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SYNTHESIS OF TRICYCLIC COMPOUNDS WITH SULFUR AND SILICON HETEROATOMS IN THE CENTRAL RING

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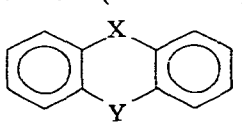
Summary

The synthesis of tricyclic derivatives which contain both silicon and sulfur in a central six-, seven- and eight-membered ring are described. Phenothiasilin-5,5-dioxides are prepared by treatment of $(o\text{-}LiC_6H_4)_2SO_2$ with dichlorosilanes. Reduction of the sulfone group is described as well as attempts to introduce aminopropyl substituents at silicon. Thiasilepins are prepared from the Grignard reagent of $(o\text{-}BrC_6H_4CH_2SC_6H_4Br\text{-}o)$ and reactions of this ring system are described. Reaction of $Me_2Si(C_6H_4CH_2Br\text{-}o)$ with Na_2S gave a thiasilocin derivative.

Introduction

Tricyclic derivatives (I) which contain appropriately functionalized side chains bonded to the central ring frequently exhibit psychotropic activity especially those which contain a side chain with a nitrogen functional group. Such derivatives may contain one or more heteroatoms in the central ring and in general these heteroatoms are O, N or S. We have previously reported the synthesis of silicon analogs of phenothiazine (Ia: X = S, Y = NR), thioxanthenes (Ib: X = S, Y = CH=CHR) and imipramine (Ic: X = CH_2CH_2, Y = NR)



(I)

[1—3]. These studies have been expanded to include derivatives which contain both silicon and sulfur heteroatoms in six-, seven- and eight-membered rings. The syntheses and reactivities of these systems are described in this report.

Preparation of thiasilins was first reported by Gilman and Wittenberg; low yields were obtained by heating diphenylsilane and thianthrene (Id: X = Y = S), a method which was also employed to prepare phenazasilins [4]. Later it was

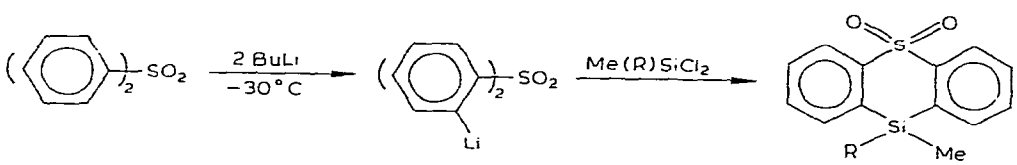
discovered that the low temperature reaction of diphenylsulfone with 2 mol of BuLi produced 2,2′-dilithiodiphenylsulfone which produced thiasilins upon reaction with R_2SiCl_2 [5]. After the initiation of our studies a third approach to the synthesis of thiasilins was published which involves bis(2-bromophenyl) sulfide, a tediously prepared derivative, as the precursor to the six-membered ring systems [6,7].

Although both thiepins [8] and silepins [3] are known, no tricyclic derivatives have been reported which contain both silicon and sulfur heteroatoms in the central ring nor have there been any reports of the formation of related thiasilocins.

Results and discussion

Initial efforts to generate thiasilins involved an exploration of the lithiation of commercially available sulfur derivatives. Monolithiation of diphenyl sulfide to give *o*-$LiC_6H_4SC_6H_5$ had been reported in the early literature [9]. Attempts to generate $(o\text{-}LiC_6H_4)_2S$ from $(C_6H_5)_2S$ and excess BuLi either at room temperature or below —20° C followed by quenching with Me_2SiCl_2 gave $(C_6H_5)_2S$ as the only isolated sulfur-containing derivative after hydrolysis work-up. Successful nuclear metalations of aryl sulfoxides have not been reported although dibenzothiophene-5-oxide is metallated in the 4-position by BuLi but reduction of the sulfoxide group occurs concurrently [10]. The reaction of diphenyl sulfoxide with BuLi in ether with added TMEDA at —20° C was briefly investigated. Carbonation and hydrolysis with dilute acid did not afford any isolable sulfur containing acid and starting material was recovered.

