

Synthesis of Dimethylsilylbis(benzoxazoles)

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Dimethylsilylbis(benzoxazoles) and related substances were required as model compounds in a study of the thermal stability of organosilicon structural units. Nitration of *p,p'*-dimethylsilyldiphenol with acetyl nitrate gave moderate yields of 4,4'-dimethylsilylbis(2-nitrophenol), which in contrast to the starting material does not undergo desilylation by acid or bromine and is resistant to cleavage by diazonium salts. Catalytic hydrogenation gave 4,4'-dimethylsilylbis(2-aminophenol) in excellent yield. The corresponding tetraacetyl derivative underwent thermal ring closure with elimination of acetic acid to give 5,5'-dimethylsilylbis(2-methylbenzoxazole) in high yield. Analogous reactions afforded 5,5'-dimethylsilylbis(2-phenylbenzoxazole). These bis(benzoxazoles), although relatively low melting (below 150°), are very stable to heat; thus 5,5'-dimethylsilylbis(2-methylbenzoxazole) was heated to 515° for 30 min in a sealed tube without decomposition.

Dimethylsilylbis(benzoxazoles) and their precursors were required as model compounds and as potential starting materials for the preparation of thermally stable organosilicon polymers. In the carbon series polymers containing the isopropylidenebis(benzoxazole) moiety in the main chain have exhibited a high degree of thermal stability as well as desirable mechanical properties.²⁻⁴ Substitution of the dimethylsilyl group for the isopropylidene group offered the possibility of further enhancement of mechanical properties, with no decrease in thermal stability.

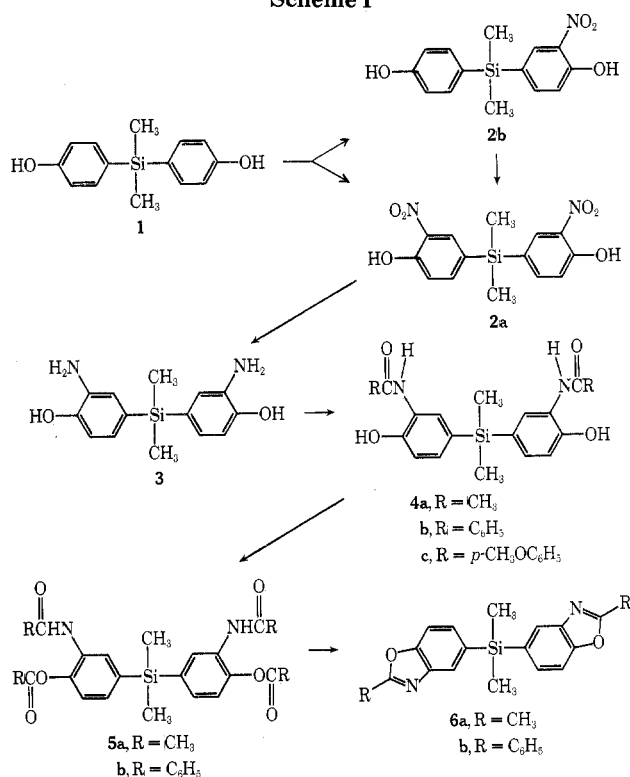
The effects of organosilicon substitution on benzoxazoles have not yet been studied. However, Kovacs⁵ reported that the solubility in organic solvents of benzimidazole derivatives containing the triphenylsilyl group was greater than the solely organic analogs, with no decrease of thermal stability or melting point. The preparation of representative substituted dimethylsilylbis(benzoxazoles) and some of their thermal properties are described in the present report.

Discussion

Preparation of Compounds 2a-6. The reactions involved in the synthesis of the dimethylsilylbis(benzoxazoles) are shown in Scheme I. The starting material, *p,p'*-dimethylsilyldiphenol (1), was prepared by known methods.⁶ Unlike the carbon analog, *p,p'*-isopropylidenediphenol,⁷ direct nitration of 1 with nitric acid in glacial acetic acid resulted in cleavage; the main product was a mixture of *o*- and *p*-nitrophenol. However, the desired nitration could be carried out in moderate yields with nitric acid in the presence of acetic anhydride. Under the reaction conditions employed it has been shown that this reagent consists largely of acetyl nitrate.⁸ It seems probable that acetyl nitrate generated in situ is responsible for the successful nitration in this case. Since the starting *p,p'*-dimethylsilyldiphenol decomposes slowly at room temperature, even under anhydrous conditions, it is important for optimum yields to use a freshly prepared sample of 1; even small amounts of decomposition products yield intractable tars during the nitration.

