Journal of Organometallic Chemistry, 194 (1980) 15—22

TRICYCLIC SYSTEMS WHICH CONTAIN SILICON AND NITROGEN HETEROATOMS IN CENTRAL SEVEN- AND EIGHT-MEMBERED RINGS

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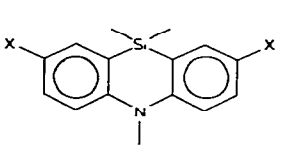
(Received January 21st, 1980)

Summary

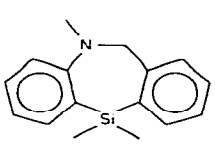
The generation of three tricyclic ring systems which contain both silicon and nitrogen heteroatoms in the central ring are described. Dibenz[*b*,*e*][1,4]azasilepines are formed in the reaction of dichlorosilanes with the lithiation product from *o*-$BrC_6H_4N(CH_3)CH_2C_6H_4Br$-*o* and n-BuLi but the direct reaction products could not be purified. Dibenz[*b*,*f*][1,4]azasilepines are prepared from the fluoride ion induced expansion of a phenazasiline. Dibenz[*c*,*f*][1,5]azasilocines are produced from reaction of $(o\text{-}BrCH_2C_6H_4)_2Si(CH_3)_2$ with primary amines. Incorporation of dimethylaminopropyl side chains at both silicon and nitrogen heteroatoms is also described.

Introduction

We have previously described routes to the synthesis of phenazasilines, I, [1]. An approach to the synthesis of related dibenzsilazepins, II and III, as well as to the dibenzsilazocine, IV, is outlined in this report. The incorporation of functionalized side chains at both the silicon center and the nitrogen center is discussed.



(Ia, X = Br;
Ib, X = H)



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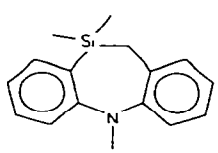

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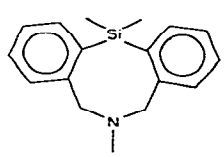
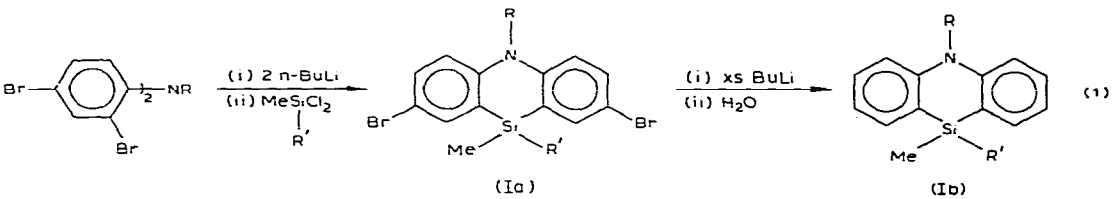


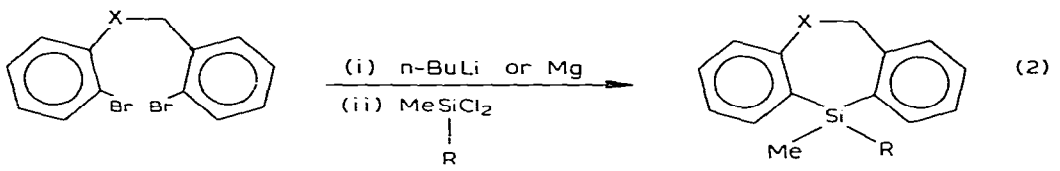
(IV)

Results and discussion

Convenient access to phenazasilines is provided in a three-step sequence which begins with conversion of commercially available diphenylamine to a tertiary amine, Ph_2NR (R = Me, Et), prior to bromination to give the 2,2',4,4'-tetrabromo-*N*-(alkyl)diphenylamines required for ring closure (Eqn. 1) [1]. The bromine substituents on Ia could be removed by treatment with excess n-butyllithium followed by hydrolysis [1].