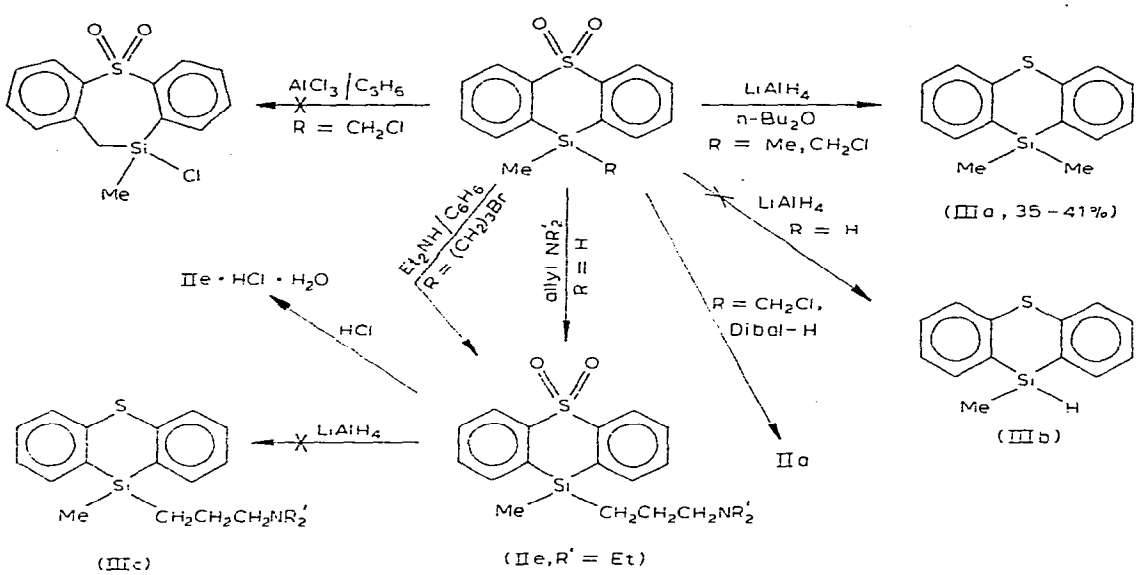
Thiasilin-5,5-dioxides (II) can be generated from diphenylsulfone and two mol BuLi at —30 to —20° C followed by quenching with a dichlorosilane (eq. 1) as originally reported by Gilman [5].



(IIa, R = Me (19%);
IIb, R = CH_2Cl (26%);
IIc, R = H (14%);
IId, R = $CH_2CH_2CH_2Br$)

The possibility of employing the thiasilin-5,5-dioxides as precursors to pharmacologically active derivatives and other ring systems was explored and is summarized in Scheme I. The sulfone group in IIa and IIb is reduced by $LiAlH_4$ in refluxing n-Bu_2O and not unexpectedly the chloromethyl group of IIb is also reduced by $LiAlH_4$. An attempt to reduce the sulfone group of IIb with a 5 molar excess of Dibal-H (diisobutylaluminum hydride) in refluxing benzene/toluene for 48 h resulted in reduction of the chloromethyl group and formation of IIa. Such conditions were employed to reduce $(C_6H_5)_2SO_2$ to $(C_6H_5)_2S$ [11]. Attempts to introduce a side chain at Si by hydride addition of IIc to *N*,*N*-dimethylallylamine in the presence of H_2PtCl_6, $Co_2(CO)_8$ or benzoyl

