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SILICON ANALOGS OF THE THIOXANTHENES

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Summary

The 9,10-dihydro-9-silaanthracene framework generated from $(o\text{-}ClMgC_6H_4)_2\text{-}CH_2$ and a dichlorosilane provides the starting point for formation of derivatives which contain a tricyclic skeleton and a three-atom side chain terminated by a nitrogen group bonded to the central ring of the framework. Reaction of the ketone, 10-oxo-9,9-dimethyl-9,10-dihydro-9-silaanthracene with either *N,N*-dimethylaminopropylmagnesium chloride or *N*-methylpiperidinylmagnesium chloride provided the alcohols which could be dehydrated with thionyl chloride/pyridine to give the silicon analogs of thioxanthene derivatives ($SiMe_2$ replaces S). Several other dehydration attempts are described as well as two other synthetic routes for introduction of an exocyclic double bond in the 10-position. Hydride addition of 9-methyl-9,10-dihydro-9-silaanthracene to *N,N*-dimethylallylamine in the presence of H_2PtCl_6 and bromination of 9,9-dimethyl-9,10-dihydro-9-silaanthracene followed by reaction with 1-methylpiperazine provided two further examples of derivatives based on the silaanthracene framework.

Introduction

Drugs which influence the mind by affecting the physiology of the brain are termed psychopharmacological agents or psychotropic drugs [1]. We are currently investigating the synthesis and structural aspects of silicon analogs of the class of psychotropics which are employed clinically as antipsychotics (neuroleptics). Recently, we reported a study of silicon derivatives (Ia) related to promazine (II), a phenothiazine ($SiMe_2$ substitutes for S), and Ib, an acridan derivative ($MeSi(CH_2)_3NMe_2$ substitutes for $HC(CH_2)_3NMe_2$) [2]. We wish to report here the isolation of silicon derivatives, such as III, that are related to thioxanthene (IV, $SiMe_2$ substitutes for S), as well as to dihydroanthracene. The structural

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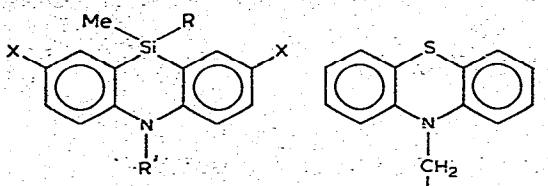
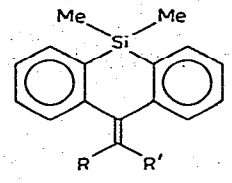
characteristics of antipsychotic derivatives which are currently in clinical use include a tricyclic skeleton with a central six-membered ring (although a few neuroleptics contain a central seven-membered ring) and a three atom side chain terminated by a nitrogen functional group [1]. These features are incorporated into the silicon compounds discussed in the next section.



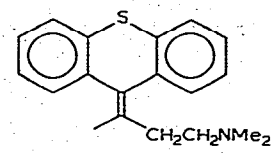
(Ia) R = Me, R′ = $(CH_2)_3NMe_2$, X = Br

(Ib) R = $(CH_2)_3NMe_2$, R′ = Me, X = H

(II)



(III)



(IV)

