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SYNTHESIS AND CHEMISTRY OF THE PHENOXASILINS AND DIHYDRO-DIBENZO-OXASILEPINS

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Summary

Formation of both sila-functional and carbo-functional phenoxasilins from diphenyl ether and *o,o'*-dibromodiphenyl ether precursors is described. Tricyclic oxasilepins are formed from *o,o'*-dibromobenzylphenyl ether by metallation with n-BuLi followed by reaction with dichlorosilanes as well as by ring expansion of an appropriate phenoxasilin. Reactions at the silicon center and at the ring methylene carbon of the oxasilepins are reported, as well as attempts to generate oxasilocins.

Introduction

The earliest report which describes the synthesis of tricyclic compounds that contain oxygen and silicon heteroatoms in the central ring appeared in the 1950's [1]. Phenoxasilins, Ia and Ib, were formed when dichlorosilanes, R_2SiCl_2, were added to solutions of the dilithio derivative prepared by the treatment of diphenyl ether with a two molar equivalent of n-butyllithium. Later studies [2] reported the effect of solvent on formation of *o,o'*-dilithiodiphenyl ether and the resultant increase in yields of phenoxasilins in tetrahydrofuran solvent. Formation of phenoxasilins from R_2SiCl_2 and *o,o'*-dilithiodiphenyl ether formed from halogen—metal exchange of *o,o'*-dibromodiphenyl ether has also been reported [2c]. The present study describes the formation of sila-functional and carbo-functional phenoxasilins as well as the syntheses of previously unreported tricyclic oxasilepins, II and III. Attempts to generate oxasilocins are also described.

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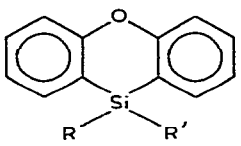
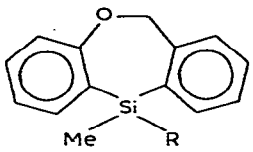
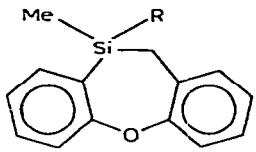


(Ia, R = R′ = Me
Ib, R = R′ = Ph
Ic, R = Me, R′ = H)



(II)



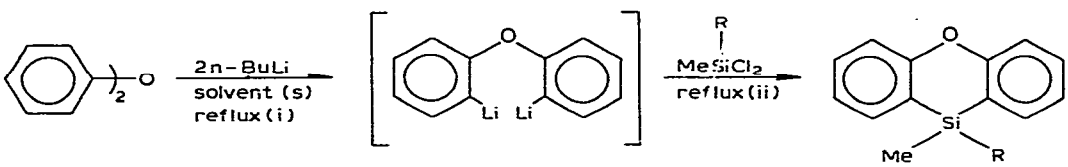
(III)

Results and discussion

The most convenient method for generation of *o,o′*-dilithiodiphenyl ether is from lithiation of commercially available diphenyl ether. In the original work, butyllithium was formed from butyl bromide and lithium in ethyl ether. When the conditions specified in the original report are followed except that commercial BuLi in hexanes is employed the yield of Ia could be reproduced (Table 1). However, when the sila-functional silane, $MeSiHCl_2$ was used as the trapping agent the yields of phenoxasilin, Ic, were either very small or not realized, but, carbo-functional derivatives could be produced by this method. The results are summarized in Table 1. When Et_2O/THF was employed as solvent (freshly prepared butyllithium) and 3-bromopropylmethyldichlorosilane as the reacting silane, no products consistent with ring closure were obtained when the addition method originally reported was used, but a product arising from trapping of monolithiated ether was detected. When an ether/hexane/THF mixture was employed (commercial BuLi), the carbon-functionalized phenoxasilins, Id and

TABLE 1

EXPERIMENTAL DATA FOR THE PREPARATION OF PHENOXASILINS I



(I)

Solvents Volume ratio	Reflux time (i) (h)	Chlorosilane	Reflux time (ii) (h)	I R (% yield)
Et_2O/hex = 4/3	72	Me_2SiCl_2	4 [a]	Ia, R = Me (25%) [b]
Et_2O/hex = 4/3	72	$MeSiHCl_2$	4	Ic, R = H (10%) [c]
Et_2O/hex = 4/3	72 [d]	$MeSiHCl_2$	4 [a]	Ic, R = H [e]
Et_2O/THF = 5/3	5	$Br(CH_2)_3Si(Me)Cl_2$	4 [a]	$Ar_2Si(Me)CH_2CH_2CH_2Br$ [f]
Et_2O/hex/THF = 2/1/1	4	$Br(CH_2)_3Si(Me)Cl_2$	18 [a]	Id, R = $CH_2CH_2CH_2Br$ (17%) [g]
Et_2O/hex/THF = 2/1/1	4	$ClCH_2Si(Me)Cl_2$	18 [a]	Ie, R = CH_2Cl (50%) [g]

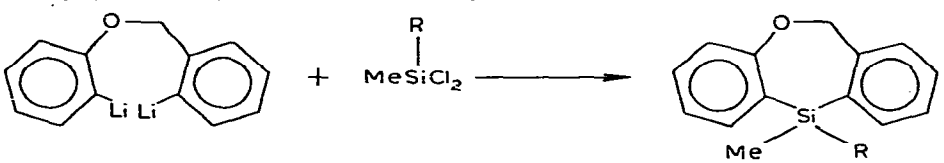
[a] Simultaneous addition of both reactants. [b] Same as reported yield in Et_2O solvent alone [1]. [c] Starting silane consumed and no Si—H observed in product(s). [d] Et_2O replaced by benzene. [e] Mixture of products with minor Ic. [f] Ar = $C_6H_5OC_6H_4$. [g] Crude yield.

