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PREPARATION OF DIMETHYLSILYLENEBISBENZOXAZOLES

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Organic derivatives and precursors of the novel bisbenzoxazole dimethylsilanes were prepared as model compounds for projected thermally stable polymers containing this moiety. 4,4'-Dimethylsilylenebis-(2-aminophenol) was obtained by reduction of the corresponding dinitro compound, which was prepared by nitration of p,p'-dimethylsilylenediphenol. Amides and ester-amides were prepared by acylation of the aminophenols. Formation of the corresponding 5,5'-disubstituted silylenebisbenzoxazoles took rapidly on heating the ester-amides to temperatures in excess of 250°C.

5,5'-Dimethylsilylenebis(2-phenylbenzoxazole) and the 2-methyl analog are very thermally stable; neither underwent any change after heating to 320°C for 3 hours or 515°C for shorter periods.

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Technical Report

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PREPARATION OF DIMETHYLSILYLENEBISBENZOXAZOLES

by

John H. Cornell and David E. Remy

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FOREWORD

The mission of this laboratory calls for the development of new materials suitable for use in fabrics resistant to flame and thermal radiation. Pursuant to this objective, a synthetic route to the novel dialkylsilylenebisbenzoxazoles has been established. This moiety is thermally very stable, and, in appropriate compounds, should form polymers with outstanding thermal properties.

The polymer and fiber forming capabilities of materials produced here are currently being evaluated. This report is concerned with the preparation and properties of the new organosilicon intermediates and model compounds synthesized in the program.

This work was carried out under the Flame and Thermal Protection Section, Chemical Modification of Textiles Branch, Textile Research and Engineering Division, under Preparation of New Flexible Thermally Stable Fibers, Project 1T062105A329.

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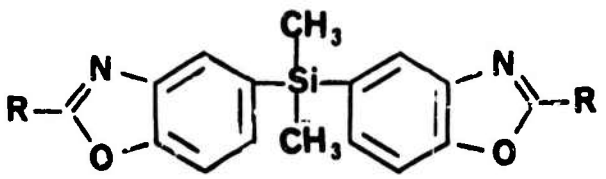
Preparation of Dimethylsilylenebisbenzoxazoles

I. Introduction

A. Purpose

The purpose of the present investigation is the preparation and study of dimethylbisbenzoxazole silanes, (I). These compounds and their precursors are potential starting materials and model compounds for the preparation of thermally stable polymers.



(Ia) R = CH_3—
(Ib) R = C_6H_5—

Organic aromatic or heterocyclic polymers are currently of great military interest for manufacture of flame resistant fabrics (e.g., Nomex, PBI, Kynol) for the protection of personnel or equipment exposed to a flame environment. The inclusion of the stable dimethylsilylene group in the polymer backbone is intended to confer outstanding properties of thermal protection and ease of processability.

B. Historical

Cornforth[1] has reviewed the chemistry of benzoxazoles and related systems. The benzoxazole nucleus was first synthesized by Ladenburg[2] in 1876 and the chemistry of the parent compound and its purely organic derivatives has been well established. Poly(azoles), including polybenzoxazoles, have recently been reviewed by Critchley[3]. These materials form a class of useful structural polymers which possess a high degree of thermal and chemical stability.

C. Thermal Stability

Thermal stability of the benzoxazoles was noted early: 2-phenylbenzoxazole boils at 314 - 317°C and 2-phenylphenanthroxazole can be distilled in small quantities at atmospheric pressure[4]. In recent years several investigators[5-12] prepared high temperature polymers in which the benzoxazole nucleus was included in the polymer backbone. In general these materials exhibited thermal stabilities roughly comparable to polybenzimidazole: thus after exposure at 500°C for one hour in nitrogen or air, representative weight losses were 1-5%[5].

D. Hydrolysis

The relative ease with which benzoxazole hydrolysis takes place varies greatly, depending on the degree and type of substitution. The parent unsubstituted benzoxazole hydrolyzes very readily whereas those substituted with bulky aromatic groups are resistant even to vigorous attack. 2-Phenylphenanthr(9,10)oxazole resists hydrolysis by both hydrochloric acid and alcoholic potassium hydroxide under strenuous conditions[4]. Incorporation of the benzoxazole moiety into a largely aromatic polymer also renders it practically invulnerable to hydrolysis[6].