In principle the dilithio- or diGrignard route can be utilized to generate the seven membered rings, the dibenz[*b*,*e*][1,4]silaheteroepins, as is illustrated in Eqn. 2 for the general case. Although the silacycle, VIc, is readily prepared

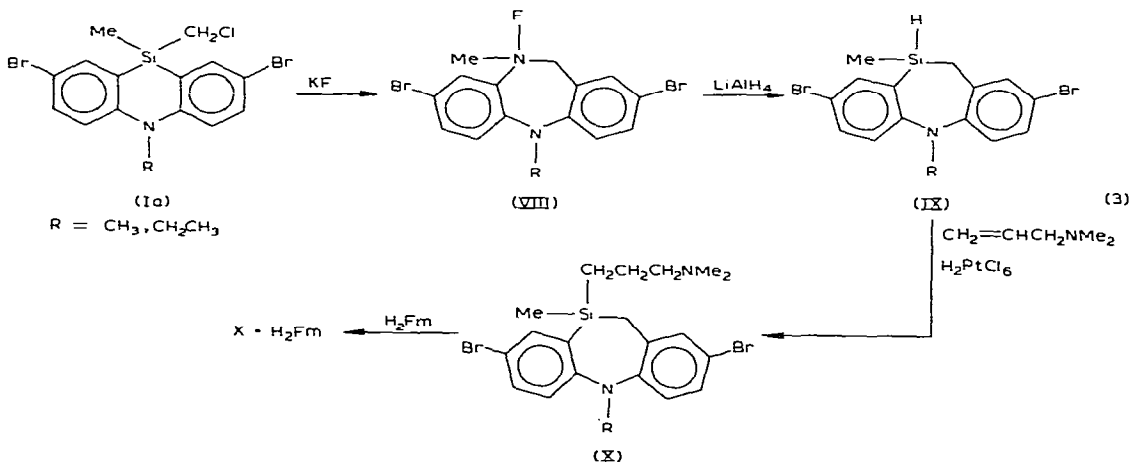


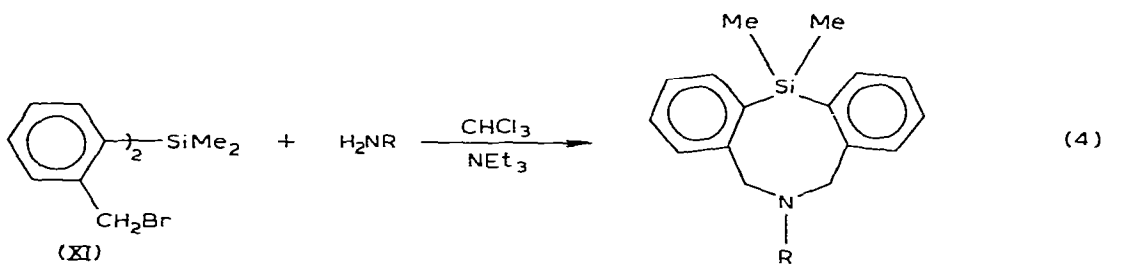
from *o*,*o*'-dibromobibenzyl and n-BuLi in yields around 50% [2], efforts to generate silaheterocycles VIa and VIb required more careful control of conditions and produced low yields (<20%) of cyclized product. The thiasilepins, VIa, could only be prepared via the Grignard reagent [3]. The oxasilepins were prepared from halogen/metal exchange of *o*,*o*'-dibromobenzylphenyl ether with n-BuLi and could not be completely separated from byproducts [4]. Not surprisingly similar difficulties were encountered in efforts to produce the silazepines, II.

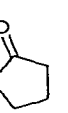
An earlier study [5] reported the formation of 10,11-dihydro-5-phenyl-5H-dibenzo[*b*,*f*][1,4]azarsepine in low yields (<5%) from trapping of the lithiated product from *o*-bromo-*N*-(*o*-bromobenzyl)aniline, VII, and BuLi/TMEDA with phenyldichloroarsine. It is likely that the high ratio of BuLi to benzylaniline of about 6/1 resulted in lithiation of =NH as well as the halogen/metal exchange and thus the trapping reaction is more complicated than the desired ring closure. Thus, our initial efforts involved methylation of VII. Since two methylated products including the desired Va, *o*-$BrC_6H_4N(CH_3)CH_2C_6H_4Br$-*o*, were formed in equal amounts from treatment of VII with n-BuLi followed by Me_2-

SO_4, an alternate methylation of VII with NaH/MeI in tetrahydrofuran was developed. The Grignard route to II proved unsuccessful and conditions for ring closure from Va and n-BuLi were found to be somewhat critical. Successful isolation of impure II occurred only when the lithiation step was performed at $\simeq 0°C$ and the reaction with dichlorosilanes, $Me(R)SiCl_2$ was conducted at room temperature. Efforts to purify the ring closure products, II (a, R = Me; b, R = H; c, R = $CH_2CH_2CH_2Br$), were uniformly unsuccessful. Conversion of IIc (R = $CH_2CH_2CH_2Br$) with $HNEt_2$ gave the diethylaminopropyl derivative, IId (R = $CH_2CH_2CH_2NEt_2$), as an oil which could be purified by elution over basic alumina. Attempts to prepare a solid hydrochloride salt of the amine, however, failed. Addition of IIb to *N,N*-dimethylallylamine produced IIe (R = CH_2CH_2-CH_2NMe_2) which had properties similar to IId.