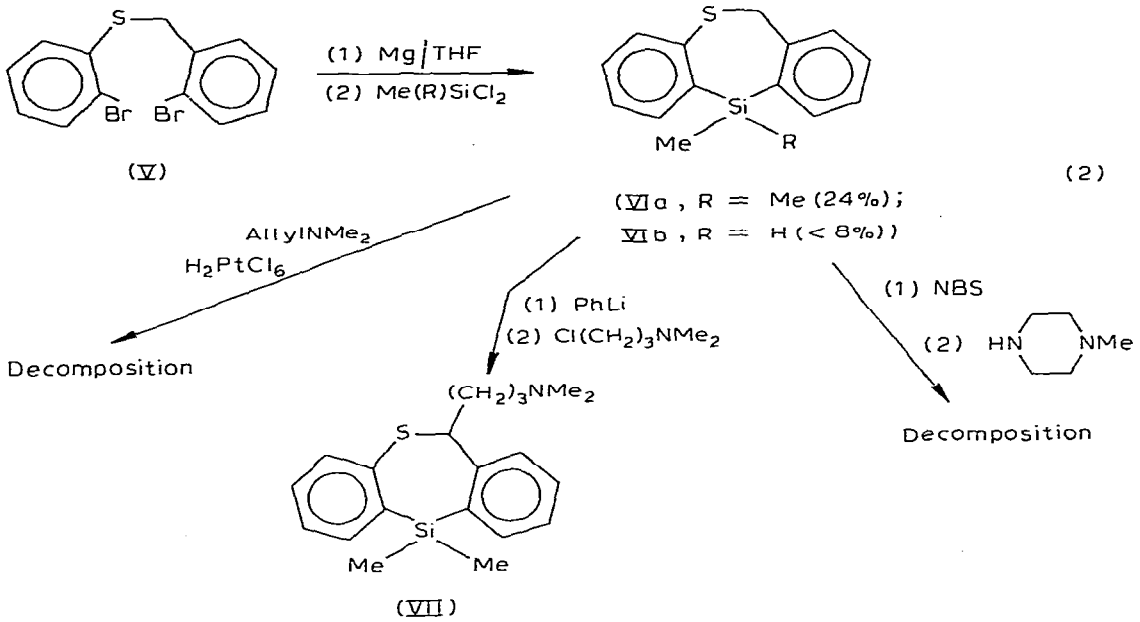
SCHEME 1



peroxide (with or without photolysis) were uniformly unsuccessful, and either starting material or decomposition products were recovered. Such addition reactions are known for the corresponding silaanthracene [2]. The formation of a thiasilindioxide (IIe) with a nitrogen functionalized side chain was eventually accomplished by reaction of IId with Et_2NH. The crystalline hydrochloride salt of IIe was obtained by bubbling dry HCl into an ether solution of IIe. Attempts to reduce the sulfone group of IIe with $LiAlH_4$ were unsuccessful.

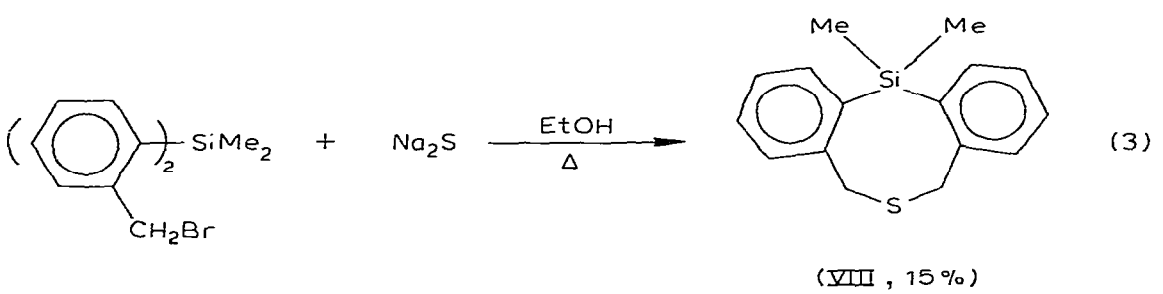
The chloromethyl derivative IIb is a potential precursor to the seven-membered ring system, 10,11-dihydro-5*H*-dibenzo[*b*,*f*][1,4]thiasilepin (IV) via an $AlCl_3$-catalyzed ring expansion [12]. However, attempts to generate IV were unsuccessful. It is probable that the sulfone group coordinates to $AlCl_3$ rendering the catalyst ineffective. Only starting material was obtained after hydrolytic work-up.