Ie, were formed in reasonable yields. A higher yield of phenoxasilin is realized with $ClCH_2Si(Me)Cl_2$ than with Me_2SiCl_2, a trend we have observed in previous ring closure reactions [3].

A quantitative conversion of diphenyl ether to *o,o'*-dilithiodiphenyl ether is unlikely and the very low yield of Ic may result from reaction of -SiH with excess n-BuLi. An improved yield of cyclized product from polyfunctional silanes such as $MeHSiCl_2$ could be realized from the dibromide precursor, bis-(2-bromophenyl) ether. Preparations of organolithium compounds may be carried out in better yields by halogen—metal exchange rather than direct metallation [4]. Bis(2-bromophenyl) ether [5] was prepared from the diazotization of 2-amino-2'-bromo-diphenyl ether [6] and reaction with copper(I) bromide (prepared "in situ" [7]). Treatment of the dibromide with n-BuLi at 0°C followed by addition of $MeHSiCl_2$ gave the desired product, Ic, in approximately 60% yield.

The route to tricyclic oxasilepins may involve reaction of a dilithio precursor which includes an oxygen heteroatom with dichlorosilanes as previously described for phenoxasilins. Alternatively, ring expansion of a phenoxasilin at the silicon heteroatom could generate the isomeric oxasilepins. Although both approaches afford cyclic products the dilithio route was only marginally successful.

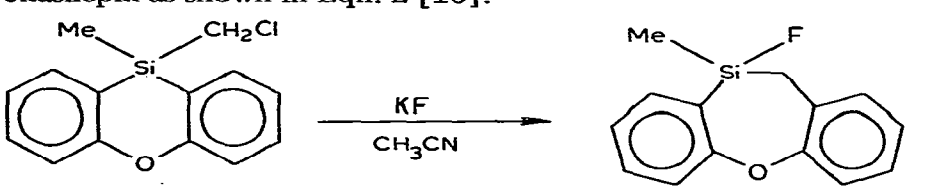
Since the action of organolithium reagents on benzylphenyl ether causes rearrangement and formation of cleavage products [8], *o,o'*-dibromobenzylphenyl ether, formed by condensation of *o*-bromobenzyl bromide and *o*-bromophenol [9] was employed as the precursor to the dilithio derivative. Quenching of *o,o'*-dilithiobenzylphenyl ether with a dichlorosilane provided the dihydro-dibenzo[b,e][1,4]oxasilepins, II (Eqn. 1). Spectroscopic evidence supports the formation of II (R = H, Me, CH_2Cl), but efforts to prepare analytically pure samples were uniformly unsuccessful.



(1)

(IIa, R = H;
b, R = Me;
c, R = CH_2Cl)

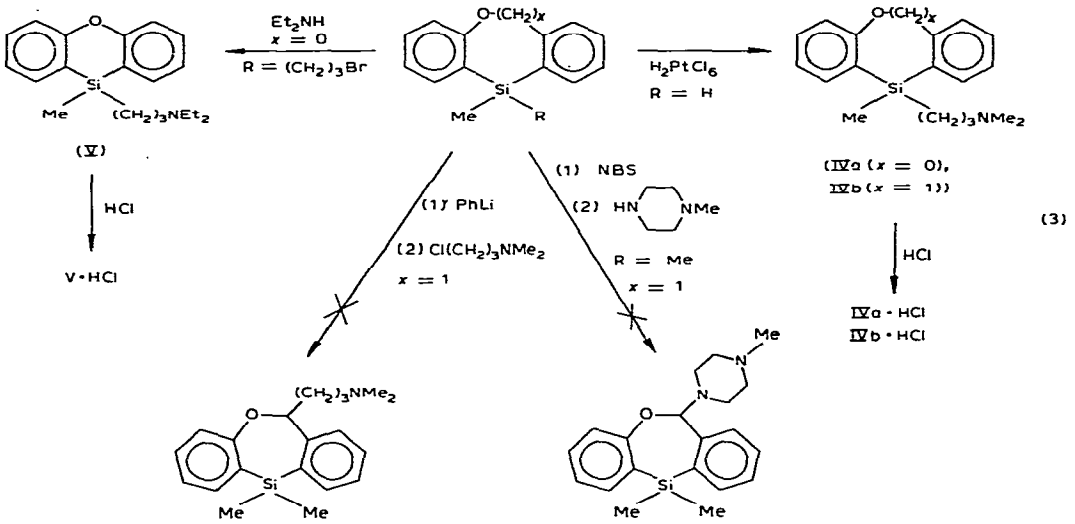
An anion-induced ring expansion reaction of the phenoxasilin, Ie, leads to the seven-membered ring system, 10-methyl-10,11-dihydrodibenzo[b,f][1,4]-oxasilepin as shown in Eqn. 2 [10].