Results and discussion

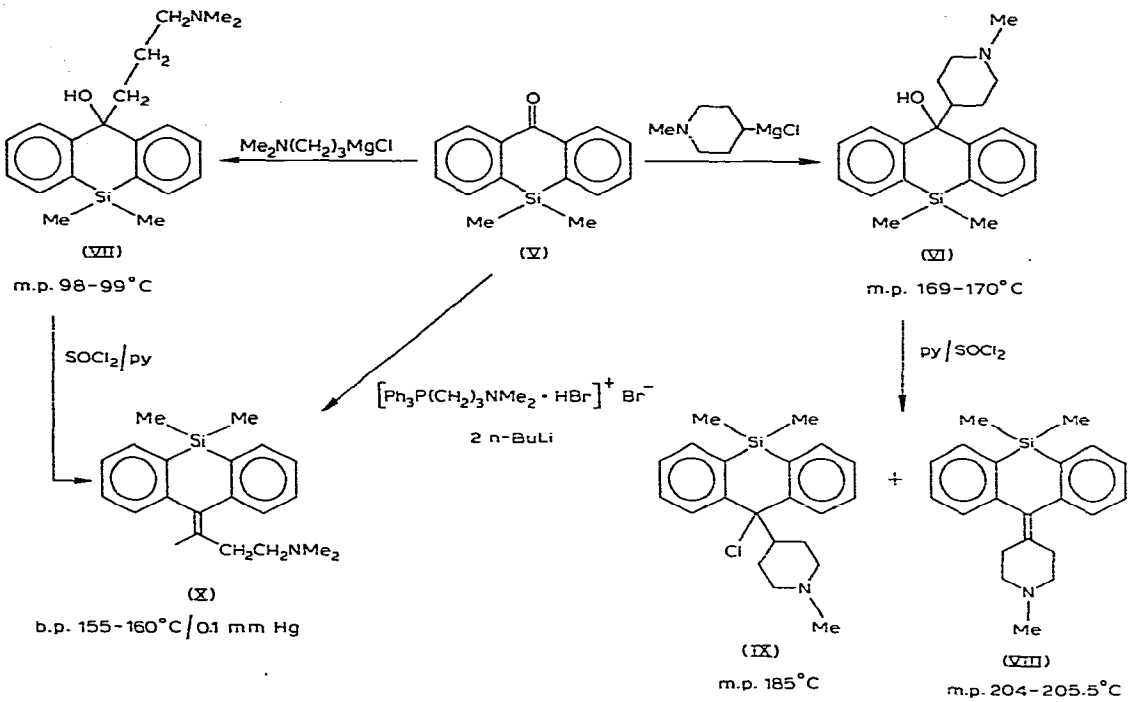
The tricyclic framework required as a precursor to the silicon analogs of thioxanthene is based upon 9,10-dihydro-9-silaanthracene. The route to the silaanthracene framework which requires the fewest steps was developed by Jutzi [3] and involves reaction of $(o\text{-}ClMgC_6H_4)_2CH_2$ with a dichlorosilane. Although formation of the Grignard reagent from *o,o′*-dichlorodiphenylmethane is frequently difficult to initiate the alternative preparation of *o,o′*-dibromodiphenylmethane is tedious [4] and ring closure via pyrolysis of $o\text{-}MeC_6H_4Si(C_6H_5)Cl_2$ requires high temperatures (670°C); in addition, these thermal reactions are normally run on a small scale [5].

Oxidation of 9,9-dimethyl-9,10-dihydro-9-silaanthracene with chromium(VI) oxide provides the ketone V. The reaction of V with *N,N*-dimethylaminopropylmagnesium chloride and *N*-methyl-4-piperidinylmagnesium chloride provides the alcohols VII and VI, respectively (Scheme 1).

A variety of dehydration methods was attempted, some of which had been reported to be successful in the generation of thioxanthenes (III). Initial investigations involved reaction of alcohol VII with 7 *N* HCl in EtOH, P_2O_5 in refluxing benzene or $SOCl_2$ in $CDCl_3$. The silicon-containing products isolated from these reactions all exhibited an upfield shift of the SiMe absorption in the ^1H NMR spectrum. Such observations are consistent with ring cleavage at silicon [6]. Attempts to effect a thermal dehydration of both alcohols VI and VII in refluxing xylene, a method which has been successfully employed in dehydration of acridan-9-ols [7], resulted only in recovery of the starting material. An attempt to dehydrate VI thermally in tetrahydronaphthalene (46 h reflux) resulted only in recovery of starting material. Attempts to dehydrate VI with methanesulfonyl chloride/sulfur dioxide in dimethylformamide or with cyclohexylcarbodiimide in ether were sunsuccessful and starting material was recovered.