Formation of the thiasilepin, dihydrodibenzo[*b*,*e*][1,4]thiasilepin, isomeric to the framework in IV, was effected from the dibromide precursor, *o*-bromobenzyl *o*-bromophenyl sulfide (V). The dibromide was prepared by condensing *o*-bromothiophenol with *o*-bromobenzyl bromide. Our original efforts to generate the dilithio reagent by reaction of (*o*-$BrC_2H_4CH_2SC_6H_4Br$-*o*) with BuLi at room temperature or at −30° C followed by quenching with Me_2SiCl_2 did not result in the isolation of the desired cyclized product. Metallation at carbon atoms adjacent to sulfur atoms by RLi and ArLi are known [13] and it is probable that a mixture of lithiated products are obtained from V. The Grignard reagent of V could be generated and quenching with a dimethyldichlorosilane provided modest yields of the dihydrodibenzo[*b*,*e*][1,4]thiasilepin, VIa (eq. 2). An attempt to react the Grignard reagent generated from V with $MeSiHCl_2$ resulted in isolation of a mixture from which pure VIb could not be isolated and attempts to obtain a hydride addition product from the mixture resulted in decomposition. Similar hydride additions to crude silepins have



been utilized to introduce the *N*,*N*-dimethylaminopropyl substituent at silicon in 10,11-dihydrodibenzo[*b*,*f*]silepins [3] (eq. 2). The methylene group adjacent to sulfur in VIa was metallated as described for a corresponding thiazepin [14]. Subsequent addition of a large excess of $Cl(CH_2)_3NMe_2$ gave VII which was converted to the maleate salt. An attempt to introduce a side chain at the methylene position by reaction of VIa with NBS followed by *N*-methylpiperazine resulted in formation of ring cleavage products.

The formation of six- and seven-membered, silicon containing, tricyclic derivatives normally involves generation of a Grignard reagent or dilithio reagent or expansion of a smaller ring. A possible alternative to such ring formation involves ring closure at a site remote to the silicon. Such indirect methods become more important as the ring size increases. The thiasilocin (VIII) was prepared by this later approach. Formation of eight-membered ring was accomplished by reaction of bis(*o*-bromomethylphenyl)dimethylsilane with sodium sulfide (eq. 3).



The molecular motions exhibited by IIa, IIb, IIIa and VIII in the solid state have been studied by pulsed NMR techniques and will be reported elsewhere [15].

An X-ray study to determine the conformation adopted by VIII in the solid is in progress [16]. Samples of IIe · HCl · H_2O and VII have been submitted for pharmacological testing.

Experimental

General

All reactions which involved organolithium reagents, Grignard reagents and chlorosilanes were carried out under an atmosphere of dry N_2 in flame-dried glassware.

The commercial reagents, Me_2SiCl_2, $MeSiHCl_2$, $Me(CH_2Cl)SiCl_2$, $(C_6H_5)_2S$, $(C_6H_5)_2SO$, $(C_6H_5)_2SO_2$, Dibal-H, $LiAlH_4$. $CH_2{=}CHCH_2NMe_2$, *o*-$BrC_6H_4NH_2$, *o*-$BrC_6H_4CH_3$, $NHEt_2$ and NBS were used as supplied.

o-Bromothiophenol was prepared by a published route from diazotization of *o*-bromoaniline and treatment with potassium ethyl xanthate followed by reduction with zinc [17]. Methyl(3-bromopropyl)dichlorosilane was prepared from allyl bromide and $MeSiHCl_2$ in the presence of H_2PtCl_6 [18] and $Me_2NCH_2CH_2CH_2Cl$ was generated from the commercially available hydrochloride salt by reaction with base followed by purification and distillation.

THF was dried by treatment with BuLi followed by distillation [19].

Proton NMR spectra were recorded in CCl_4 or $CDCl_3$ on a Varian T-60 spectrometer (internal TMS as a reference unless otherwise specified). Mass spectral data were collected at 70 eV on an AEI MS-1201B mass spectrometer.

Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

10,10-Dimethylphenothiasilin-5,5-dioxide (IIa)

To a well stirred solution of diphenylsulfone (22 g, 0.10 mol) in 300 ml anhydrous ether, at approximately —30°C, was added dropwise BuLi (0.2 mol) during a 20 minutes period. The mixture was stirred for 3 h at —30°C. A solution of dimethyldichlorosilane (0.10 mol) in 75 ml anhydrous ether was then added slowly. The mixture was allowed to come to room temperature and stirred overnight. The reddish-brown suspension was hydrolyzed with water, the ether layer extracted and dried over Na_2SO_4. After stripping the ether, the light brown oil was vacuum distilled.