(2)

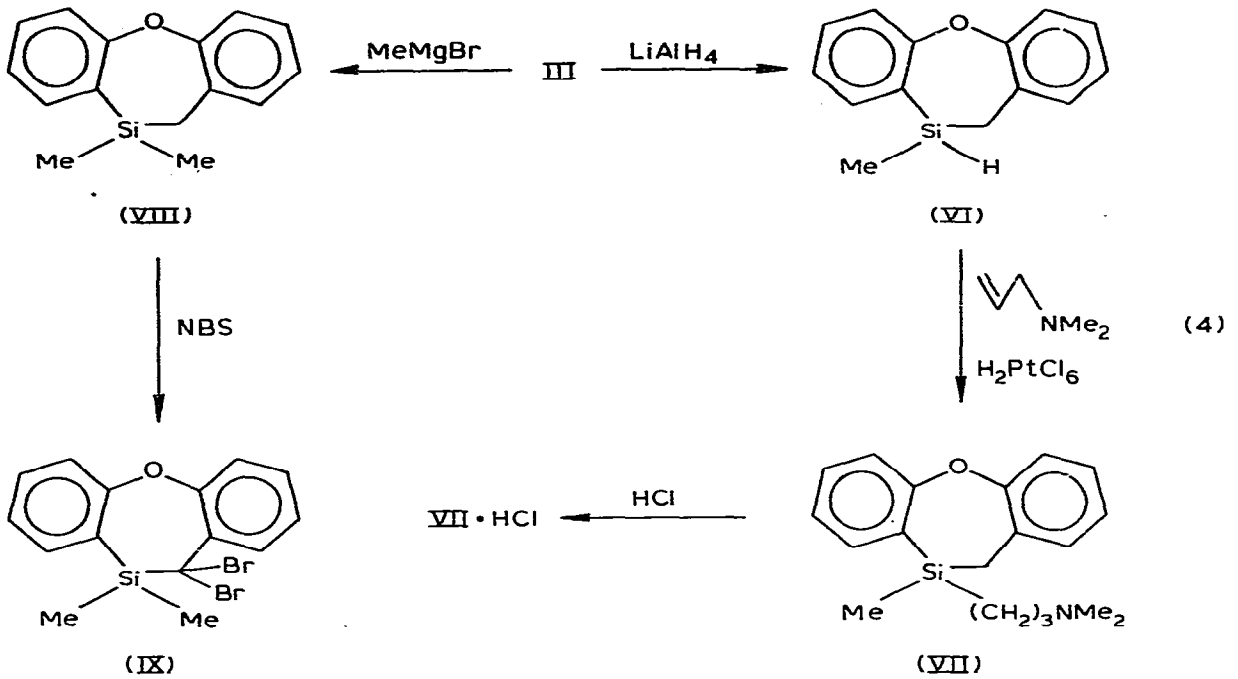
(Ie) (III)

Substitution reactions at silicon in both Ic and IIa were briefly explored as well as substitution at the methylene carbon in IIb. Introduction of an aminopropyl side chain and formation of IV was effected by hydride addition of Ic and IIa to *N,N*-dimethylallylamine in the presence of chloroplatinic acid. Alternatively, Id could be converted to V by reaction with diethylamine. The three amines, IVa, IVb and V are all oils which could not be induced to crystallize and thus were converted to the solid hydrochloride salts. An attempt to introduce a side chain at the methylene position adjacent to oxygen in IIb by reaction with either NBS * followed by *N*-methylpiperazine or with organolithium reagents (PhLi, BuLi) followed by $Cl(CH_2)_3NMe_2$ resulted in ring cleavage. These results are not surprising in view of the fact that benzylphenyl ether reacts with NBS [11] or organolithium reagents [8] to give cleavage products. These results are summarized in Eqn. 3.