The only chemical dehydration method that was successful involved reaction

SCHEME 1

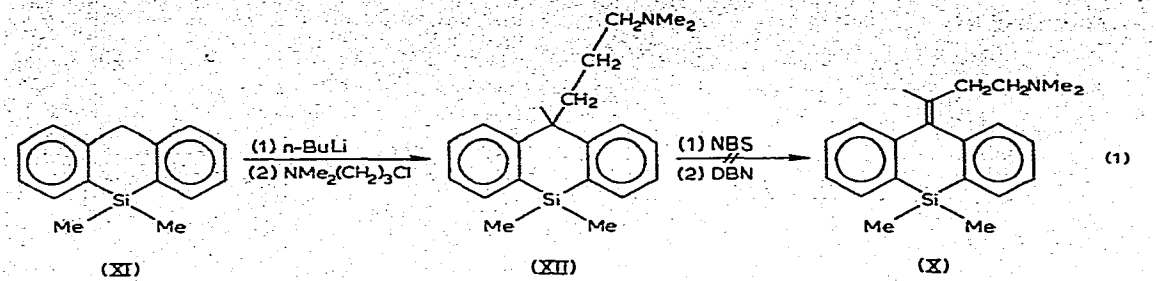


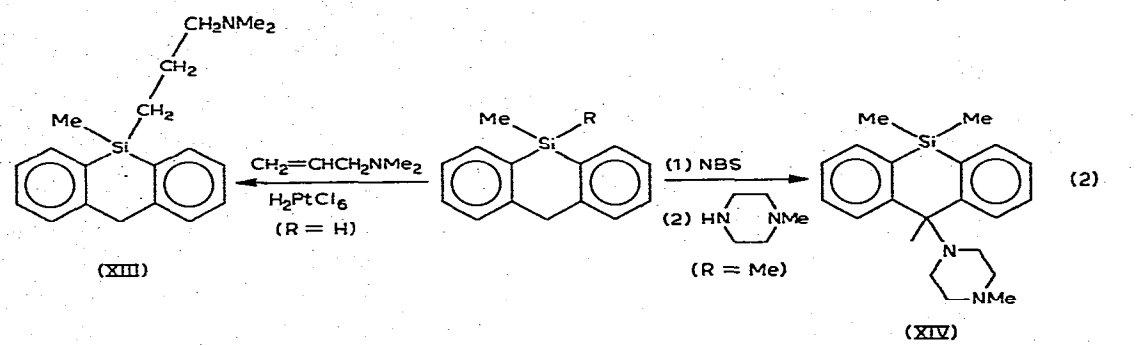
of either alcohol VI or VII with a mixture of thionyl chloride plus pyridine in benzene at room temperature. The reaction of alcohol VI may actually proceed in part via the chloride IX which undergoes elimination of HCl during distillation since the dehydration product VIII was isolated only when the products of the reaction were distilled. The yields of isolated VIII were about one-third those obtained for X.

An alternative route to X is reaction of the ketone V with the Wittig reagent generated from the reaction of $[Ph_3P(CH_2)_3NMe_2 \cdot HBr]^+Br^-$ [8] with a two molar equivalent of n-BuLi. The desired coupling product X was obtained admixed with starting ketone and presumably Ph_3PO after distillation of the reaction residue obtained from hydrolysis. The attempts to separate X and the reaction product tentatively identified as Ph_3PO by distillation or chromatographic methods were unsuccessful. The maximum yield of X produced by the Wittig reaction is less than 18%.

A third route to X, which is outlined in eq. 1, was also briefly explored. The 9,10-dimethyl-9-[3-dimethylaminopropyl]-9,10-dihydro-9-silaanthracene (XII) can be prepared from the coupling of lithiated XI (as described by Jutzi [9]) with *N,N*-dimethylaminopropyl chloride. However, attempts to brominate XII with NBS in CCl_4 with the aid of benzoyl peroxide or irradiation were unsuccessful [10].

Additional derivatives of the 9,10-dihydro-9-silaanthracene framework which also contain a side chain bonded to the central ring of the framework were also prepared as outlined in eq. 2. XIII was successfully converted into a solid hydrochloride salt.



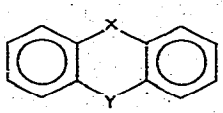


In conjunction with the synthetic studies a program is also in progress to determine the solid state structural features of tricyclic systems which contain a silicon heteroatom. Replacement of S in phenothiazines such as XIV by an $SiMe_2$ unit produced no major structural change. Table 1 summarizes the comparison of S and $SiMe_2$ heterocycles.