A white crystalline solid was obtained in the fraction, b.p. 100°C/0.5 mmHg. Recrystallization from isopropyl alcohol gave 5.3 g (19%) white, plate-like crystals, m.p. 156—158°C (lit. 160.5—161.5°C [5]). ^{1}H NMR ($CDCl_3$) δ(ppm): 8.5—7.5 (m, 8.4, aromatics); 0.75 (s, 5.6, Si—CH_3).

10-Chloromethyl-10-methylphenothiasilin-5,5-dioxide (IIb)

The chloromethyl derivative was prepared in a similar manner as described for IIa, from diphenylsulfone (0.10 mol), BuLi (0.20 mol) and chloromethylmethyldichlorosilane (0.10 mol). Unreacted diphenylsulfone (3.2 g) was recovered and the crude product was obtained after vacuum distillation, b.p. 210—230°C/0.1 mmHg. Recrystallization from isopropyl alcohol gave 4.2 g (26.6%) pure IIb, m.p. 136—137°C. (Found: C, 54.58; H, 4.38. $C_{14}H_{13}SiSO_2Cl$ calcd.: C, 54.44; H, 4.25%.) ^{1}H NMR ($CDCl_3$) δ(ppm): 8.7—7.7 (m, 8.0, aro-

matics); 3.5 (s, 2.0, CH_2Cl); 0.9 (s, 3.0, Si—CH_3). *Caution*: This compound was a skin irritant.

10-Methylphenothiasilin-5,5-dioxide (IIc)

The methylsilin derivative was prepared as described for IIa, from diphenylsulfone (0.10 mol) BuLi (0.20 mol) and methyldichlorosilane (0.10 mol). Vacuum distillation of the reaction mixture gave the crude product, b.p. 180—200°C/0.1 mmHg. Recrystallization from isopropyl alcohol gave 3.6 g (14%) IIc, m.p. 146—148°C. ^{1}H NMR ($CDCl_3$) δ(ppm): 7.1—8.2 (m, 7.8, aromatics); 4.8—5.1 (q, 1.1, SiH); 0.78—0.80 (d, 3.1, SiMe). *m/e* 218.

10-Methyl-10-(3-bromopropyl)phenothiasilin-5,5-dioxide (IId)

IId was prepared as described for IIa from diphenylsulfone (0.10 mol) BuLi (0.20 mol) and methyl(3-bromopropyl)dichlorosilane. Kugelrohr distillation resulted in collection of a fraction (175—200°C/0.5 mmHg) which consisted of a white solid and a yellow oil, 8.0 g, which contains between 60 and 70% of IId.

10-Methyl-10-(γ-N,N'-diethylaminopropyl)phenothiasilin-5,5-dioxide hydrochloride (IIe · HCl)

Approximately 3.0 g of the crude IId was treated with an excess of diethylamine (10 ml) in dry benzene (50 ml) and the solution was refluxed overnight. Filtration removed the white solid (diethylammonium bromide, 0.7 g) and stripping the solvent (benzene) left a light yellow oil. Kugelrohr distillation gave a fraction, b.p. 130—150°C/0.5 mmHg, which contained a white solid and a yellow oil, 2.1 g. Crude IIe was separated from starting material on a basic alumina column and collected principally in the methanol/benzene, 2/3, fraction (1.5 g). ^{1}H NMR ($CDCl_3$) δ(ppm): 7.6—8.4 (m, 6.6, Ar); 2.3—2.8 (m, 4.6, $CH_2CH_2CH_2N$ (CH_2CH_3)$_2$; 0.8—1.6, 0.6 (m, $CH_2CH_2CH_2N(CH_2CH_3)_2$; s, Si*Me*, 15.8). Purified IIe was then dissolved in anhydrous ether and dry HCl was slowly bubbled through the solution until complete precipitation of the salt had occurred. The salt was recrystallized from hexane/xylene mixtures, m.p. 185—187°C. (Found: C, 55.68; H, 6.84. $C_{20}H_{28}O_2NSiSCl \cdot H_2O$ calcd.: C, 56.18; H, 7.01%). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.5—8.4 (m, 7.6, aromatics); 2.7—3.3 (m, 5.6, $CH_2N(CH_2CH_3)_2H$); 1.7—2.3 (m, 3.4, $CH_2CH_2CH_2NEt_2H$); 1.1—1.5 (brd t, 8.2, $CH_2CH_2CH_2N$ (CH_2CH_3)$_2$H); 0.75 (s, 3.1, $SiCH_3$). Recrystallization from the same mixture followed by drying (24 h) resulted in partial removal of water. (Found: C, 57.74; H, 6.66. $C_{20}H_{28}O_2NSiSCl$ calcd.: C, 58.58; H, 6.88%).