E. Effect of Organosilicon Substitution

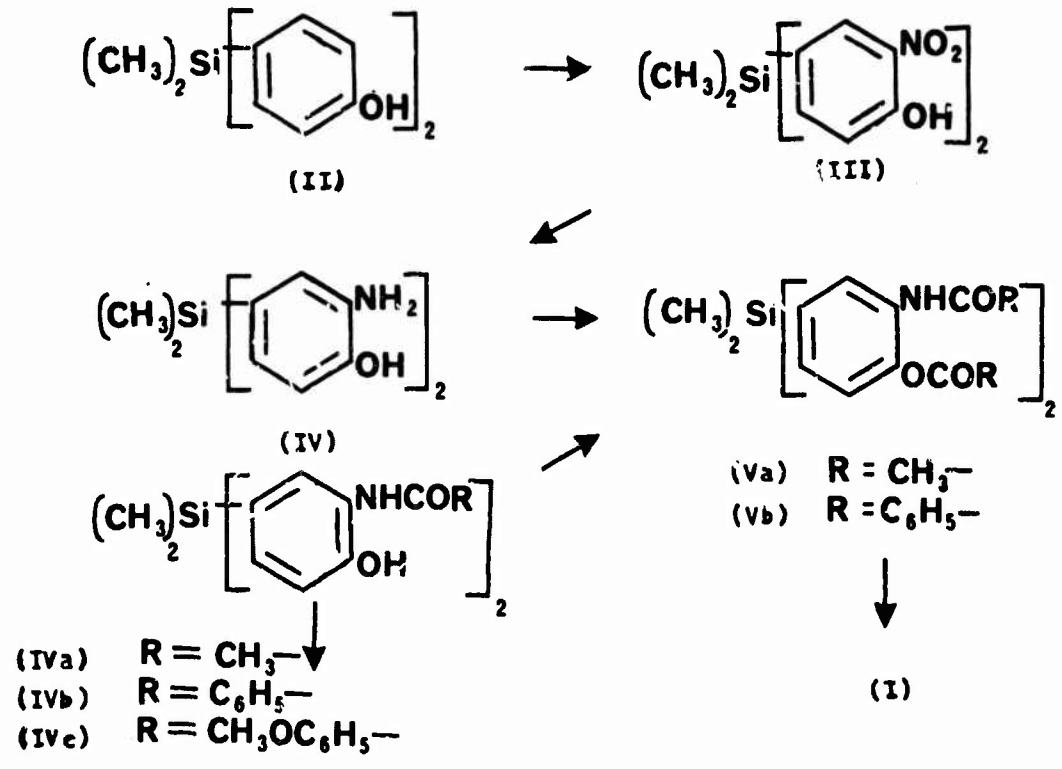
The effects of organosilicon substitution on benzoxazoles have not yet been studied. However, Kovacs[13] prepared several Schiff bases and benzimidazole derivatives containing the triphenylsilyl group, and compared their properties with the purely organic analogs. It was concluded that solubility in organic solvents was greatly improved by this substitution, without any corresponding impairment of thermal stability or melting point. Many high temperature resins prepared either from polybenzoxazoles or polybenzimidazoles are either insoluble or soluble only in concentrated sulfuric acid. Ease of fabrication or spinning would be greatly enhanced if solubility in organic solvents could be improved by organosilicon substitution.

II. Discussion

A. Synthetic Route

The following route was adapted for preparation of the new

series of silylenebisbenzoxazoles and precursors:



B. Starting Materials

The indicated route was chosen because of the availability of p,p'-dimethylsilylenediphenol. The starting material was generously made available by Dr. Wenzel Davidsohn, US Army Materiel and Mechanics Research Center, Watertown, Massachusetts, who has developed a relatively large scale method for its preparation from p-bromophenol, dimethylsilicon dichloride and butyllithium[14]. Preparation of p,p'-dimethylsilylenediphenol by other methods has been described[15-17].

C. Synthetic Intermediates

1. Preparation of 4,4'-Dimethylsilylenebis(2-nitrophenol)(III)

This compound was prepared in 60% yield by treatment of

p,p'-dimethylsilylenediphenol with a solution of 70% nitric acid in acetic anhydride at room temperature. Direct nitration with nitric acid in glacial acetic acid resulted in cleavage of the starting material; the main product was a mixture of ortho and para nitrophenols. Direct nitration of the analogous carbon compound, p,p'-isopropylidenediphenol, can be carried through without difficulty[18,19].