The dibenz[*b,f*][1,4]silazepine system, VIII, was formed by ring expansion of phenazasiline, Ia (R′ = CH_2Cl) with potassium fluoride in acetonitrile. The fluorosilane, VIII, was reduced to the hydrosilane, IX, with $LiAlH_4$ and hydride addition of IX to *N,N′*-dimethylallylamine afforded X which was successfully converted to the crystalline fumarate salt. The reaction sequence is shown in Eqn. 3. The conformation of VIII in the solid state has been determined by an





(XIIa, R = $CH_2C_6H_5$;
XIIb, R = t-Bu;
XIIc, R = c-C_6H_{11};
XIId, R = CH_3;
XIIe, R = $CH_2CH_2CH_2N$  ;
XIIf R = $CH_2CH_2CH_2NMe_2$)

X-ray study [6]. The tricycle exhibits a folded boat conformation and contains features that are similar to the psychotropic drug, imipramine.

Although there are several possible tricyclic systems which contain both silicon and nitrogen atoms in a central eight-membered ring, the only readily accessible derivative is prepared from the condensation of primary amines with bis(*o*-bromomethylphenyl)dimethylsilane (Eqn. 4). All the azasilocins which were prepared were characterized by a singlet ring methylene absorption in the ^{1}H NMR spectra. Such behavior is consistent with the flexible boat conformer [7]. The boat conformation of XII (R = tBu) has been confirmed in the solid state [8] and the molecular motions of XII (R = Me) have also been analyzed in the solid [9]. Thiasilocins related to XII have been prepared from XI and Na_2S [3] but the oxasilocins could not be generated from XI [4].

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, Me_2SiCl_2, $Me(ClCH_2)SiCl_2$, *o*-$BrC_6H_4NH_2$, CH_2=$CHCH_2NMe_2$, $HNEt_2$, *o*-$BrC_6H_4CH_3$, $LiAlH_4$, $MeNH_2$, t-$BuNH_2$, c-$C_6H_{11}NH_2$, $H_2N(CH_2)_3\overline{N}CH_2CH_2CH_2\dot{C}$=O and n-BuLi were used as supplied.

Methyl(3-bromopropyl)dichlorosilane was prepared from allyl bromide and $MeSiHCl_2$ in the presence of H_2PtCl_6 [10]. 2,2′,4,4′,-tetrabromo-(*N*-alkyl)-diphenylamines were prepared by bromination of *N*-alkyldiphenylamine [1] and *o*-Bromo-*N*-(*o*-bromobenzyl)aniline was prepared from *o*-bromobenzyl bromide and *o*-bromoaniline [5]. *o*-Bromobenzyl bromide was obtained by the bromination of *o*-bromotoluene [11] and bis-(*o*-bromomethylphenyl)dimethylsilane was prepared by bromination of bis-(*o*-tolyl)dimethylsilane [3].

Tetrahydrofuran was dried by treatment with n-BuLi followed by distillation [12].

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

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

o-Bromo-N-(o-bromobenzyl)methyl aniline

Sodium hydride (4.0 g, 50% oil dispersion, 0.083 mol) was washed with petroleum ether (3—30 ml portions) and dried under vacuum. *o*-Bromo-*N*-(*o*-bromobenzyl)aniline (10 g, 0.028 mol) and methyl iodide (15 ml) dissolved in dry THF were added to the sodium hydride and the reaction mixture stirred at room temperature overnight. Ethyl acetate (50 ml) was added slowly to the mixture followed by water (50 ml). The volatile material was removed from the aqueous mixture and the water/oil residue extracted with ether and the ether layer dried over anhydrous sodium sulfate. After removal of the ether the oil

was distilled to give *o*-$BrC_6H_4CH_2N(Me)C_6H_4Br$-*o*, b.p. 142—148°C/0.10 mm Hg (8.8 g, 83%). ^1H NMR δ (ppm): 8.0—6.9 (m, 8.3, Arom); 4.5 (s, 1.9, NCH_2); 2.8 (s, 2.7, NCH_3). *m/e* = 351 (M^+ based on ^{79}Br). The distilled product was used for ring closure reactions.