As can be seen from Table 1 XVI with an sp^3-C atom opposite the sulfur

TABLE 1

STRUCTURAL COMPARISON OF TRICYCLES WHICH CONTAIN S OR Si HETEROATOMS



	X	Y	C_{Ar}—X—C_{Ar}	C—A [a] (Å)	Dihedral angle [b]	Reference
XIV	S	N—Et	97°	1.776	135°	11
XV	MeSiMe [c]	N—Et	99°	1.85	141°	12
XVI	S	MeCPr-i	100°	1.763	144°	13
XVII	S	C=C(H)R [d]	101°	1.749	142°	14
XVIII	S	C=C(H)R [e]	103°	1.75	152°	15
XIX	S	C=C(R)H [f]	101°	1.758	143°	16
XIII	MeSiR [g]	CH_2	101°	1.864	132°	17
XIV	MeSiMe	HCR [h]	99°	1.872	128°	18

[a] Mean value. [b] Angle between benzo group planes. [c] 2,8-Dibromo derivative. [d] R = $CH_2CH_2NMe_2$ · HCl; 2-Cl derivative. [e] R = CH_2CH_2N⟨⟩NCH_2CH_2OH; *cis*-2-CF_3 derivative. [f] R = CH_2CH_2N⟨⟩NCH_2CH_2OH; *trans*-2CF_3 derivative. [g] $CH_2CH_2CH_2NMe_2$ · HCl (axial). [h] N⟨⟩NMe (axial).

heteroatom and the thioxanthenes XVII through XIX which contain an sp^2-C atom opposite sulfur have similar structural features; i.e., there is little change in the dihedral angle upon introduction of the exocyclic double bond. Structural work has been completed on silicon systems which contain sp^3-C atoms opposite silicon (XIII and XIV) and it appears that replacement of silicon for sulfur in thioxanthenes produces a more bent tricycle (comparison of XIII and XIV with XVI) in contrast to phenothiazines-phenazasilines (XIV and XV). It is probable that the silicon analogs of thioxanthenes will also be more bent than XVII, XVIII and XIX and a solid state structural analysis of VIII is currently in progress to verify this point.

Experimental

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

Organosilicon halides, *N,N*-dimethylallylamine and *N*-methylpiperazine were obtained commercially and were used without further purification. Dimethylaminopropyl chloride and *N*-methyl-4-chloropiperidine were generated from the commercially available hydrochloride salts by reaction with base and purified by distillation prior to use. 9,9-Dimethyl-9,10-dihydro-9-silaanthracene [3b], *o,o'*-dichlorodiphenylmethane [3b] and $[Ph_3P(CH_2)_3NMe_2 \cdot HBr]^+Br^-$ [8] were prepared according to published procedures.

THF was dried by treatment with BuLi followed by distillation [19], benzene by azeotropic distillation and pyridine by distillation from KOH.

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

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

10-Oxo-9,9-dimethyl-9,10-dihydro-9-silaanthracene (V). A modified version of the published procedure was utilized [3b]. To a stirred solution of 9,9-dimethyl-9,10-dihydro-9-silaanthracene (6.1 g, 0.027 mol) in 80 ml glacial acetic acid at room temperature was added chromium trioxide (3.6 g, 0.036 mol) (exothermic reaction). Fifteen minutes after the addition the reaction mixture was heated at reflux for one hour and then stirred at room temperature overnight. The reaction mixture was poured into 150 ml of ice water and extracted with two 100 ml portions of ether. The organic layer was separated, dried and stripped. The oil residue was distilled in a Kugelrohr apparatus to give a thick oil, b.p. 135—150°C/0.1 mmHg (lit. [3b] b.p. 110—111°C/0.04 mmHg), 5.0 g (78%), which crystallized on standing (m.p. 78°C). The ketone was used without further purification.