Bordwell and Garbisch[20] have shown that a solution of nitric acid in acetic anhydride under the reaction conditions consists largely of acetyl nitrate. It seems probable that acetyl nitrate generated *in situ* is responsible for the successful nitration of the silyl phenol. Purity of the starting material also has a marked effect on the success of the nitration step. Even under anhydrous conditions p,p'-dimethylsilylenediphenol slowly decomposes on storage. Presence of decomposition products in the starting material tends to cause tarry by-products which inhibit crystallization of the silyl nitrophenol, thus complicating the product isolation and reducing yield.

2. Structure and Properties of 4,4'-Dimethylsilylenebis(2-nitrophenol)

4,4'-Dimethylsilylenebis(2-nitrophenol), unlike the starting material, is very stable. It resisted acidic hydrolysis under successively more vigorous conditions. Cleavage was finally obtained by heating at 150° for 50 hours with concentrated hydrochloric acid in a sealed tube. Under these conditions ortho-nitrophenol was obtained cleanly and in good yield. In a control experiment under identical conditions 2,5-dinitrophenol gave at least seven different products which could be resolved by thin layer chromatography. These results suggested that the nitration product was indeed 4,4'-dimethylsilylenebis(2-nitrophenol) rather than the isomeric dimethylsilylene-4-(2,5-dinitrophenol)-4'-phenol.

Benzenediazonium chloride solutions cleave p,p'-isopropylidenediphenol and its homologs quantitatively under mild conditions to give para-hydroxyazobenzene and acetone (or a homologous ketone)[21,22]. In the present work, it was shown that p,p'-dimethylsilylenediphenol was also rapidly cleaved by cold benzenediazonium chloride solutions to give the same coupling compound. However, 4,4'-dimethylsilylenebis-(2-nitrophenol) is recovered unchanged under similar conditions.

Attempted brominolysis of 4,4'-dimethylsilylenebis(2-nitrophenol) in a sealed tube at 115°C failed, and the starting material was largely recovered. It is also stable to refluxing 20% sodium hydroxide for long periods. Cleavage with 57% hydrogen iodide led to complete

tarification of the reaction mixture from which no identifiable product could be isolated.

4,4'-Dimethylsilylenebis(2-nitrophenol) consumes two equivalents of 0.01 M sodium hydroxide per mole when titrated in methanolic solution. A pH meter was used to determine the equivalence point, which in this case occurred at pH 9.3 for both phenolic groups. Dimethylsilylene-4-(2-nitrophenol)-4-phenol consumed a single equivalent of base; the higher pH required to observe the second equivalence point was not obtained under these conditions.

These results are further evidence that 4,4'-dimethylsilylenebis-(2-nitrophenol) is in fact symmetrically nitrated, since the other structure would be expected to consume a single equivalent of base as observed with the foregoing mononitrated diphenol.

3. Spectral Data on 4,4'-Dimethylsilylenebis(2-nitrophenol)

The ir spectrum of (III) conforms to the structure 4,4'-dimethylsilylenebis(2-nitrophenol), but is insufficient to differentiate between this structure and its possible isomers.

The early nmr spectra of (III) at 60 mhz were incompletely resolved, and the aromatic protons exhibited a singlet, with a symmetrical quartet upfield. This spectrum could be interpreted as the superposition of the A_2 and $A_2'B_2'$ patterns, corresponding to 1,3,4,5, and 1, 4 substitutions respectively in the rings, and suggested the structure might be dimethylsilylene-4-(2,6-dinitrophenol)-4'-phenol.

However at 100 mhz or with improved resolution at 60 mhz, splitting of the singlet and downfield doublets was observed, forming three new doublets. This new pattern is consistent with two equivalent ABX systems (1,3,4 substitution in both rings) and therefore confirms the postulated structure for (III), 4,4'-dimethylsilylenebis(2-nitrophenol).

The mass spectrum of this compound showed an abundant molecular ion which confirmed its molecular weight. The fragmentation pattern is consistent with its postulated symmetrical structure.

4. Preparation of 4,4'-Dimethylsilylenebis(2-aminophenol)(IV)

This intermediate was prepared in excellent yield by hydrogenation of (III) in ethanol in a Parr shaker using ten percent palladium on charcoal as catalyst.

The aminophenol(IV) is quite stable in crystalline form, and can

be kept for a considerable period without noticeable decomposition. In solution or as a syrup it darkens rapidly on exposure to air and light. Accordingly a novel method involving recrystallization from sulfurous acid was devised to purify and isolate this product. The excess sulfurous acid present acts as a mild reducing agent keeping the product in a constant reducing environment. This allows removal of the hydrogenation catalyst and purification of product without the decomposition encountered in the conventional methods. Removal of residual solvent and sulfur dioxide under mild conditions results in precipitation of the 4,4'-dimethylsilylenebis-(2-aminophenol) in a highly crystalline, analytically pure form.