Catalytic hydrogenation of 2a gave 4,4'-dimethylsilylbis(2-aminophenol) (3) in good yield. Although this intermediate is quite stable in crystalline form, its isolation and purification by crystallization from aqueous sulfurous acid according to the procedure given in the Experimental Section is recommended. Alternatively the hydrogenation can be conducted in acetic anhydride as solvent. Under the latter conditions the product is 4,4'-dimethylsilylbis(2-acetaminophenol) (4), a stable intermediate for 5,5'-dimethylsilylbis(2-methylbenzoxazole) (6a).

Scheme I



Heating of 3 under reflux with excess acetic anhydride gave 4,4'-dimethylsilylbis(2-acetaminophenol) diacetate (5a), which upon distillation at reduced pressure lost the elements of acetic acid to give 5,5'-dimethylsilylbis(2-methylbenzoxazole) (6a). 4,4'-Dimethylsilylbis(2-benzamidophenol) dibenzoate (5b) was obtained by treatment of 3 in pyridine with the stoichiometric quantity of benzoyl chloride.

When 5b was heated in programmed increments between 200 and 275° in a thermobalance, 5,5'-dimethylsilylbis(2-phenylbenzoxazole) (6b) was formed almost quantitatively with the elimination of 2 mol of benzoic acid. This reaction was also carried out in good yield on a preparative scale under similar conditions.

Structure and Properties of Compounds 2a-6b. Unlike its precursor 1, 4,4'-dimethylsilylbis(2-nitrophenol) (2a) is very stable. It resisted acidic hydrolysis under progressively more vigorous conditions until cleavage was finally obtained with concentrated hydrochloric acid in a sealed tube after 50 hr at 150°. Under these conditions *o*-nitrophenol was obtained cleanly and in good yield. At-

tempted brominolysis of **2a** in a sealed tube at 115° failed, and the resulting material consisted largely of unchanged starting material.

Benzenediazonium chloride solutions cleaved *p,p'*-isopropylidenediphenol and its homologs quantitatively under mild conditions to give *p*-hydroxyazobenzene and acetone or homologous ketones.⁹

An analogous cleavage takes place with *p,p'*-dimethylsilyldiphenol, but its dinitro derivative **2a** is recovered unchanged under similar conditions.

The postulated structure of **2a** is supported by its NMR spectrum, the aromatic portion of which is consistent with an ABX system (symmetrical 1,2,4 substitution in both rings). One half of the AB quartet ($J_{ab} = 8.1$ Hz) is split into a doublet of doublets ($J_{ax} = 1.5$ Hz) by the meta proton.

Further evidence for the presence of a nitro group in each ring of **2a** is adduced by titration of both phenolic groups (equivalence point pH 9.7) with sodium hydroxide in methanol-water. In contrast, only one of the phenolic groups of 4,4'-dimethylsilyl(2-nitrophenol)phenol (**2b**) was titrated under these conditions.

4,4'-Dimethylsilylbis(2-aminophenol) (**3**) is quite stable in crystalline form, but in solution it darkens rapidly on exposure to air or light. It is most easily recrystallized from aqueous sulfurous acid by vacuum stripping of the sulfur dioxide; under these conditions a stable, crystalline product is obtained with minimum decomposition.

If the hydrogenation of **2a** is conducted in acetic anhydride, 4,4'-dimethylsilylbis(2-acetaminophenol) (**4a**), a stable derivative, is obtained. The amino groups of **3** could be acetylated with acetic anhydride in a buffered aqueous solution to give **4a**. Acetylation of **3** under more drastic conditions results in esterification of the hydroxyl groups also to give 4,4'-dimethylsilylbis(2-acetamino)phenol diacetate (**5a**). This is a crystalline substance which is stable to 250°, at which temperature ring closure to the corresponding bis(benzoxazole) takes place.