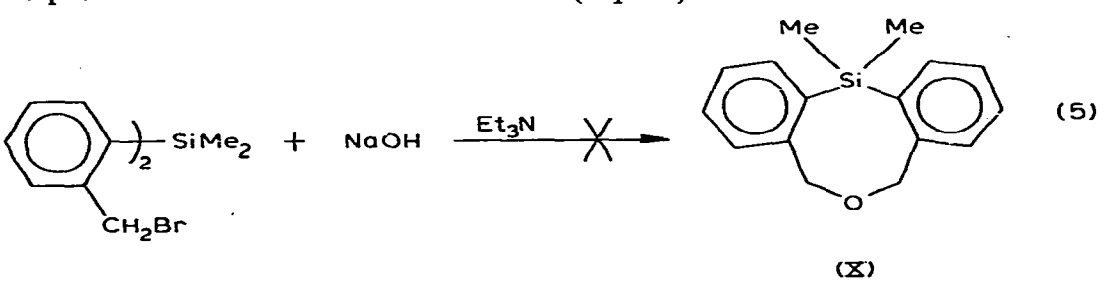


The conversions of oxasilepin, III, were briefly examined. Reduction of III with $LiAlH_4$ provides the silane, VI, which adds to allylamine in the same fashion as Ie and IIa, to give the carbo-functional silane, VII. The amine, VII, was also converted to the crystalline hydrochloride salt. Reaction of III with MeMgBr afforded the methylated derivative, VIII, as an oil which could not be completely separated from traces of starting material. A solid derivative was prepared by reaction of crude VIII with NBS. When VIII was brominated with a one molar equivalent of NBS only the dibrominated derivative, IX, was formed and starting material was recovered. There are several cases where α,α'-dibromobenzylsilanes are more readily synthesized than α-bromobenzylsilanes [12]. An attempt to introduce a side chain at the methylene position of VIII with n-BuLi at room temperature followed by addition of a large excess of $Cl(CH_2)_3NMe_2$ failed. When the product produced from VIII and n-BuLi was quenched with D_2O however, incorporation of deuterium into VIII was observed. The various reactions of III are summarized in Eqn. 4.

* NBS = *N*-bromosuccinimide.



The possibility of synthesis of the tricyclic oxasilocin, IX, by direct ring closure was also examined. Metallation of bis(2-bromobenzyl) ether with n-BuLi followed by quenching with dimethyldichlorosilane gave no evidence for the formation of IX. An alternative ring closure at a site remote to silicon is suggested from the observation that *o*-bromobenzyl bromide condenses in the presence of NaOH/Et_3N. When bis(*o*-bromomethylphenyl)dimethylsilane and NaOH were refluxed for 2 h at 80—90°C, starting material was consumed but no product identifiable as X was isolated (Eqn. 5).



(5)

Formation of oxasilocins from the fluoride ion induced ring expansion of IIc are under current exploration.

Experimental

General

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

The commercial reagents, Ph_2O, Me_2SiCl_2, $Me(CH_2Cl)SiCl_2$, n-BuLi/hexane, NBS, bromobenzene, $CH_2{=}CHCH_2NMe_2$, $NHEt_2$, *o*-bromotoluene, and *o*-bromophenol were used as supplied.

Methyl(3-bromopropyl)dichlorosilane was prepared from allylbromide and $MeHSiCl_2$ in the presence of H_2PtCl_6 [14] and $Me_2NCH_2CH_2CH_2Cl$ was generated from the commercially available hydrochloride salt by reaction with base followed by purification by distillation. 2-Amino-2′-bromo-diphenyl ether [5] was generated from 2-bromo-2′-nitrodiphenyl ether [6] by reaction with iron powder in ethanol and *o*-bromobenzyl bromide was obtained by the bromination of *o*-bromotoluene with Br_2 in CCl_4 [15] followed by purification and distillation. Bis(*o*-bromomethylphenyl)dimethylsilane was prepared according to the literature method [3].

THF was dried by treatment with BuLi followed by distillation [16].

Proton NMR spectra were recorded in $CDCl_3$ on a Varian T-60 spectrophotometer (internal TMS as a reference, δ(ppm), unless otherwise specified). Mass spectral data were collected at 70 eV on an AEIMS-1201B Mass spectrophotometer. The Kuglrohr distillation method was employed in all vacuum distillations unless otherwise specified.

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

o,o′-Dibromobenzylphenyl ether [9]. Small pieces of freshly cut sodium metal, (6.6 g, 0.28 mol), were added to absolute C_2H_5OH (133 ml) with stirring until completely dissolved and then 50 g (0.28 mol) *o*-bromophenol were added to the solution. After an additional 10 minutes, *o*-bromobenzyl bromide (0.28 mol) in 10 ml absolute C_2H_5OH was added to the phenoxide solution, the mixture stirred another 20 minutes and then refluxed until the solution was neutral. After extraction with ether and stripping the solvent, a solid containing C_2H_5OH was obtained. After removal of the C_2H_5OH by heating under vacuum, 86 g of a brown red solid was obtained (87%), m.p. 60°C; *m/e* 342 (M^+). ^1H NMR ($CDCl_3$) δ(ppm): 6.8—7.9 (m, 7.9, arom.); 5.4 (s, 2.1, O—CH_2—Ph). (Found: C, 45.32; H, 3.05. $C_{13}H_{10}Br_2O$ Calcd.: C, 45.31; H, 2.92%).

o,o′-Dibromodiphenyl ether. 2-Bromo-2′-amino-diphenyl ether, (28.3 g, 0.100 mol), which was prepared by the method of Mann and Millar [5], 90 ml of 48% HBr, 210 ml of H_2O, and 100 ml of glacial acetic acid were heated until the amine had dissolved completely and then cooled to 0°C (ice bath). With vigorous stirring, a solution of 7.37 g of $NaNO_2$ in 50 ml of H_2O was added slowly over 1 h to the suspension of the amine hydrobromide (the reaction temperature was kept between 0°C and —2°C). The diazonium salt solution was filtered rapidly without allowing it to warm, and the filtrate added in a fine stream in the course of 40 minutes, with stirring, to a boiling solution of the catalyst which was prepared by heating for 4 h a mixture of 48 g of $CuSO_4$, 117 g of NaBr, 98 ml of H_2O, 12 ml of concentrated H_2SO_4 and 9 g of copper powder. The combined solutions were heated for another 10 minutes after the addition. When the mixture cooled to room temperature it was extracted with $CHCl_3$ and the extract washed with 20% NaOH solution, concentrated HCl and water, and then dried. The product, 16.7 g (48%), was collected at b.p. = 120—138°C/0.4 mmHg [Lit. 134—136°C/0.5 mmHg] [5]. *m/e* = 330 (M^+).