As an alternate to this procedure, the hydrogenation can be conducted in an excess acetic anhydride. Under these conditions the product isolated is 4,4'-dimethylsilylenebis(2-acetaminophenol) (IVa), a stable precursor for many derivatives, including benzoxazoles. This compound can also be prepared by selective acetylation of the aminophenol by acetic anhydride in aqueous sodium acetate-acetic acid buffer.

Chemical reduction of the nitro groups was not attempted, since the reduction of the corresponding carbon analog with stannous chloride gave only intractable complexes[18].

5. 5,5'-Dimethylsilylenebis-(2-methylbenzoxazole)(Ia)

Refluxing the aminophenol, (IV), with excess acetic anhydride gave 4,4'-dimethylsilylenebis-(2-acetaminophenol) diacetate (Va) which upon distillation at about 220°C/10 mm lost the elements of acetic acid to give 5,5'-dimethylsilylenebis-(2-methylbenzoxazole)(Ia).

Characteristic infrared bands for the benzoxazole system[23] and disappearance of the amide and ester bands of the precursor (Va) indicated ring closure. Although the bis-silylene benzoxazole (Ia) is somewhat volatile at high temperatures, it is very thermally stable. This compound was recovered unchanged after heating to 515°C in a sealed tube for 30 minutes.

6. Preparation of 5,5'-Dimethylsilylenebis-(2-phenylbenzoxazole)(Ib)

Treatment of 4,4'-dimethylsilylenebis-(2-aminophenol), (IV), with the stoichiometric quantity of benzoyl chloride in pyridine gave 4,4'-dimethylsilylenebis-(2-benzamidophenol) dibenzoate, (Vb), a precursor for 5,5'-dimethylsilylenebis-(2-phenylbenzoxazole), (Ib). The latter compound was formed by elimination of two moles of benzoic acid per mole of precursor by heating (Vb) in programmed increments between 200 and 275°C in a thermobalance under nitrogen sweep. The

bisbenzoxazole was also prepared on a larger scale in more conventional equipment under essentially the same conditions.

The assigned structure of 5,5'-dimethylsilylenebis-(2-phenylbenzoxazole) is supported by the nmr spectrum and by the disappearance of ester and amide bands which were present in the original spectrum of the precursor, (Vb). Further support is given by the appearance of new bands characteristic of the benzoxazole nucleus[23].

The mass spectrum exhibits a predominant molecular ion at 446 amu, corresponding to the calculated molecular weight. There are weak fragment ions corresponding to cleavage of one or more methyl groups and/or a phenylbenzoxazole moiety. However, the abundance of the molecular ion in relation to the minor amounts of fragmentation ions is evidence for the high stability of the silicon benzoxazole system.

III. Experimental

A. General

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 mass spectrometer.

Melting points were determined by the capillary method in a Thomas-Hoover apparatus and are not corrected. TLC medium was Eastman Chromagam silica gel sheets with fluorescent indicator (Eastman No. 6060).

The majority of the elemental analyses were obtained with a F&M 185 CHN Analyzer although some were performed by Midwest Microchemical Laboratories.

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

B. Preparative

1. Preparation of 4,4'-Dimethylsilylenebis-(2-nitrophenol)(III)

Freshly prepared dimethylsilylenediphenol (14.07 g, 0.0575 mole) was briefly degassed under reduced pressure and dissolved in 100

ml of acetic anhydride. The solution was cooled by stirring in a dry ice/acetone bath for about 45 minutes.

During this time the nitrating solution was prepared by adding concentrated nitric acid (10.8 g, 0.160 mole) slowly with stirring and cooling to 75 ml of acetic anhydride. During the addition the temperature was maintained between 35 and 40°C. The nitrating solution was cooled to just above the appearance of crystals, and was added dropwise to the stirred cooled solution of dimethylsilylenediphenol. The addition required about 90 minutes at the end of which the bath was removed and the stirring continued for 15 minutes. The reaction mixture was poured onto 800 ml of cracked ice and 600 ml of water, stirred, and the hydrolysis 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 (2.25 in ID, 1.5 ft.) packed with silica gel (Grace 950, 60-200 mesh) with benzene as solvent.