10-Hydroxyl-10-(N-methylpiperidinyl)-9,9-dimethyl-9,10-dihydro-9-silaanthracene (VI). A Grignard solution was prepared by addition of freshly distilled 4-chloro-*N*-methylpiperidine (2.0 g, 0.015 mol) in 50 ml anhydrous THF to a slurry of Mg mesh (0.40 g, 0.015 mol) in 10 ml THF. Ethylene bromide was added to initiate the reaction. After heating the Grignard mixture for 3 h a solution of the ketone V (2.9 g, 0.012 mol), in THF was added and the mixture heated an additional 2 h. After addition of a saturated NH_4Cl solution the THF

layer was separated and the inorganic salts washed with ether. The combined organic layers were stripped and the residue distilled in a Kugelrohr apparatus to give 2.8 g crude product, b.p. 185—200°C/0.05 mmHg. Two recrystallizations from hexanes afforded an analytical sample, m.p. 169—170°C. (Found: C, 74.71; H, 8.00. $C_{21}H_{27}NOSi$ calcd.: C, 74.78; H, 8.01%.) *m/e* 337. ^1H NMR ($CDCl_3$) δ (ppm): 8.2—7.7 (m, 7.6 aromatics); 2.8—2.5 (m, 1.6, CH); 1.75 (s, 3.4, NMe); 1.7—0.8 (m, 7.0, CH_2); 0.5 (s, 6.1, $SiMe_2$).

10-Hydroxyl-10-(N,N-dimethylaminopropyl)-9,9-dimethyl-9,10-dihydro-9-silaanthracene (VII). In a manner similar to the preparation of VI, *N,N*-dimethylaminopropylmagnesium chloride was generated in THF from freshly distilled *N,N*-dimethylaminopropyl chloride (4.7 g, 0.039 mol) and Mg mesh (4.25 g, 0.18 mol). After addition of the ketone V (4.25 g, 0.018 mol) the solution was heated at reflux for 13 h and then treated with a saturated NH_4Cl solution. The precipitated magnesium salts were washed with ether and the ether washings added to the THF solution, whereupon a white precipitate formed. After filtration, the THF/ether filtrate was stripped to give a yellow oil which crystallized on standing to give 4.5 g crude alcohol. Recrystallization of the crude alcohol provided an analytical sample, m.p. 98—99°C. (Found: C, 74.39; H, 8.08. $C_{20}H_{27}NOSi$ calcd.: C, 73.84; H, 8.31%.) ^1H NMR ($CDCl_3$) δ (ppm): 8.1—7.9 and 7.6—7.1 (m, 7.9, Ar); 2.30 (s, 5.7, NMe_2); 2.30—1.65 and 1.4—1.1 (m, 6.8; $(CH_2)_3$); 0.50 (d, 5.4, $SiMe_2$) *m/e* 325 (20 eV).

The white solid which precipitated upon addition of the ether to the THF solution was recrystallized from $EtOAc/Et_2O$ to give long white needles, m.p. 186.5—187.5°C. Analysis corresponds to the dihydrate of the HCl salt of the alcohol VII. (Found: C, 59.61; H, 7.01. $C_{20}H_{27}NOSi \cdot HCL \cdot 2\ H_2O$ calcd.: C, 60.36; H, 8.05%.) ^1H NMR ($CDCl_3$) δ (ppm) (dilute solution; partial listing): 2.6 (s, $NHMe_2$); 0.55—0.45 (d, $SiMe_2$). Attempts to remove water by heating in vacuo at 80°C were unsuccessful. A sample of the HCl salt was treated with 4 *M* NaOH and evaporation of the ether extract provided alcohol VII identical with that isolated from the THF/Et_2O layer.

Dehydration of 10-hydroxyl-10,10-(N-methylpiperidinyl)-9,9-dimethyl-9,10-dihydro-9-silaanthracene. To a sample of the crude alcohol VI (1.2 g, 0.0036 mol), dissolved in 50 ml dry benzene was added pyridine (0.60 g, 0.0071 mol) followed by freshly distilled thionyl chloride (0.85 g, 0.0071 mol) and the mixture stirred for 15 min. After addition of a 4 *M* NaOH solution and extraction with ether, the ether layer was dried over Na_2SO_4 and stripped to give an oil. Kugelrohr distillation afforded 0.75 g of oil, b.p. 150—195°C/00.15 mmHg. Elution of the distilled oil over 70 g of basic alumina with 20% MeOH in benzene afforded 0.48 g of solid. Recrystallization from cyclohexane, followed by rerecrystallization from isopropyl alcohol, gave pure VIII, m.p. 204—205.5°C, 0.20 g (16%). (Found: C, 79.11; H, 7.97. $C_{21}H_{25}NSi$ calcd.: C, 79.00; H, 7.84%.) *m/e* 319. ^1H NMR ($CDCl_3$) δ (ppm): 7.6—7.0 (m, 8.0, Ar); 2.9—2.4, 2.3—1.6 (m, CH_2) and 2.25 (s, NMe) (rel. int. 11.5); 0.6, 0.3 (d, 5.5, $SiMe_2$).