5,5'-Dimethylsilylbis(2-methylbenzoxazole) (**6a**) and 5,5'-dimethylsilylbis(2-phenylbenzoxazole) (**6b**) are crystalline solids which possess a remarkable degree of thermal stability. They can be recovered unchanged after heating to 515° in a sealed tube for 30 min, or at 320° for 3 hr. The ir spectra showed bands which are characteristic of the benzoxazole moiety¹⁰ and the other spectral data support the assigned structures.

Experimental Section

Elemental microanalyses were performed by Midwest Micro-labs, Ltd., Indianapolis, Ind.

Infrared spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer, uv spectra with a Perkin-Elmer Model 202 visible-ultraviolet spectrophotometer, NMR data with Varian A-60 and HA-100 spectrometers, and mass spectra with a C. E. C. Model 21-110 spectrometer.

Thermogravimetric analyses were performed with a custom-made instrument comprising a Cahn RG electrobalance with a R. I. Data-Trak temperature programmer.

Preparation of 4,4'-Dimethylsilylbis(2-nitrophenol) (2a). Dimethylsilyldiphenol (14.07 g, 0.0575 mol), freshly prepared,⁶ was briefly exposed to reduced pressure at room temperature to remove volatiles, and dissolved in 100 ml of acetic anhydride. The solution was cooled by stirring in a Dry Ice-acetone bath for about 45 min.

During this time the nitrating solution was prepared by adding concentrated nitric acid (10.8 g, 0.160 mol) slowly with stirring and cooling to 75 ml of acetic anhydride. During the addition the temperature was maintained between 35 and 40°. The nitrating solution was cooled to just above the appearance of crystals, and was added dropwise to the stirred cooled solution of dimethylsilyldiphenol. The addition required about 90 min, at the end of which

the bath was removed and the stirring continued for 15 min. The reaction mixture was poured onto 800 ml of cracked ice and 600 ml of water and stirred, and the hydrolysis was completed at room temperature.

The mixture was extracted with four 200-ml portions of dichloromethane and the combined extracts were washed twice with 300-ml portions of water and dried over anhydrous magnesium sulfate. The filtrate was concentrated to give an orange-brown oil, which was freed from tars by passing it through a column (5.7 × 46 cm) packed with silica gel (Grace 950, 60–200 mesh) with benzene as solvent.

The product, together with a trace of *o*-nitrophenol, emerged in the first fraction (ca. 700 ml) and crystallized upon concentration of the eluate and addition of *n*-hexane. The crude product (11.9 g, 61.8%) was obtained as bright yellow crystals, mp 88–95°.

The foregoing product is of adequate purity for the reduction step; however, pure 4,4'-dimethylsilylbis(2-nitrophenol) was obtained by recrystallization of the crude product from *n*-hexane. The product crystallized very slowly as long, yellow needles: mp 101.1–101.5°; uv max (CH₃OH) 225 mμ (ϵ 15,700), (aqueous NaOH) 249 mμ (ϵ 39,700); ir (KBr) 3250, 3030, 2950, 1610, 1520, 1310, 1245, 1155, 895, and 670 cm⁻¹; NMR (CCl₄) δ 10.7 (s, 2 H), 8.25 (d, 2 H, $J_{ac} = 1.5$ Hz), 7.55 (m, 4 H, $J_{bc} = 8.1$ Hz), and 0.66 ppm (s, 6 H); mass spectrum m/e 334 (M), 319, 303, 289, 273, 258, 227, 212, 196, 150, 135, 85, 73, and 55.

Anal. Calcd for C₁₄H₁₄O₆N₂Si: C, 50.28; H, 4.22; N, 8.38. Found: C, 50.50; H, 4.20; N, 8.75.

Cleavage of 4,4'-Dimethylsilylbis(2-nitrophenol) (2). A small sample (0.10 g, 0.3 mmol) of **2** was heated with 3 ml of concentrated (36 N) hydrochloric acid in a sealed tube for 50 hr at 150°. A yellow aqueous layer and a gummy residue were formed. The gummy residue proved to be dimethylsilicone polymer; the aqueous phase was separated and extracted with dichloromethane. Chromatography (TLC) of the dried (MgSO₄) extracts indicated presence of only one component, a nitro compound having the same R_f as *o*-nitrophenol. Evaporation of the extracts gave yellow crystals of *o*-nitrophenol, 0.06 g (84%), mp 42.5–43.5°; no melting point depression with authentic *o*-nitrophenol (Eastman No. 191), mp 44.5–45°, was noted and the two samples had identical infrared spectra.