The product, together with a trace of ortho-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°C.

The foregoing product is of adequate purity for the reduction step; however, pure 4,4'-dimethylsilylenebis(2-nitrophenol) was obtained by recrystallization of the crude product from n-hexane. The product crystallized very slowly in the absence of seed crystals to yield long yellow needles. With seed crystals rapid crystallization took place.

4,4'-Dimethylsilylenebis-(2-nitrophenol)

mp 101.0-101.5; ir ν_{max}^{KBr} 3250, 3030(vw), 2950(w), 1610(s), 1520(s), 1310(vs), 1245, 1155,895, 670 cm^{-1}; nmr(CCl_4) δ 0.66(s,6H, 7.55 (m,4H,Jbc 8.1), 8.25(d,2H,Jac 1.5), 10.7(s,2H); uv $\lambda_{Max}^{CH_3OH}$ 225 nm (ϵ =15,700), λ_{max}^{NaOH} 249nm (ϵ =39,700); ms m/e 334(M), 319, 303, 289, 273, 258, 227, 212, 196, 180. 135, 85, [illegible], 55

Anal. Calcd. for $C_{14}H_{14}O_6N_2Si$: C, 50.28; H, 4.22: N, 8.38 Found: C, 50.10: H, 4.20: N, 8.75

Titration Calcd. 16.9ml; required 16.5ml 0.01M NaOH to titrate 19.77mg (III) as dibasic acid: pH 9.7 at equivalence point.

2. Acidic Hydrolysis of 4,4'-Dimethylsilylenebis-(2-nitrophenol) (III)

A small sample (0.10 g, 0.3 mmol) of (III) was heated with 3 ml of concentrated (36N) hydrochloric acid in a sealed tube for 50 hours at 150°C. 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 (magnesium sulfate) extracts indicated presence of only one component, a nitro compound having the same Rf as ortho-nitrophenol. Evaporation of the extracts gave yellow crystals of ortho-nitrophenol (0.06 g, 84%) mp 42.5-43.5°C; no melting point depression with authentic ortho-nitrophenol (Eastman No. 191), mp 44.5-45°C, was noted and the two samples had identical infrared spectra.

A control experiment was run under identical conditions to determine stabilities of the expected nitro products from the alternate isomer under these rather vigorous conditions. A sample of 2,6-dinitrophenol (Aldrich D19,880) when subjected to the foregoing treatment was completely destroyed, giving at least seven different compounds (tlc). Most were yellow nitro compounds, including one whose Rf value coincided with that of ortho-nitrophenol.

Thus 4,4'-dimethylsilylenebis-(2-nitrophenol) underwent acidic hydrolysis cleanly under rigorous conditions to give only ortho-nitrophenol and dimethylsilicone polymer. The relatively complex nature of the hydrolyzate in the case of 2,6-dinitrophenol tends to further support structure (III).

3. Attempted Cleavage of 4,4'-Dimethylsilylenebis-(2-nitrophenol) with Other Reagents

Diazonium Chlorides

4,4'-Dimethylsilylenebis-(2-nitrophenol) (0.32 g, 0.96 mmole) failed to react with a slight excess benzenediazonium chloride at 0° in excess 10% sodium hydroxide. However, in a control experiment under similar conditions dimethylsilylenediphenol was instantly cleaved by benzenediazonium chloride to give para-hydroxyazobenzene and dimethylsilicone polymer.

Basic Hydrolysis

4,4'-Dimethylsilylenebis-(2-nitrophenol) (1.1 g, 3.4 moles)

was refluxed with 20% sodium hydroxide for 64 hours. The starting material was quantitatively recovered.

Bromodesilylation

4,4'-Dimethylsilylenebis-(2-nitrophenol)(0.16 g, 0.43 mmole) was treated for several days at room temperature with an excess of bromine in carbon tetrachloride. The starting material was quantitatively recovered unchanged.

4. Preparation of 4,4'-Dimethylsilylene(2-nitrophenol)phenol

Nitric acid, (70%), (3.61 g, 0.04 mole) was dissolved dropwise with stirring in 25 ml of acetic anhydride, maintaining the temperature between 25 and 35°C. The nitrating solution was added dropwise with stirring to 4.69 g, (0.0194 mole) of dimethylsilylene-diphenol dissolved in 200 ml of dry ether. During the addition, which required 0.5 hour, the reaction mixture was maintained at about -40°C by stirring in a dry ice/dichloromethane bath. The solution was allowed to warm to room temperature and stood overnight (16 hrs.). It turned from light yellow (2 hrs.) to amber at the end of this time.