10,10-Dimethylphenothiasilin (IIIa)

To 10,10-dimethylphenothiasilin-5,5-dioxide (2.6 g, 0.0090 mol) in 100 ml butyl ether was added $LiAlH_4$ (1.1 g, 0.030 mol) and the mixture was refluxed 48 h. The solution was cooled then quenched with dilute HCl. The ether layer was separated, dried over Na_2SO_4, and stripped. The crude product, a dark brown oil, was separated on a neutral alumina column and collected principally in the benzene/heptane, 1/4, fraction. The product slowly crystallized from cold aqueous isopropyl alcohol to yield 0.72 g (35%), m.p. 60—61°C (Lit. 50—

52°C [6]; 66—67°C [7]. (Found: C, 68.72; H, 5.95. $C_{14}H_{14}SiS$ calcd.: C, 69.38; H, 5.83%). ^{1}H NMR ($CDCl_3$) δ(ppm): 7.7—7.2 (m, 8.7, aromatics); 0.8 (s, 5.3, $SiMe_2$). *m/e* 242.

Yields were increased in the above reaction when the chloromethyl derivative IIb was used as the initial reactant (41%).

o-Bromobenzyl-o-bromophenyl sulfide (V)

To *o*-bromothiophenol (42 g, 0.22 mol) and KOH (12 g, 0.22 mol) dissolved in 75 ml 95% ethanol was slowly added *o*-bromobenzyl bromide (48 g, 0.22 mol). After the addition was completed the mixture was refluxed for 3 h and then poured into water. The product was extracted into ether, and the ether layer was washed with aqueous KOH and several times with water. The solution was dried over Na_2SO_4 and the ether evaporated. Kugelrohr distillation of the brown oil gave V, 48 g (74%), which was collected as a yellow oil, b.p. 140°C/0.5 mmHg. ^{1}H NMR ($CDCl_3$) δ(ppm): 7.8—7.0 (m, 8.3, aromatics); and 4.3 (s, 1.7, S—CH_2).

5,5-Dimethyl-5,11-dihydrodibenzo[b,e][1,4]-thiasilepin (VIa)

The dibromo derivative V (7.5 g, 0.021 mol) dissolved in 50 ml THF was slowly added to Mg turnings (2.0 g, 0.083 mol) at room temperature and then heated at reflux for 1.5 h. After cooling to room temperature, Me_2SiCl_2 (0.21 mol) in 50 ml THF was slowly added and then the mixture heated at reflux an additional 2 h. The solution was cooled to room temperature and hydrolyzed with saturated NH_4Cl solution. The THF layer was removed, dried and stripped to give a brown oil. The crude product was isolated as a light yellow oil, b.p. 150—165°C/0.1 mmHg, 1.3 g (24%). An analytical sample was prepared by elution over neutral alumina with hexane/benzene, 1/4. (Found: C, 70.51; H, 6.55. $C_{15}H_{16}SiS$ calcd.: C, 70.32; H, 6.30%). ^{1}H NMR ($CDCl_3$) δ(ppm): 7.0—7.2 (m, 7.8, aromatics); 4.2 ((br)s, 2.2, SCH_2); 0.6 (s, 6.0, $SiMe_2$). *m/e* 256.

