% solutions in CDCl₃. ¹³C NMR spectra were run with broad-band proton decoupling. For most bis(aryl)sulfur diimides, ¹H NMR spectral data are less characteristic than ¹³C NMR data. IR spectra were acquired on a Perkin-Elmer 281 spectrometer. Ultraviolet (UV) spectra were determined on a Shimadzu UV-260 instrument. Spectral quality *n*-hexane was utilized as solvent to prepare solutions for determination of UV spectra. Mass spectra were run at the University of California Riverside Mass Spectrometry Laboratory. Melting points and boiling points are uncorrected. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

N-(Trimethylsilyl)anilines were prepared by literature methods.⁴

N-Sulfinylanilines were prepared by literature methods.¹⁰

(3) Pump, J.; Wannagat, U. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 112.

(4) Porskamp, P. A. T.; Zwanenberg, B. *Synthesis* **1981**, 368.

(5) Johnson, C. R. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon: Oxford, 1979; Vol. 3, pp 233-235.

(6) Kresze, G.; Wucherpennig, *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 149.

(7) Scherer, O. J.; Hornig, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 729.

(8) Ruppert, I.; Bastian, V.; Appel, R. *Chem. Ber.* **1975**, *108*, 2329.

(9) Hörhold, H. H. *Z. Chem.* **1972**, *12*, 41.

(10) Kresze, G.; Maschke, A.; Albrecht, R.; Bederke, K.; Patzschke, H. P.; Smalla, H.; Trede, A. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 89.

General Procedure. All reactions were carried out under an atmosphere of prepurified nitrogen in flame-dried apparatus. *n*-Butyllithium (20 mmol) in hexane (12 mL, 1.67 M) was added to a stirred solution of *N*-(trimethylsilyl)aniline (20 mmol) in dry THF at -70 °C. After 0.5 h, the temperature was raised to 0 °C for 1 h. The reaction mixture was then cooled to -70 °C, and freshly distilled thionyl chloride (10 mmol) dissolved in THF (10 mL) was slowly added. After 1 h, the mixture was allowed to warm to room temperature. After 3 h, the reaction mixture was neutralized with acetic acid. Ether was added, and the solution was filtered to remove salts. Solvent was removed from the filtrate by evaporation under reduced pressure. Distillation, crystallization, or column chromatography afforded the pure bis(aryl)sulfur diimide.

The reaction of lithium (trimethylsilyl)anilides with *N*-sulfinylanilines to give unsymmetrical bis(aryl)sulfur diimides was carried in an analogous manner with the exception that the *N*-sulfinylaniline was used in place of the thionyl chloride.

Diphenylsulfur diimide was purified by distillation: bp 125-128 °C (0.3 mm) [lit.¹¹ bp 126 °C (0.5 mm)]; 75% yield; ¹³C NMR δ 145.40, 128.79, 126.69, 123.10; UV λ_{max} 411 nm (log ε 4.045); IR (film) ν 1297, 1265, 1218, 1060 cm⁻¹.

Bis(*p*-bromophenyl)sulfur diimide was recrystallized from *n*-hexane: mp 106-107 °C (lit.¹² mp 106-107 °C); 82% yield; ¹³C NMR δ 144.34, 132.10, 124.73, 120.50; UV λ_{max} 426.6 nm (log ε 4.185); IR (CHCl₃) ν 1290, 1245, 1226, 1055 cm⁻¹.

Bis(*p*-chlorophenyl)sulfur diimide was recrystallized from *n*-hexane: mp 64-65 °C (lit.¹² mp 60-61 °C); 92% yield; ¹³C NMR δ 143.96, 132.53, 129.12, 124.50; UV λ_{max} 425 nm (log ε 4.133); IR (CHCl₃) ν 1292, 1260, 1228, 1057 cm⁻¹.

Bis(2,4,6-trimethylphenyl)sulfur diimide was purified by column chromatography. Silica gel was used as the adsorbent and *n*-hexane/THF (95:5) was used as the eluant: mp 46 °C (lit.¹³ mp 47.5 °C); 77% yield; ¹H NMR δ 2.08 (s, 12 H), 2.19 (s, 6 H), 6.60-6.85 (m, 4 H); ¹³C NMR δ 140.11, 134.26, 128.63, 128.09, 20.66, 18.87. UV λ_{max} 329.6 nm (log ε 3.45); IR (film) ν 1310, 1250, 1206, 1060 cm⁻¹.

Di-*p*-tolylsulfur diimide was purified by distillation: bp 125-128 °C (0.25 mm); mp 46-48 °C (lit.⁶ mp 48-50 °C); 89% yield; ¹H NMR δ 2.40 (s, 6 H), 7.0-7.6 (m, 8 H); ¹³C NMR δ 143.53, 136.59, 129.33, 123.10, 21.09; UV λ_{max} 425 nm (log ε 4.09); IR (CHCl₃) ν 1490, 1395, 1363, 1220, 1060 cm⁻¹.

(3,4-Dichlorophenyl)(4'-chlorophenyl)sulfur diimide was prepared by the reaction of *N*-sulfinyl-*p*-chloroaniline with lithium (trimethylsilyl)-3,4-dichloroanilide in 44% yield. A dark red solid was recrystallized from *n*-hexane: mp 60-61 °C; ¹³C NMR δ 144.45, 143.96, 143.80, 133.02, 132.53, 130.52, 129.12, 124.73, 124.51, 122.40; UV λ_{max} 425 nm (log ε 4.19); IR (CHCl₃) ν 1295, 1248, 1227, 1092 cm⁻¹; MS, *m/e* (rel intens) 319 (1.0), 318 (1.8), 317 (2.3), 316 (1.8) M⁺ 283 (30.4), 247 (100), 157 (19), 111 (24). Anal. Calcd for C₁₅H₉N₂SCl₃: C, 45.38; H, 2.22; S, 10.09. Found: C, 46.0; H, 2.33; S, 9.99. In addition, small amounts of bis(*p*-chlorophenyl)sulfur diimide was isolated.

(*p*-Chlorophenyl)(2',4',6'-trimethylphenyl)sulfur diimide was prepared by the reaction of lithium (trimethylsilyl)-2,4,6-trimethylanilide with *N*-sulfinyl-*p*-chloroaniline in 59% yield. It was purified by column chromatography on silica gel. A mixture of hexane and THF (95:5) was used as eluant: ¹H NMR δ 2.06 (s, 6 H), 2.19 (s, 3 H), 6.6-7.0 (m, 6 H); ¹³C NMR δ 141.96, 141.36, 134.91, 130.96, 128.19, 127.65, 127.38, 123.48, 20.55, 18.76; UV λ_{max} 354.4 nm (log ε 3.805); IR (film) δ 1306, 1262, 1210, 1057 cm⁻¹; MS, *m/e* (rel intens) 292 (2.8), 291 (1.8), 290 (7.3) M⁺, 277 (36.9), 276 (16.9), 275 (100), 164 (50), 149 (11.7), 132 (5.6), 127 (6.7), 111 (6.1); high-resolution MS calcd for C₁₅H₁₅N₂S³²S³³Cl 290.0640, found 290.0644. In addition, small amounts of bis(*p*-chlorophenyl)sulfur diimide were found.

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(11) Hörhold, H. H.; Floppmann, K. D. *Z. Chem.* **1967**, *7*, 346.

(12) Levchenko, E. S.; Kirsanov, A. V. *Zh. Org. Khim.* **1965**, *1*, 300.

(13) Kuyper, J.; Vrieze, K. *J. Organomet. Chem.* **1975**, *86*, 127.