4,4'-Dimethylsilylbis(2-nitrophenol) (0.32 g, 0.96 mmol) failed to react with a slight excess of benzenediazonium chloride at 0° in excess 10% sodium hydroxide. However, in a control experiment under similar conditions dimethylsilyldiphenol was rapidly cleaved by benzenediazonium chloride to give *p*-hydroxyazobenzene and dimethylsilicone polymer.

Treatment of **2** with refluxing 20% sodium hydroxide for 64 hr, or with an excess of bromine in carbon tetrachloride at room temperature, failed to cleave it. The starting material was quantitatively recovered.

4,4'-Dimethylsilyl(2-nitrophenol)phenol (2b). Nitric acid, (70%, 3.61 g, 0.04 mol) was dissolved dropwise with stirring in 25 ml of acetic anhydride, maintaining the temperature between 25 and 35°. The nitrating solution was added dropwise with stirring to 4.69 g (0.0194 mol) of dimethylsilyldiphenol dissolved in 200 ml of dry ether. During the addition, which required 0.5 hr, the reaction mixture was maintained at about -40° by stirring in a Dry Ice-dichloromethane bath. The solution was allowed to warm to room temperature and stood overnight (16 hr). It turned from light yellow (2 hr) to amber at the end of this time.

The solution was poured on water and stirred for 1.5 hr, and the ethereal layer was thoroughly washed with water and dried over anhydrous magnesium sulfate. The crude product was obtained as an amber oil by evaporation on a rotary evaporator. It was chromatographed on a silica gel column with dichloromethane as developing solvent. The small forerun consisted of 4,4'-dimethylsilylbis(2-nitrophenol) (**2a**), but was soon followed by a larger fraction containing 4,4'-dimethylsilyl(2-nitrophenol)phenol (**2b**). This fraction (2.1 g, 36%) partly solidified on standing, and TLC showed it to be almost completely **2b**. This product was purified by recrystallization from *n*-hexane: mp 84–85.5°; uv max (CH₃OH) 232 mμ (ϵ 19,400), (aqueous NaOH) 252 mμ (ϵ 35,900); ir (CHCl₃) 3270, 2995, 1625, 1575, 1525, 1480, 1400, 1310, 1240, 1190, 1160, 1110, 1080, 813, and 786 cm⁻¹; NMR (CCl₄) δ 10.6 (s, 2 H), 8.1 (d, 2 H), 7.1 (m, 6 H), and 0.4 ppm (s, 6 H); mol wt (vapor pressure osmometry, CHCl₃) calcd, 289; found, 281. Titration: calcd, 10.0 ml; required 9.9 ml of 0.01 M NaOH to titrate 19.93 mg of **2a** as monobasic acid, single inflection at pH 9.5 in aqueous methanol.

Anal. Calcd for C₁₄H₁₅O₄NSi: C, 58.11; H, 5.23; N, 4.84. Found: C, 58.26; H, 5.47; N, 4.95.

Conversion of 4,4'-Dimethylsilyl(2-nitrophenol)phenol (2b) to 2a. 4,4'-Dimethylsilyl(2-nitrophenol)phenol (0.25 g, 0.86 mmol) was dissolved in 100 ml of acetic anhydride. A nitrating solution was prepared by dropwise addition of 0.5 g of 70% nitric acid to 20 ml of acetic anhydride, such that the temperature remained between 20 and 25°. The nitrating solution was added dropwise to the solution of the phenol at -5 to -10° with stirring. The reaction mixture was allowed to warm to 0° and held at that temperature for 1 hr, and then for 1 hr at 20°. At this time TLC indicated complete conversion of the starting material. The reaction mixture was poured into cold water and stirred for 1 hr. After cooling, yellow crystals separated which were collected by filtration (0.20 g, 70%), mp 93–100.5°. After recrystallization from *n*-hexane, this product had the same melting point as 4,4'-dimethylsilylbis(2-nitrophenol), produced no depression in a mixture melting point with an authentic sample, and exhibited identical ir spectra with the latter.