All preparations which employed NaH from an oil dispersion were successful but use of solid NaH produced irratic results.

Reaction of o-bromo-N-(o-bromobenzyl)methylaniline with n-BuLi followed by chlorosilanes.

1) $MeSi(CH_2CH_2CH_2Br)Cl_2$. A solution of *o*-bromo-*N*-(*o*-bromobenzyl)methylaniline, Va (6.0 g, 0.017 mol), dissolved in 50 ml ethyl ether was stirred in an ice bath for 0.5 h. Butyllithium (0.036 mol, 1.6 *M*) was added dropwise to the cooled aniline solution, the mixture stirred for an additional 0.5 h and then allowed to warm to room temperature. A solution of 3-bromopropylmethyldichlorosilane (4.2 g, 0.018 mol) in ether (50 ml) was added dropwise and the solution stirred at room temperature overnight. After aqueous workup and evaporation of the solvent the ring-closed product, IIc (R = $CH_2CH_2CH_2Br$) was obtained in the fraction, b.p. = 180—200°C/0.4 mm Hg, 3.2 g. ^1H NMR δ (ppm): 8—6.9 (m, Ar); 4.6—4.0 (q, CH_2); 3.5—3.1 (t, CH_2Br), 2.95 (s, NCH_3); 2.1—0.9 (m, $SiCH_2CH_2$); 0.5 (s, $SiCH_3$). *m/e* = 359 (M^+, based on ^{79}Br). Attempts to purify the product were unsuccessful (all preparations were characterized by enhanced CH absorption in the region between 2—1 ppm). The crude product was used for the formation of II (R = $CH_2CH_2CH_2NEt_2$).

When the lithiation reaction and trapping reaction were both conducted at room temperature or at ice bath temperatures ring-closure products were either not obtained or obtained in low yields.

2) Me_2SiCl_2. According to the same procedure, the lithiation of Va (6.2 g, 0.017 mol) with n-BuLi (24 ml, 1.6 *M*) followed by reaction with dimethyldichlorosilane (2.3 ml, 0.019 mol) gave product in the distilled fraction, b.p. 150—200°C/0.1 mm Hg, 2.2 g. Elution of the distilled oil over basic alumina and redistillation of the oil which eluted in the $MeOH/C_6H_6$ = 1/9 fraction failed to generate an analytically pure sample. ^1H NMR δ (ppm): 7.9—6.9 (m, Arom); 4.5 (s, N—CH_2); 3.0 (s, N—CH_3); 0.6 (s, Si—CH_3). *m/e* = 253 (M^+).

3) $MeSiHCl_2$. According to the same procedure, the lithiation of Va (13 g, 0.037 mol) with n-BuLi (46 ml, 1.6 *M*) followed by reaction with methyldichlorosilane (3.8 ml, 0.037 mol) gave product in the distilled fraction, b.p. 140—150°C/0.2 mm Hg, 2.4 g. ^1H NMR δ (ppm): 8.0—6.8 (m, Arom); 5.2—5.0 (q, SiH); 4.3 Brd s, NCH_2); 2.9 (s, NMe); 0.59—0.57 (d, SiMe). All preparations contained byproducts which resulted from incorporation of butyl groups (broad absorption in ^1H NMR from 0.7 to 1.6 ppm) which could not be removed by redistillation or elution chromatography over basic alumina.

5,10-Dimethyl-5-(γ-diethylaminopropyl)-10,11-dihydro-5H-dibenz[b,e][1,4]-azasilepine

IIc (3.2 g, 0.0089 mol), benzene (50 ml) and diethylamine (5 ml) were heated at reflux, with stirring, for 20 h. After removal of the precipitated diethylammonium bromide the volatiles were removed and the residue purified by elution over basic alumina. The product was obtained as an oil from the

MeOH/C_6H_6, 1/9, fractions. ^{1}H NMR δ (ppm): 7.9—6.9 (m, 8.7, Ar); 4.6—4.0 (q, 1.9, N—CH_2); 2.9 (s, 3.2, N—CH_3); 2.7—2.1 (t + q, 6, $CH_2N(CH_2CH_3)_2$); 1.8—0.7 (m + t, 9.2, $SiCH_2CH_2CH_2N(CH_2CH_3)_2$); 0.56 (s, 3.0, $SiCH_3$). *m/e* = 352 (M^+). (Found: C, 74.48; H, 9.15. $C_{22}H_{32}N_2Si$ Calcd.: C, 75.00; H, 9.09%.) Efforts to further purify the eluted sample by distillation resulted in decomposition.