The solution was poured on water, stirred for 1.5 hours 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 (1.25 ft., 1 in. ID) with dichloromethane as developing solvent. The small forerun (245 ml) contained mostly 4,4'-dimethylsilylenebis-(2-nitrophenol)(III), but was soon followed by a larger fraction (620 ml) containing 4,4'-dimethylsilylene-(2-nitrophenol) phenol. This fraction, (2.1g), (36 percent) partly solidified on standing, and tlc showed it to be almost pure product, mp 82-84°C (2.1 g, 35%). An analytical sample was purified by recrystallization from n-hexane.

4,4'-Dimethylsilylene (2-nitrophenol)phenol

mp 84-85 C; ir $\nu_{MAX}^{CDCl_3}$ 3270(vw), 1625(vs), 1575, 1525(vs), 1480, 1400, 1310(s), 1240(s), 1190, 1160, 1110, 1080, 813, 786, cm^{-1}; nmr (CCl_4) δ 0.4(s,6H), 7.1(m,6H), 8.1(d,2H), 10.6(s,2H); uv $\lambda_{max}^{CH_3OH}$ 232nm(ϵ=19,400); λ_{max}^{NaOH} 252nm (ϵ=35,900)

Anal. Calcd. for $C_{14}H_{15}O_4NSi$: C, 58.11; H, 5.23; N, 4.84: MW 289.35

Found: C, 58.26; H, 5.47; N, 4.95; MW (Osmometer, $CHCl_3$) 281.

Titration: Calcd. 10.0ml; required 9.9 ml 0.01 M NaOH to titrate 19.93 mg (IIIa) as monobasic acid; pH 9.5 at equivalence point.

5. Conversion of 4,4'-Dimethylsilylene(2-nitrophenol)phenol to (III)

4,4'-Dimethylsilylene(2-nitrophenol)phenol (0.25 g, 0.86 mmole) 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 20-25°C. The nitrating solution was added dropwise to the solution of the phenol at -5 to -10°C with stirring. The reaction mixture was allowed to warm to 0°C and held at that temperature for one hour, and then for one hour at 20°C. At this time tlc indicated complete conversion of the starting material. The reaction mixture was poured into cold water and stirred one hour, during which time it became quite warm. After cooling, yellow crystals separated which were collected by filtration (0.20 g, 70%) mp 93-100.5°C. After recrystallization from n-hexane, this product had the same mp as 4,4'-dimethylsilylene-bis (2-nitrophenol), and produced no depression in a mixed melting point with an authentic sample. Both samples exhibited identical ir spectra and Rf on tlc.

6. Preparation of 4,4'-Dimethylsilylenebis(2-nitrophenol) Diacetate

4,4'-Dimethylsilylenebis(2-nitrophenol), (1.1 g, 4.53 mmoles) was refluxed for four hours 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.

4,4'-Dimethylsilylenebis(2-nitrophenol) Diacetate

mp 119.5-120.0 -- ν^{KBR} 3080(w), 2960(w), 1775(vs), 1600(s), 1530(vs), 1350(s), max 1190(vs), 1085(vs), 920(vs), 885, 825(s), cm^{-1}.

Analysis: Calcd. for: $C_{18}H_{18}N_2O_8Si$; C, 51.67; H, 4.04; N, 6.70.

Found: C, 51.40; H, 4.12; N, 6.75.

7. Preparation of 4,4'-Dimethylsilylenebis(2-aminophenol)(IV)

4,4'-Dimethylsilylenebis(2-nitrophenol)(III) (4.0 g, 0.012

mole) was dissolved in 250 ml of dry ethyl ether. Approximately 100 mg 10% palladium on charcoal was suspended in 10 ml 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 three hours.

A saturated solution of sulfurous acid was prepared by bubbling sulfur dioxide through water and 100 ml was added to the hydrogenation solution. This dissolved precipitated (IV) 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, mp 150-151°C. A second crop 1.1 g, mp 148-150°C was obtained by decolorization of the filtrate with charcoal, further concentration and adjustment to pH 6 with dilute ammonium hydroxide. The combined yield of (IV) was 2.3 g (70%).