4,4'-Dimethylsilylbis(2-nitrophenol) Diacetate (2c). 4,4'-Dimethylsilylbis(2-nitrophenol) (1.51 g, 4.53 mmol) was refluxed for 4 hr with 50 ml of acetic anhydride. The solution turned from a bright to light yellow, and was poured on boiling water at the termination of refluxing. The cooled hydrolyzate was extracted with dichloromethane, which was then evaporated to dryness. The residue was recrystallized from 250 ml of boiling petroleum ether to give 0.79 g (63.8%) of product as fine yellowish-white needles: mp 119.5–120.0°; ir (KBr) 3080, 2960, 1775, 1600, 1530, 1350, 1190, 1085, 920, and 825 cm⁻¹.

Anal. Calcd for C₁₈H₁₈N₂O₈Si: C, 51.67; H, 4.04; N, 6.70. Found: C, 51.40; H, 4.12; N, 6.75.

4,4'-Dimethylsilylbis(2-aminophenol) (3). 4,4'-Dimethylsilylbis(2-nitrophenol) (2a, 4.0 g, 0.012 mol) was dissolved in 250 ml of dry ethyl ether. Approximately 100 mg of 10% palladium on charcoal was suspended in 10 ml of absolute ether and added to the ethereal solution, which was then shaken at an initial hydrogen pressure of 50 psig in a Parr hydrogenator. Shaking was continued with replenishment of hydrogen when necessary until the calculated pressure drop (100 psi) was obtained after about 3 hr.

The hydrogenation mixture was treated with 100 ml of a saturated solution of sulfurous acid which dissolved precipitated 3 and allowed removal of the catalyst by filtration. The combined ethereal and aqueous filtrates were evaporated on a rotary evaporator at room temperature. When approximately one-half of the aqueous phase remained, yellowish-white crystals of the product began to appear. The solution was chilled and the first crop collected by filtration (1.2 g). A second crop (1.1 g), mp 148–150°, was obtained by decolorization of the filtrate with charcoal, further concentration, and adjustment to pH 6 with dilute ammonium hydroxide. The combined yield of 3 was 2.3 g (70%). The first crop was of sufficient purity for analysis: mp 150–151°; ir (KBr) 3360, 3290, 1500, 1270, 805, and 775 cm⁻¹; NMR (DMSO-*d*₆) δ 6.6 (m, 6 H), 0.3 (s, 6 H).

Anal. Calcd for C₁₄H₁₈N₂O₂Si: C, 61.05; H, 6.95; N, 10.17. Found: C, 61.40; H, 6.60; N, 10.15.

4,4'-Dimethylsilylbis(2-acetamidophenol) (4a). Method A. 4,4'-Dimethylsilylbis(2-aminophenol) (1.3 g, 4.74 mmol) was dissolved in dilute hydrochloric acid and the brownish solution was decolorized by stirring with activated charcoal at ca. 50°. The filtered solution was shaken with 1.0 g (10 mmol) of acetic anhydride, to which was immediately added an excess of saturated sodium acetate solution with further shaking. After stirring for several minutes in an ice bath, crystallization took place. The precipitate was collected by filtration, washed several times with water, and recrystallized from acetone–water. The product was obtained as fine white needles, mp 209.5–211.0°, 0.7 g (30%). An analytical sample was recrystallized from methanol: mp 212.5–213.0°; ir (Nujol) 3410, 1655, 1530, 1400, 1100, 1090, and 700 cm⁻¹.

Anal. Calcd for C₁₈H₂₂N₂O₄Si: C, 60.31; H, 6.19; N, 7.82. Found: C, 60.24; H, 5.99; N, 7.49.

Method B. 4,4'-Dimethylsilylbis(2-nitrophenol) (2a) was catalytically hydrogenated in a Parr apparatus under the same conditions as were used to prepare 3, with the exception that the solvent was acetic anhydride. After uptake of the theoretical quantity of hydrogen, the catalyst was removed by filtration and the excess acetic anhydride was removed by rotary evaporation. The residue was recrystallized from aqueous acetone to give 4,4'-dimethylsilylbis(2-acetamidophenol), mp 209–212°, in 73% yield. A small sample, recrystallized from methanol, had an ir spectrum identical with that of 4a prepared by method A and exhibited no depression of mixture melting point.