Bis(o-bromobenzyl) ether [13]. A mixture of *o*-bromobenzyl bromide (0.10

mol), Et_3N (0.01 mol) and 46% NaOH solution (8.4 g) was refluxed for 2 h at 80—90°C. After extraction with ether, the solvent was stripped and a light-yellow crystalline solid precipitated. Recrystallization from ethanol gave a white solid, 7.2 g, (40%), m.p. = 61—62°C. ^{1}H NMR δ(ppm) (external TMS): 7.0—7.8 (m, 8.5, arom.); 4.1 (s, 3.5, Ph—CH_2—O).

10,10-Dimethyl-phenoxasilin, Ia [1]. The phenoxasilin was prepared according to the literature method from diphenyl ether (17.0 g, 0.10 mol), commercial n-BuLi (235 ml, 1.6 *M* in hexane) in anhydrous ether (200 ml) followed by addition of dimethyldichlorosilane (18.5 g, 0.120 mol). After workup, 8.0 g (25%) of product were obtained, b.p. = 100—120°C/0.2 mmHg. The liquid was solidified by cooling in an acetone/dry ice-bath, m.p. = 74—76°C [Lit. 78.5—79°C] [1]. ^{1}H NMR δ(ppm): 7.0—7.7 (m, 8.1, arom.); 0.3 (s, 5.9, Si—*Me*).

Attempt to synthesize Ic from diphenyl ether/n-BuLi. To a mixture of diphenyl ether (17 g, 0.10 mol), n-BuLi (0.25 mol; 1.6 *M* in hexane) and anhydrous ether (200 ml) which had been refluxed for 72 h, a solution of $HMeSiCl_2$ (5.8 g, 0.050 mol) in 100 ml ether was added. After another 4 h reflux, the mixture was hydrolyzed and after workup, the residue was vacuum distilled. There was no NMR evidence for the desired product in the fractions which distilled below 200°C/0.1 mmHg.

In a second attempt, dry benzene (100 ml) was added to the $(C_6H_5)_2O$/n-BuLi mixture after the 72 h reflux period and distilled to remove ether/hexane. Two-thirds of the remaining solution and $HMeSiCl_2$ (0.05 mol) in 100 ml benzene were simultaneously added to 1/3 portion of the solution over 0.5 h. After another 4 h reflux, the mixture was hydrolyzed. After workup, NMR evidence showed the presence of a Si—H peak but at low intensity.

10-Hydrido-10-methyl-phenoxasilin, (Ic). A solution of 28 ml of BuLi (0.045 mol, 1.06 *M* in hexane) in 50 ml anhydrous ether was added dropwise to 7.4 g (0.22 mol) of *o,o'*-dibromophenyl ether in 75 ml Et_2O which had been cooled to 0°C. The mixture was stirred and refluxed 1 h. A solution of methyldichlorosilane (0.020 mol) in Et_2O and the former mixture were added simultaneously over a period of 1 h and then refluxed for another 1 h. After aqueous workup the light yellow oil was vacuum distilled. The fraction which distilled from 106—136°C/0.2 mmHg (3.0 g) contained the desired product, Ic. ^{1}H NMR ($CDCl_3$) δ(ppm): 7.0—7.8 (m, 8.3, arom.); 5.1 (q, 1.0, Si—H); 0.5 (d, 2.7, Si—CH_3). *m/e* = 212 (M^+).

Efforts to produce an analytical sample by redistillation and elution over neutral alumina failed. The crude product was employed for reaction with *N,N*-dimethylallylamine (formation of IVa).

10-Methyl-10-(3-bromopropyl)-phenoxasilin (Id). n-BuLi (0.092 mol, 1.06 *M* in hexane) was added slowly to 0.045 mol of diphenyl ether in the mixture of 120 ml dry THF and 278 ml anhydrous ether and refluxed for 5 h. A solution of 3-bromopropylmethyldichlorosilane (0.045 mol) in 150 ml THF and the n-BuLi/Ph_2O solution were added simultaneously to about 100 ml THF over a period of 1.5 h and the mixture heated at reflux for 18 h. After aqueous workup the crude product, 2.3 g, was obtained in the fraction, b.p. = 106—140°C/0.3 mmHg. ^{1}H NMR ($CDCl_3$) (ppm): 7.0—7.8 (m, 7.2, arom.); 3.3 (t, 1,8, CH_2Br); 0.8—2.0 (m, 4.2, Si—CH_2—CH_2—); 0.4 (s, 2.9, Si—*Me*). *m/e* = 334 (M^+). The crude product was used without further purification in the formation of V.