5,5-Dimethyl-11-(γ-N,N'-dimethylaminopropyl)-5,11-dihydrodibenzo[b,e]-[1,4]thiasilepin (VII)

A solution of VIa (1.7 g, 0.0070 mol) in 22 ml ether was slowly added to a freshly prepared solution of phenyllithium (prepared from 3.1 g bromobenzene and 0.15 g Li in 20 ml ether). The mixture was stirred for 3 h at room temperature. Approximately 30 ml of freshly distilled dimethylaminopropyl chloride was then added slowly to the reaction mixture. After an additional 5 h of reflux the solution was cooled and unreacted Li metal removed. The solution was washed with water and extracted with dilute HCl. The extract was made alkaline to Litmus paper with a 10% solution of NaOH. The yellow oil was extracted with $CHCl_3$ and washed with H_2O, dried over Na_2SO_4 and the $CHCl_3$ stripped. Kugelrohr distillation gave a yellow oil, b.p. 180—205°C/0.1 mmHg, 1.4 g, which was consistent with the crude product. The product was separated from starting material on a basic alumina column and collected principally in the methanol/benzene, 3/2, fraction, 290 mg (12%). ^{1}H NMR ($CDCl_3$) δ(ppm): 7.4—7.8 (m, 9.4, aromatics); 4.0—4.3 (t, 1.0, CH); 1.3—2.4 + 0.5—0.7 (m + d, 20.5, $CH_2CH_2CH_2NH(CH_3)_2$ + $Si(CH_3)_2$). The pure product was treated with an equimolar ratio of maleic acid in ether. After a light yellow oil settled the ether

was decanted and 20 mg of maleic acid was recovered. The product, as an oil, could not be induced to crystallize. (Found: C, 61.07; H, 7.49. $C_{24}H_{31}SiSNO_4 \cdot H_2O$ calcd.: C, 60.63; H, 6.94%).

Di-o-tolyldimethylsilane

Dimethyldichlorosilane (30 ml, 0.25 mol) was added to *o*-lithiotoluene (prepared from addition of 275 ml of 2 *M* BuLi to 0.50 mol *o*-bromotoluene) and the mixture heated at reflux for 15 h. After hydrolysis the ether layer was dried, stripped and distilled to give $(o\text{-}CH_3C_6H_4)_2Si(CH_3)_2$, 36 g (60%), b.p. 110—114°C/100 mmHg.

Bis(o-bromomethylphenyl)dimethylsilane

To di-*o*-tolyldimethylsilane (13 g, 0.048 mol) in 70 ml CCl_4 was added portion-wise, *N*-bromosuccinimide (16 g, 0.10 mol). The mixture was heated at reflux for 4 h. After removal of the succinimide and stripping of the CCl_4, distillation of the residue gave the crude dibromide, 16 g, b.p. 144—170°C/0.05 mmHg. Recrystallization from heptane gave $(o\text{-}BrCH_2C_6H_4)_2SiMe_2$, m.p. 67.5—70°C. ^{1}H NMR (CCl_4) δ (ppm) (external TMS): 6.7—7.2 (m, 8.3, Ar); 3.9 (s, 3.2, CH_2Br); 0.4 (s, 6.4, $SiMe_2$).

12,12-Dimethyl-7,12-dihydro-5H-dibenzo[c,f][1,5]thiasilocin (VIII)

To bis(*o*-bromomethylphenyl)dimethylsilane (9.2 g, 0.023 mol) in absolute ethanol (15 ml) was added dropwise, Na_2S (1.5 g, 60% technical grade) dissolved in 2 ml H_2O. The mixture was heated at reflux for 14 h then poured onto ice. The resultant sludge was extracted with ether and the ether layer dried over $MgSO_4$ and stripped. The residue was distilled to give 4.3 g oil, b.p. 135—150°C/0.150 mmHg. The distillate (1.2 g) was eluted over 50 g silica gel. The portion which eluted in C_6H_6/hexanes, 4/1, solidified (0.25 g). Recrystallization from absolute ethanol provided an analytical sample of VIII, m.p. 123.5—125°C. (Found: C, 70.30; H, 6.34. $C_{16}H_{18}SiS$ calcd.: C, 71.11; H, 6.67%). ^{1}H NMR ($CDCl_3$) δ (ppm); 7.1—7.7 (m, 8.5, Ar); 3.45 (s, 3.5, CH_2S); 0.50 (s, 6.0, $SiMe_2$). *m/e* 270.

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