4,4'-Dimethylsilylbis(2-acetamidophenol) Diacetate (5a). 4,4'-Dimethylsilylbis(2-aminophenol) (1.0 g, 3.66 mmol) was re-

fluxed for 6 hr with 50 ml of acetic anhydride. The reaction mixture was evaporated to dryness and the residue was boiled with water. The resulting slurry was extracted with dichloromethane; the extracts were washed thoroughly with water and dried over Drierite. The residue obtained by evaporation of the filtered extracts was recrystallized from carbon tetrachloride to give 5a, 1.38 g (85.3%), as colorless needles: mp 149.5–151°; ir (KBr) 1780, 1710, 1365, 1250, 1180, 1100, and 780 cm⁻¹.

Anal. Calcd for C₂₂H₂₆N₂O₆Si: C, 59.71; H, 5.92; N, 6.34. Found: C, 59.77; H, 5.91; N, 6.19.

4,4'-Dimethylsilylbis(2-benzamidophenol) (4b). 4,4'-Dimethylsilylbis(2-aminophenol) (3, 0.4 g, 1.46 mmol) was slurried in a mixture consisting of 10 ml of dimethylacetamide and an equal amount of carbon tetrachloride. Benzoyl chloride (0.41 g, 2.92 mmol) dissolved in 15 ml of carbon tetrachloride was added while the mixture was stirred in ice. The solution was further stirred in the cold, after addition of sufficient carbon tetrachloride to dissolve the solids. After about 1 hr, 50 ml of ethanol was added and the reaction mixture warmed to room temperature. The volatiles were evaporated and the remaining orange-brown oil was stirred with petroleum ether and water until it crystallized. The brownish crude product was recrystallized from acetone–water with decolorizing charcoal. Fine yellowish crystals of 4b (0.703 g, 57%) were obtained: mp 205–206°; ir (Nujol) 3420, 3400, 1640, 1540, 1530, 1400, and 700 cm⁻¹.

Anal. Calcd for C₂₈H₂₆N₂O₄Si: C, 69.75; H, 5.40; N, 5.81. Found: C, 69.43; H, 5.64; N, 5.69.

4,4'-Dimethylsilylbis[2-(*p*-anisamido)phenol] (4c). This compound was prepared by the foregoing method starting with *p*-anisoyl chloride (Eastman 2668). It was obtained in 63% yield as a yellowish solid by recrystallization from ethanol–water: mp 245–246°; ir (Nujol) 3410, 2950, 2840, 1640, 1605, 1535, 1505, 1495, and 1255 cm⁻¹; NMR (DMSO-*d*₆) δ 7.4 (m, 14 H), 3.75 (s, 6 H), and 0.35 ppm (s, 6 H).

Anal. Calcd for C₃₀H₃₀N₂O₆Si: C, 66.40; H, 5.57; N, 5.16. Found: C, 66.10; H, 5.71; N, 5.00.

4,4'-Dimethylsilylbis(2-benzamidophenol) Dibenzoate (5b). 4,4'-Dimethylsilylbis(2-aminophenol) (4, 0.4 g, 1.46 mmol) was dissolved in 10 ml of dimethylacetamide and cooled in an ice–salt bath. Benzoyl chloride (0.41 g, 2.92 mmol) in 10 ml of carbon tetrachloride was added with stirring. Additional carbon tetrachloride was added to dissolve the slurry that formed. After 1 hr the solution was removed from the bath and 10 ml of ethanol was added. It was then evaporated to an orange-brown oil which crystallized on stirring with water and petroleum ether. The product was recrystallized from acetone–water to give yellowish needles: 0.4 g (57%); mp 216–217°; ir (KBr) 3200–3500 (broad), 2950, 1730, 1645, 1515, 1480, 1390, 1240, 1035, 800, and 700 cm⁻¹; NMR [(CD₃)₂CO] δ 10.27 (s, 2 H), 8.1 (m, 6 H), 7.6 (d, 10 H), and 0.7 (s, 6 H).

Anal. Calcd for C₄₂H₃₄N₂O₈Si: C, 73.05; H, 4.96; N, 4.06. Found: C, 73.01; H, 5.06; N, 3.96.