When the procedure recommended in the original report describing the generation of phenoxasilins [1] was followed, ring closure products were not obtained. To a solution of n-BuLi in 300 ml ether [prepared from n-BuBr (0.34 mol) and Li wire (0.68 mol)] was added diphenyl ether (0.14 mol) in 200 ml dry THF which had been cooled to 0°C. The 3-bromopropylmethyldichlorosilane (0.14 mol) in THF and two thirds of the dilithio solution were simultaneously added dropwise to the remaining one third solution, followed by reflux for another 4 h. After hydrolysis and workup, an oil was collected at 210—240°C/0.3 mmHg, 16 g. ^{1}H NMR δ(ppm) (external TMS): 6.8—7.8 (m, 17.6, arom.); 3.4 (t, 3.1, —C*H*$_2$—Br); 1.2—2.3 (m, 4.3, Si—C*H*$_2$C*H*$_2$); 0.7 (s, 3.0, Si—Me).

10-Methyl-10-(chloromethyl)-phenoxasilin (Ie). Following the procedure outlined for the preparation of Id, reaction of *o,o'*-dilithiodiphenyl ether [prepared from diphenyl ether (14 g, 0.080 mol) and n-BuLi (0.18 mol)] with chloromethylmethyldichlorosilane (13 g, 0.080 mol) gave Ie, 10.3 g (50%), b.p. = 140—184°C/0.1 mmHg. The oil was solidified by cooling it in an acetone-dry ice bath and the analytical sample was prepared by recrystallization from C_2H_5OH to give a white solid, m.p. = 48.5—49.5°C. ^{1}H NMR δ(ppm) (external TMS): 6.8—7.6 (m, 8.5, arom.); 2.7 (s, 1.7, SiC*H*$_2$Cl); 0.4 (s, 2.7, Si—*Me*). *m/e* = 261 (*M*$^+$). (Found: C, 64.91; H, 5.59. $C_{14}H_{13}OSiCl$, Calcd.: C, 64.37; H, 4.98%).

11-Methyl-5,11-dihydro-dibenzo[b,e][1,4]oxasilepin (IIa). To a well stirred solution of *o,o'*-dibromobenzylphenyl ether (17.2 g, 0.0500 mol) which had been cooled to —5°C, was added dropwise BuLi (64.5 ml, 0.100 mol) over a 30 minute period. The mixture was heated to boiling for 15 minutes and then cooled to —20°C. A solution of dichloromethylsilane (5.2 ml, 0.050 mol) in 20 ml anhydrous ether was then added slowly to the former mixture followed by a 30 minute reflux. The suspension was hydrolyzed with water, and the ether layer extracted and dried over Na_2SO_4. After stripping the ether, the oil was distilled. The crude product was obtained in the fraction, b.p. = 120—140°C/0.2 mmHg, 2.8 g. ^{1}H NMR ($CDCl_3$) δ (ppm): 6.8—7.8 (m, 8.0, arom.); 5.0—5.3 (m, 3.0, Ph—O—C*H*$_2$—Ph and Si—*H*); 0.5 (d, 3.0, Si—*M*e). *m/e* = 226 (*M*$^+$). Attempts to prepare a purified sample by redistillation and elution over neutral alumina failed. The crude product could be employed for reaction with *N,N*-dimethylallylamine (formation of IV b).

11,11-Dimethyl-5,11-dihydro-dibenzo[b,e][1,4]oxasilepin (IIb). The compound IIb was prepared in a similar manner as described for IIa, from the *o,o*-dibromobenzylphenyl ether (0.050 mol), BuLi (0.10 mol) and dichlorodimethylsilane (0.050 mol). The crude product, 2.5 g, was obtained at b.p. = 172—180°C/0.2 mmHg. The oil (1.2 g) was eluted over a neutral alumina column and purified product, 0.8 g, was obtained from a 50—50 hexane-benzene mixture. ^{1}H NMR ($CDCl_3$) δ(ppm): 7.0—7.8 (m, 8.3, arom.); 5.3 (s, 1.7, Ph—O—C*H*$_2$—Ph); 0.5 (s, 6.0, Si—*Me*). *m/e* = 240 (*M*$^+$). An analytically pure sample was not obtained.

11-Chloromethyl-11-methyl-5,11-dihydro-dibenzo[b,e][1,4]oxasilepin (IIc). The compound IIc was generated by a procedure similar to the preparation of IIa, from *o,o'*-dibromobenzylphenyl ether (0.050 mol), BuLi (0.10 mol) and chloromethylmethyldichlorosilane (0.050 mol). After aqueous workup, distil-

lation of the residue afforded 5.8 g oil, b.p. 142—188°C/0.6 mmHg which contained the desired product. Redistillation of this fraction gave purified IIc, 3.6 g, b.p. 120—140°C/0.1 mmHg. ^{1}H NMR δ(ppm): 6.8—7.8 (m, 8.1, arom.); 5.2 (q, 2.0, Ph—O—CH_2—Ph); 3.2 (s, 3.0, SiCH_2Cl); 0.7 (s, 2.9, Si—Me). *m/e* = 275 (M^+). Attempts to produce an analytical sample from elution over neutral alumina failed as did efforts to initiate crystallization.