If the reaction residue was passed directly over a basic alumina column, elution with benzene gave a portion which after several recrystallizations from cyclohexane afforded a pure sample of 10-chloro-10-(*N*-methylpiperidinyl)-9,9-dimethyl-9,10-dihydro-9-silaanthracene, m.p. 185°C (4.6%). (Found: C, 70.71; H, 7.45. $C_{21}H_{26}ClNSi$ calcd.: C, 70.91; H, 7.32%.) *m/e* 355 (^{35}Cl; 20 eV).

Dehydration of 10-hydroxyl-10-(N,N-dimethylaminopropyl)-9,9-dimethyl-9,10-dihydro-9-silaanthracene. In a manner described for the dehydration of alcohol VI, crude alcohol VII (2.0 g, 0.0062 mol) was dissolved in benzene, and dry pyridine (1.4 g, 0.018 mol) and $SOCl_2$ (2.5 g, 0.021 mol) were added. After stirring overnight at room temperature the reaction mixture was hydrolyzed with 5% NaOH and extracted with ether. Kugelrohr distillation of the oil which remained after removal of the ether afforded crude IX, b.p. 140—160°C/0.1 mmHg, 0.9 g. An analytical sample was obtained by elution over 50 g of basic alumina and Kugelrohr distillation of the fraction collected in 20% MeOH in C_6H_6 (b.p. 155—160°C/0.1 mmHg). (Found: C, 78.26; H, 8.29. $C_{20}H_{25}NSi$ calcd.: C, 78.17; H, 8.14%.) *m/e* 307.

Attempts to prepare the fumarate or maleate salts produced only oils which could not be induced to crystallize.

Reaction of 10-oxo-9,9-dimethyl-9,10-dihydro-9-silaanthracene and $[Ph_3P(CH_2)_3NMe_2 \cdot HBr]^+Br^-$. To a suspension of freshly prepared phosphonium salt $[Ph_3P(CH_2)_3NMe_2 \cdot HBr]^+Br^-$, (12.4 g, 0.0244 mol) in 50 ml THF was added n-BuLi (0.050 mol, 2.29 *M*). To the red solution was added dropwise a solution of the ketone V (4.5 g, 0.019 mol) in 40 ml THF; thereupon, the reaction mixture was heated at reflux for 8 h. After the solvents were stripped the residue was hydrolyzed with 40 ml 10% NaOH and extracted with benzene. The benzene extracts were dried over $MgSO_4$ and stripped. The oil residue was distilled on a Kugelrohr apparatus to give a fraction, 120—165°C/0.2 mmHg, 1.1 g. Elution of 0.2 g of distilled product over 25 g of basic alumina provided 0.15 g of material which eluted with benzene. The NMR spectrum was identical with that exhibited by X prepared from VII and $SOCl_2$/py, except for enhanced absorption in the aromatic region. The characteristics of the thin-layer chromatogram exhibited by the oil obtained from elution over alumina were identical with those obtained from a mixture of authentic samples of X and Ph_3PO.