4,4'-Dimethylsilylenebis(2-aminophenol)(IV)

mp 150-151 ir ν_{max}^{KBR} 3360, 3290(w), 2950(w), 1500(s), 1270(vs), 805(s), 775(s)$_{cm}^{-1}$ nmr (DMSO-d_6) δ 0.3 (s, 6H), 6.6 (m, 6H)

Analysis: Calc. for: $C_{14}H_{19}N_2O_2Si$: C, 61.05; H, 6.95; N, 10.17

Found: C, 61.40; H, 6.60; N, 10.15.

8. Preparation of 4,4'-Dimethylsilylenebis(2-acetamidophenol)(IVa)

Method A. 4,4'-Dimethylsilylenebis(2-aminophenol)(IV) (1.3 g 4.74 mmoles) was dissolved in dilute hydrochloric acid and the brownish solution was decolorized by stirring with activated carbon at about 50°C. The filtered solution at 50°C was shaken with 1.0 g (10 mmoles) of acetic anhydride, to which was immediately added an excess of saturated sodium acetate solution with further shaking. After stirring 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°C (0.7 g, 30%). An analytical sample was recrystallized from methanol.

Method B. 4,4'-Dimethylsilylenebis(2-nitrophenol)(III) was catalytically hydrogenated in a Parr apparatus under the same conditions as were used to prepare (IV), 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 removed by rotary evaporation. The residue was recrystallized from aqueous acetone to give 4,4'-dimethylsilylenebis-(2-acetamidophenol) mp 209-212°C, in 73% yield. A small sample recrystallized from methanol was identical with an authentic sample, exhibiting the same ir spectra and no depression of mixed melting point.

4,4'-Dimethylsilylenebis(2-acetamidophenol)

mp 212.5-213 C, ir ν_{max}^{Nujol} 3410, 1655, 1530, 1400, 1100, 1090, 700 cm^{-1}

Anal. Calc. for $C_{18}H_{22}N_2O_4Si$: C, 60.31; H, 6.19; N, 7.82.

Found: C,60.24; H, 5.99; N, 7.49.

9. 4,4'-Dimethylsilylenebis(2-acetamidophenol) diacetate(Va)

4,4'-Dimethylsilylenebis(2-aminophenol), (1 g,3.66 mmole) was refluxed for 6 hours with 50 ml of acetic anhydride. The reaction mixture was evaporated to dryness and the residue 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 (Va), (1.38 g ,85 3%) as colorless needles, mp 149.5-151°.

4,4'-Dimethylsilylenebis(2-acetamidophenol) diacetate

mp 149.5-151 ir ν_{max}^{KBr} 1780(s), 1710(vs), 1365(s), 1250(vs), 1100, 780 cm^{-1}.

Anal. Calc. for $C_{22}H_{26}N_2O_6Si$: C, 59.71; H, 5.92; N, 6.34.

Found: C, 59.77; H, 5.91; N, 6.19.

10. 4,4'-Dimethylsilylenebis(2-benzamidophenol)(IVb)

4,4'-Dimethylsilylenebis(2-aminophenol)(IV) (0.4 g,1.46 mmoles) 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 mmoles) 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 one hour, 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 (IVc), (0.703 g 57%) were obtained.

4,4'-Dimethylsilylenebis(2-benzamidophenol)

mp 205-206 ir ν_{max}^{Nujol} 3420(w), 3400(w), 1640(s), 1540, 1530(s), 1400, 700(s)cm^{-1}.

Anal. Calc. for $C_{28}H_{26}N_2O_4Si$: C, 69.75; H, 5.40; N, 5.81.

Found: C, 69.43; H, 5.64; N, 5.69.

11. 4,4'-Dimethylsilylenebis(2-(p-anisamido)phenol)(IVc)

This compound was prepared by a method similar to that for (IVb) starting with p-anisoyl chloride (Eastman 2668). It was obtained in 63% yield as a yellowish solid (mp 245-246°C) by recrystallization from ethanol-water.

mp 245-246° ir ν_{max}^{Nujol} 3410, 2950(w), 2840(w), 1640, 1605(s), 1535, 1505(s), 1495, 1255(s)cm^{-1}, nmr (DMSO-d_6) δ 0.35 (s, 6H), 3.75 (s, 6H), 7.4 (m, 14H)

Anal. Calc. for $C_{30}H_{30}N_2O_6Si$: C, 66.40, H, 5.57; N, 5.16.

Found: C, 66.1; H, 5.71; N, 5.00.