10-Fluoro-10-methyl-10,11-dihydro-dibenzo[b,f][1,4]oxasilepin (III). Ie (1.7 g, 0.0065 mol) and KF (0.76 g, 0.013 mol) were added to 45 ml CH_3CN. After a 24 h reflux, CH_3CN was removed and a mixture of ether/water was added. The ether layer was removed, dried and stripped to give an oil. Distillation afforded the crude product, b.p. = 108—120°C/0.1 mm Hg, 0.94 g (60%). An analytical sample was prepared by elution over silica gel with heptane/benzene = 1/4. ^{1}H NMR ($CDCl_3$) δ(ppm): 7.0—7.6 (m, 8.4, arom.); 2.6—3.0 (m, 1.7, Si—CH_2Ph); 0.4 (d, 2.8, Si—*Me*); (*J*(*HC*Si*F*) = 7.2 Hz). *m/e* = 244 (M^+). (Found: C, 69.36; H, 5.50. $C_{14}H_{13}SiOF$ Calcd.: C, 68.81; H, 5.32%).

10-Methyl-10(γ-N,N-dimethylaminopropyl)phenoxasilin (IVa). Approximately 4.8 g of crude Ic, *N,N*-dimethylallyl amine (10 ml) and two drops of H_2PtCl_6/t-BuOH were refluxed for 4 h. The platinum residue was filtered out prior to vacuum distillation of the oil to give crude product, IV (3.2 g), b.p. = 138—180°C/0.2 mmHg. ^{1}H NMR ($CDCl_3$) δ(ppm): 7.1—7.7 (m, 8.0, arom.); 2.2 (m, 7.3, —CH_2N (CH_3)$_2$); 1.6—0.6 (m, 4.3, Si—CH_2—CH_2); 0.4 (s, 2.3, Si—*Me*). *m/e* = 297 (M^+). The free base was dissolved in an ether/$CHCl_3$ mixture and dry HCl was slowly bubbled through the solution until precipitation of the salt was complete. The salt was recrystallized from isopropyl alcohol, m.p. = 160—161°C. (Found: C, 64.38; H, 7.50. $C_{18}H_{24}SiNO$ Calcd.: C, 64.76; H, 7.19%).

11-Methyl-11-(γ-N,N-dimethylaminopropyl)-5,11-dihydrodibenzo[b,e][1,4]-oxasilepin (IVb) and IVb · HCl. The preparation of IVb is similar to the preparation of IVa from Ic. A mixture of IIa (2.8 g), CH_2=$CHCH_2NMe_2$ (3 ml) and H_2PtCl_6/t-BuOH was heated at reflux for 3 h. After filtering to remove the Pt residues the oil was distilled to give the slightly impure product in the fraction of b.p. = 145—160°C/0.1 mm Hg (1.1 g). ^{1}H NMR ($CDCl_3$) δ(ppm): 7.0—7.8 (m, 8.4, arom.); 5.2 (q, 1.9, Ph—O—CH_2—Ph); 0.8—2.2 (m, 12.1, Si—(CH_2)$_3$-NMe_2); 0.6 (s, 2.5, Si—*Me*). *m/e* = 311 (M^+). (Found: C, 72.13; H, 7.96. $C_{19}H_{25}$-ONSi Calcd.: C, 73.31; H, 8.03%).

The distilled product was further purified by elution over basic alumina (55 g) with MeOH/benzene = 1/4 to give a pale yellow oil (0.86 g). The free base was dissolved in ether and dry HCl gas was bubbled into the solution until no further oil separated. After pumping on the oil for 24 h a solid was obtained. Recrystallization of the solid from EtOAc followed by recrystallization from xylenes provided an analytical sample of IVb · HCl, m.p. 149—150°C. (Found: C, 65.69; H, 7.73. $C_{19}H_{26}SiONCl$ Calcd.: C, 65.61; H, 7.48).

10-Methyl-10-(γ-N,N-diethylaminopropyl)phenoxasilin (V) and V · HCl. Approximately 2.3 g of crude II was refluxed with 4.8 ml Et_2NH in dry benzene (25 ml) for 16 h. Filtration removed the white solid (diethylammonium bromide, 0.4 g) and the solvent was stripped. The crude product 1.2 g (45%) was collected by vacuum distillation, b.p. = 140—158°C/0.1 mmHg. The free base was dissolved in ether and dry HCl gas was bubbled into the solution until

no further oil separated. Chloroform was added to the oil/ether mixture until the oil dissolved. Cooling the solution in dry ice resulted in formation of a precipitate, which was recrystallized from $CHCl_3$/xylene mixture, m.p. = 152—153°C. ^1H NMR ($CDCl_3$) δ(ppm): 7.0—7.8 (m, 8.4, arom.); 2.2—2.8 (m, 6.5, —CH_2—N—(CH_2)$_2$); 0.8—1.8 (m, 9.1, —Si—CH_2—CH_2— and —N(CH_2CH_3)$_2$); 0.6 (s, 2.9, Si—*Me*). *m/e* = 325 (M^+). Two further recrystallizations from i-PrOH/xylenes provided the analytical sample, m.p. 155.5—157°C. (Found: C, 65.75; H, 7.84. $C_{20}H_{28}OSiNCl$ Calcd.: C, 66.39; H, 7.74).