9-Methyl-9,10-dihydro-9-silaanthracene. To a slurry of Mg (mesh, 8.088 g, 0.337 mol) in 20 ml of anhydrous THF, which had been activated by addition of 0.5 ml ethylene bromide, was added, dropwise, *o,o'*-dichlorodiphenylmethane (13.14 g, 0.0557 mol) dissolved in 100 ml THF, while maintaining a gentle reflux. The reaction mixture was heated an additional 3 to 18 h, during which time a dark reddish-brown solution was obtained which gave a positive Grignard test [20]. After the Grignard solution had cooled to room temperature, a solution of $MeSiHCl_2$ (6.0 ml, 0.057 mol) in 30 ml of THF was added dropwise, and the mixture heated at reflux for 5 h. After stripping the THF layer, 150 ml of ether were added and the slurry heated for 0.5 h before hydrolysis with saturated ammonium chloride. The ether layer was stripped and a Kugelrohr distillation of the residue afforded 5.32 g oil, b.p. 115—130°C/0.15 mmHg (46% crude yield). A purified sample was prepared from a twice-distilled portion which afforded a solid, m.p. 65—66°C after recrystallization from EtOH. ^1H NMR (CCl_4) δ (ppm) (external TMS): 7.55—7.80 (m, Ar); 4.90—4.65 (q, SiH); 4.05—3.85 (br, s, CH_3); 0.65—0.55 (d, SiMe). *m/e* 310.

9-Methyl-9-(N,N-dimethylaminopropyl)-9,10-dihydro-9-silaanthracene hydrochloride. To a 1.7 g sample of crude 9-methyl-9,10-dihydro-9-silaanthracene were added 2 ml allylamine and 3 drops of H_2PtCl_6/t-BuOH. After the initial foaming had subsided, the mixture was refluxed for 16 h. The volatiles were stripped and

the residue eluted over 60 g of basic alumina. The spectral properties of the pale yellow oil, 1.1 g, eluted with 40% MeOH/C_6H_6, were consistent with the desired product, XIII: ^{1}H HMR ($CDCl_3$) δ (ppm): 7.65—6.80 (m, 8.0, Ar); 4.15—3.95 (q, 1.8, $ArCH_2Ar$); 2.35—1.8 (t + s, 7.8, CH_2NMe_2); 1.8—0.65 (m, 4.1, CH_2CH_2); 0.50 (s, 3.0, SiMe).

Hydrogen chloride gas was bubbled into a solution of a 1.0 g sample of purified XIII dissolved in 25 ml Et_2O. Chloroform was added until the oil which had separated redissolved. Upon cooling, 0.5 g of hydrochloride salt was obtained. An analytical sample of XIII · HCl was obtained from recyrstallization from $CHCl_3$/xylenes, m.p. 162—63°C. (Found: C, 68.41; H, 7.97. $C_{19}H_{26}ClNSi$ calcd.: C, 68.78; H, 7.84%.)

10-Piperazinyl-9,9-dimethyl-9,10-dihydro-9-silaanthracene (XIV). A slurry of 9,9-dimethyl-9,10-dihydro-9-silaanthracene (3.3 g, 0.015 mol) dissolved in 25 ml of CCl_4 and *N*-bromosuccinimide (2.6 g, 0.015 mol) was heated to reflux and illuminated with a G.E. sunlamp. Upon completion of the reaction, as indicated by the formation of succinimide (which is insoluble in CCl_4 but less dense), the cooled reaction mixture was filtered and the filtrate stripped to give an oil which was dissolved in 30 ml toluene and then treated with 7 ml *N*-methylpiperazine. After a 12 h reflux the reaction mixture was filtered to remove the HBr salt of *N*-methylpiperazine and the filtrate stripped of all volatile material. The residue was crystallized from EtOH to give 1.6 g (34%) white solid, m.p. 164—165°C. ^{1}H NMR ($CDCl_3$) δ (ppm); 7.65—6.9 (m, 8.0, Ar); 4.0 (s, 0.7, CH); 2.25, 2.20 (s, br s, 11, piperazinyl); 0.65—0.55 (d, 6.2, $SiMe_2$). An analytical sample was prepared by recrystallization from EtOH, m.p. 166—167°C. (Found: C, 74.50; H, 8.25. $C_{20}H_{26}N_2Si$ calcd.: C, 74.53; H, 8.07%.) *m/e* 322.

Biological testing. The HCl salt of XIII and the neutral base XIV have been tested for CNS activity. XIV exhibited no activity whereas XIII · HCl exhibited patterns of activity similar to that shown by silipramine and related derivatives *.

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