Thermal Analysis of 5b. 4,4'-Dimethylsilyl(2-benzamidophenol) dibenzoate (5b, 101 mg, 0.146 mmol) was charged to the pan of a thermobalance and heated by increments under a nitrogen flow until a significant weight loss began (between 200 and 250°). The temperature was maintained at 250° for 25 min, and was then increased to 275° for an additional 25 min. At the end of this time the rate of loss had become slow and heating was terminated. The total weight loss was 40 mg; elimination of two molecules of benzoic acid to form 6b corresponds to 35.6 mg. The amber glassy residue which remained in the pan was recrystallized from ethanol–water. It proved to be identical with 6b by mixture melting point and ir spectra. Examination of the sublimate deposited in the thermobalance suggested that it consisted of benzoic acid mixed with a small amount of 6b. The benzoic acid was separated from the sublimate by recrystallization and its identity established by comparison with an authentic sample.

5,5'-Dimethylsilylbis(2-methylbenzoxazole) (6a). 4,4'-Dimethylsilylbis(2-acetamidophenol) diacetate (5a, 0.34 g, 0.77 mmol) was refluxed for 1 hr in a small distilling flask (oil bath at 230°) and was then distilled at 10 mm. The distillate solidified and was recrystallized from acetone–hexane to give 6a (0.2 g, 80%) as a fine white powder: mp 111.5–113.5°; ir (KBr) 3050, 2960, 1610, 1570, 1410, 1275, 1240, 1180, 1070, 930, 920, 820, 785, 665, and 400 cm⁻¹.

Anal. Calcd for C₁₈H₁₈N₂O₂Si: C, 67.05; H, 5.63; N, 8.69. Found: C, 67.05; H, 5.84; N, 8.43.

Thermal Stability of 6a. Two portions of the distillate (6a) were sealed in Pyrex tubes at 0.1 mm. One tube was heated at 320° for 3 hr and the other at 515° for 0.5 hr. A slight discoloration was

noted in the sample heated to the higher temperature. The contents were otherwise identical in melting point and ir spectra with the original 6a.

5,5'-Dimethylsilylbis(2-phenylbenzoxazole) (6b). 4,4'-Dimethylsilylbis(2-benzamidophenol) dibenzoate (**5b**, 1.6 g, 2.32 mmol) was placed in a 100-ml three-neck round-bottom flask provided with a metal bath, cold finger, connections for nitrogen flow, and an outlet cold trap. The reaction mixture was heated under identical conditions as previously described for the thermal analysis of **5b**. The residue was dissolved in chloroform and extracted three times with 5% sodium bicarbonate solution and finally twice with water. The chloroform layer was separated, dried (Drierite), filtered, and evaporated to dryness. The product was recrystallized twice from absolute ethanol and from carbon tetrachloride-hexane (1:1). **6b** (8.86 g, 83%) was obtained as white needles: mp 148–148.5°; ir (KBr) 3040, 2960, 1610, 1550, 1485, 1445, 1325, 1280, 1265, 1230, 1065, 1050, 1020, 920, 810, 800, 775, 705, 690, and 420 cm^{-1} ; NMR (CCl_4) δ 8.4 (m, 4 H), 8.2 (s, 2 H), 7.6 (m, 10 H), 0.9 ppm (s, 6 H); mass spectrum m/e 446 (M^+), 431, 254, 222, 215.

Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_2\text{Si}$: C, 75.31; H, 4.97; N, 6.27. Found: C, 75.40; H, 4.76; N, 6.19.

Thermal Analysis of 6b. A 5-mg sample of **6b** was sealed in a Pyrex capillary tube and run on a differential scanning calorimeter using an empty sealed Pyrex capillary as reference. The instrument was operated under nitrogen at a heating rate of 50°/min to a maximum temperature of 550°. With the exception of the expected melting endotherm at 149° the DSC scan exhibited no additional features.

Registry No.—1, 2915-36-8; **2a**, 54677-68-8; **2b**, 54677-69-9; **2c**, 54677-70-2; **3**, 54677-71-3; **4a**, 54677-72-4; **4b**, 54677-73-5; **4c**,

54677-74-6; **5a**, 54677-75-7; **5b**, 54677-76-8; **6a**, 54677-77-9; **6b**, 53543-27-4; acetic anhydride, 108-24-7; benzoyl chloride, 98-88-4; *p*-anisoyl chloride, 100-07-2.

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