10-Methyl-10,11-dihydro-dibenzo[b,f][1,4]oxasilepin (VI). The reduction reaction of 10-fluoro-10-methyl-10,11-dihydro-dibenzo[b,f][1,4]oxasilepin (1.9 g, 0.0070 mol) was carried out by refluxing with excess $LiAlH_4$ (0.7 g) in 40 ml anhydrous ether for 70 minutes. After hydrolytic work up, the ether layer was separated, dried over Na_2SO_4 and stripped. The desired product was obtained in the fraction, b.p. = 96—110°C/0.1 mmHg (1.6 g). ^1H NMR ($CDCl_3$) (ppm): 7.0—7.6 (m, 8.1, arom.); 4.6 (m, 1.0, Si—H); 2.4—2.9 (m, 2.0, Si—CH_2—Ph); 0.3 (d, 2.9, Si—*Me*). *m/e* = 226 (M^+).

The distilled product was used without further purification in reaction with *N,N*-dimethylallylamine to form VII.

10-Methyl-10-(γ-N,N-dimethylaminopropyl)-10,11-dihydro-dibenzo[b,f]-[1,4]oxasilepin (VII). The compound VII and its HCl salt were prepared in a manner similar to IVa and IVb, from compound VI, 2.0 g (0.0080 mol), CH_2 = $CHCH_2NMe_2$ (6.5 ml) and H_2PtCl_6/t-BuOH. The crude oil product was obtained at 166°C/0.2 mmHg, 1.5 g (60%). After the salt was generated by bubbling dry HCl through the free base in ether/$CHCl_3$ mixture, recrystallization from isopropyl alcohol gave a solid, m.p. = 156—157°C. ^1H NMR ($CDCl_3$) δ(ppm): 6.9—7.5 (m, 8.1, arom.); 0.6—2.9 (m, 14.2, Si—CH_2—Ph and Si(CH_2)$_3$—NMe_2); 0.2 (s, 2.7, Si—*Me*). (Found: C, 65.73; H, 7.44. $C_{19}H_{26}OSiNCl$ Calcd.: C, 65.61; H, 7.48%).

10,10-Dimethyl-10,11-dihydro-dibenzo[b,f][1,4]oxasilepin (VIII). To a solution of III (2.2 g, 0.0091 mol) in 40 ml anhydrous ether, was added 4 ml CH_3MgBr (2.5 *M*) and the mixture was heated at reflux for 1.5 h. After aqueous workup the product was obtained in the fraction, b.p. 98—102°C/0.1 mm Hg (1.4 g). ^1H NMR δ(ppm): 7.0—7.6 (m, 8.2, arom.); 2.5 (s, 1.9, Si—CH_2—Ph); 0.2 (s, 5.9, Si—*Me*). *m/e* = 240 (M^+).

Efforts to prepare an analytical sample failed and a solid derivative (IX) was formed by reaction with NBS.

10,10-Dimethyl-11,11-dibromo-10,11-dihydro-dibenzo[b,f][1,4]oxasilepin (IX). *N*-Bromosuccinimide (0.4 g, 0.002 mol) and compound VIII (0.3 g, 0.001 mol) were stirred at reflux in 30 ml CCl_4. A small amount of benzoyl peroxide was added to the solution and the mixture was refluxed for 30 minutes under a sun lamp. Removal of the solvent after the succinimide was filtered gave a solid which was recrystallized from n-hexane to give the desired product, 0.4 g (50%), m.p. = 120—121°C. ^1H NMR δ(ppm): 7.2—8.2 (m, 8.2, arom.); 0.6 (s, 5.8, Si—*Me*). *m/e* = 398 (M^+). (Found: C, 45.33; H, 3.65. $C_{15}H_{14}OSiBr_2$ Calcd.: C, 45.22; H, 3.52%).

10,10-Dimethyl-11-deutero-10,11-dihydro-dibenzo[b,f][1,4]oxasilepin. A solution of compound VIII (0.40 g, 0.0016 mol) in 30 ml ether was treated with n-BuLi (4 ml, 1.06 *M*) in hexane. Stirring for 18 h at room temperature

gave a cloudy yellow solution to which was added, all at once, 10 ml D_2O. After stirring for 0.5 h, work up gave an oil. A crude product was collected at b.p. = 100—120°C/0.4 mmHg, 0.2 g (50%). m/e = 241 (M^+). The NMR spectrum is similar to the starting material except that the intensity of $SiCH_2Ph$ unit is half that of VIII.

Attempt to synthesize oxasilocin, X. (1) To the solution of bis(*o*-bromobenzyl) ether (0.02 mol) in 120 ml ether which had been cooled in an ice bath, n-BuLi (0.04 mol) was added. After stirring the above solution for 15 minutes, Me_2SiCl_2 (0.02 mol) in 40 ml ether was added dropwise followed by a 0.5 h reflux. After hydrolysis and removal of the solvent, the residue was vacuum distilled. There was no NMR evidence for the desired product.

(2) Bis(*o*-bromomethylphenyl)dimethylsilane (0.017 mol), Et_3N (0.3 ml) and 1 ml NaOH (46%) were refluxed for 2 h. After extraction by ether and removal of the solvent, the residue was vacuum distilled. There was no NMR evidence for the desired product.

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