12. 4,4'-Dimethylsilylenebis(2-benzamidophenol) dibenzoate(Vb)

4,4'-Dimethylsilylenebis(2-aminophenol) (IV), (0.4 g 1.46 mmoles was dissolved in 10 ml of dimethylacetamide, and cooled in an ice-salt bath. Benzoyl chloride (0.41 g, 2.92 mmoles) in 10 ml of carbon tetrachloride was added with stirring. Additional carbon tetrachloride was added to dissolve the slurry that formed. After 1 hour the solution was removed from the bath and 10 ml of ethanol 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%).

4,4'-Dimethylsilylenebis(2-benzamidophenol) dibenzoate

mp 205-206°C ir ν_{max}^{KBr} 3200-3500 (broad) 2950(w), 1730(vs), 1645(s), 1515(vs), 1480(vs), 1390(s), 1240(vs), 1035(s), 800, 700(vs)cm^{-1} nmr ($(CD_3)_2CO$) δ 10.27(s), 2H, 8.1(m), 6H, 7.6(d), 10H, and 0.7(s), 6H

Anal. Calc. for $C_{42}H_{34}N_2O_6Si$: C, 73.05; H, 4.96; N, 4.06.

Found C, 73.0; H, 5.06; N, 3.96

Thermal Analysis: See paragraph 14.

13. 5,5'-Dimethylsilylenebis(2-methylbenzoxazole)(Ia)

4,4'-Dimethylsilylenebis(2-acetamidophenol)diacetate (Va), (0.34 g, 0.77 mmole) was refluxed for one hour 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 (Ia) (0.2 g, 80%) as a fine white powder, mp 111.5-113.5°C.

5,5'-Dimethylsilylenebis(2-methylbenzoxazole)

mp 111.5-113.5° ir ν_{max}^{KBr} 3050(w), 2960(w), 1610(s), 1570(s), 1410(s), 1275(vs), 1240(vs), 1180(s), 930, 920, 820(vs), 785(s), 665, 400

Anal: Calc. for $C_{18}H_{18}N_2O_2Si$: C, 67.05; H, 5.63; N, 8.69.

Found: C, 67.05; H, 5.84; N, 8.43.

Thermal Stability of (Ia) - Two portions of the distillate (Ia) were sealed in Pyrex tubes at 0.1 mm. One tube was heated at 320°C for three hours and the other at 515 C for 0.5 hour. A slight discoloration was noted in the sample heated to the higher temperature. The contents were otherwise identical in mp and ir spectra to the original (Ia).

14. 5,5'-Dimethylsilylenebis(2-phenylbenzoxazole)(Ib)

4,4'-Dimethylsilylenebis(2-benzamidophenol) dibenzoate(Vb), (1.6 g, 2.32 mmole) was placed in a 100-ml 3-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 incrementally from 210 C to 260 C for a total of two hours, during which time a sublimate of benzoic acid formed. The residue was dissolved in chloroform, 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 twice from carbon tetrachloride-hexane (1:1); Ib was obtained as white needles, mp 148-148.5°C, (0.86 g, 83%).

mp 148-148.5° ir ν_{max}^{KBr} 3040, 2960(w), 1610, 1550(s), 1485, 1445, 1325, 1280, 1265, 1230(vs), 1065(s), 1050(vs), 1020, 920, 810(vs), 800(vs), 775(vs), 705(vs), 690(s), 420 cm^{-1}.

nmr (CCl_4) δ 0.9 (s, 6H), 7.6 (m, 10H), 8.2 (s, 2H), 8.4 (m, 4H); ms m/e 446 (M+), 431, 254, 222, 215.

Anal.: Calc. for $C_{28}H_{22}N_2O_2Si$ (446.56): C, 75.31; H, 4.97; N, 6.27.

Found: C, 75.40; H, 4.76; N, 6.19.

Thermal Analysis: 4,4'-Dimethylsilylene(2-benzamidophenol) dibenzoate (Vb), (101 mg, 0.146 mmole) was charged to the pan of a thermobalance and heated by increments under a nitrogen flow until a significant weight loss began (between 200-250oC). The temperature was maintained at 250o C for 25 minutes, and was then increased to 275°C for an additional 25 minutes. 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 (Ib) corresponds to 35.6 mg. The amber glassy residue which remained in the pan was recrystallized from ethanol-water. It proved to be identical to (Ib) by mixed mp and ir spectra.

Examination of the sublimate deposited in the thermobalance suggested that it consisted of benzoic acid mixed with a small amount of (Ib). The benzoic acid was separated from the sublimate by recrystallization and its identity established by comparison with an authentic sample.

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