Attempts to prepare a solid salt with HCl or fumaric acid failed.

Reaction of IIb with N,N-Dimethylallylamine

A mixture of crude IIb (2.4 g) and *N,N*-dimethylallylamine (3 ml) and the catalyst, H_2PtCl_6, were heated at reflux for three hours. After removal of the excess amine the residue was distilled. The fraction, b.p. 140—160°C/0.05 mm Hg, 1.0 g, was eluted over 60 g of basic alumina and the product, IIe, was obtained as an oil from the fraction, MeOH/C_6H_6 = 1/9, 0.70 g. ^{1}H NMR δ (ppm): 7.7—6.7 (m, 7.9, Arom); 4.6—4.0 (q, 1.8, NCH_2); 3.0 (s, 3.0, NCH_3); 2.4—2.0 (s + t, 7.7, $CH_2N(CH_3)_2$); 1.9—0.8 (brd m, 4.9, $SiCH_2CH_2$); 0.53 (s, 3.0, $SiCH_3$). *m/e* = 322 (M^+). Attempts to induce the oil crystallize failed as did efforts to prepare solid salts with HCl, fumaric and maleic acids. Redistillation of the IIe which had been eluted over basic alumina failed to produce an analytical sample.

2,8-Dibromo-5,10-dimethyl-10-chloromethyl-5,10-dihydrophenazasiline, Ia

The phenazasiline was prepared according to the published procedure [1] from 2,2′4,4′-tetrabromodiphenylmethylamine (8.0 g, 0.016 mol) in diethyl ether (150 ml) and n-BuLi (20 ml, 1.6 *M*) followed by addition of methylchloromethyldichlorosilane (2 ml, 0.016 mol). After aqueous workup and removal of the volatiles, the product was obtained in the fraction, b.p. = 190—210°C/0.1 mm Hg, 4.5 g. Trituration with heptanes gave a solid and three recrystallizations from heptane gave a purified sample, m.p. 122.5—124°C. ^{1}H NMR δ (ppm): 7.7—6.8 (m, 6.1, Arom); 3.5 (s, 3.0, NCH_3); 2.9 (s, 1.8, $SiCH_2Cl$); 0.73 (s, 3.1, $SiCH_3$). (Found: C, 42.31; H, 3.49. $C_{15}H_{14}Br_2ClNSi$ Calcd.: C, 41.71; H, 3.24%.) The corresponding N—CH_2CH_3 derivative was similarly prepared, and characterized by m.p. = 114—116°C.

2,8-Dibromo-5,10-dimethyl-10-fluoro-10,11-dihydro-5H-dibenz[b,f][1,4]azasilepine, VIII

A mixture of Ia (5.9 g, 0.014 mol), KF (0.81 g technical grade which had been dried in an oven at 110°C for 24 h) and CH_3CN (50 ml) were heated at reflux for 24 h. Water was added to dissolve the inorganic salts and the mixture was extracted with Et_2O. After evaporation of the ether layer the oil was triturated with heptanes and the solid product, VIII (4.0 g) was obtained. ^{1}H NMR δ (ppm): 7.6—6.8 (m, 5.9, Arom); 3.2 (s, 3.0, N—CH_3); 2.9—2.1 (m, 2.1, NCH_2); 0.4—0.28 (d, 3.0, $SiCH_3$; $CHSiF$ = 7.2 Hz). *m/e* = 413 (M^+ based on ^{79}Br). Recrystallization from heptane provided the analytical sample, m.p. 129.5—130.5°C. (Found: C, 43.73; H, 3.64. $C_{15}H_{14}Br_2SiNF$ Calcd.: C, 43.37; H, 3.37%.) The corresponding N—CH_2CH_3 derivative was similarly prepared and characterized by m.p. = 105—107°C.

2,8-Dibromo-5,10-dimethyl-10-(γ-dimethylaminopropyl)-10,11-dihydro-5H-dibenz[b,f][1,4]azasilepine, X and X · H_2Fm

The ring expansion product produced from Ia (5.2 g) was dissolved in Et_2O and added to a slurry of $LiAlH_4$ (2 g) in Et_2O (150 ml) and heated at reflux for 1 h. After hydrolysis with saturated NH_4Cl the ether layer was removed, dried, concentrated, and distilled to give the silane (IX) as an oil, b.p. 170—190°C/0.05 mm Hg, 3.2 g. ^1H NMR δ (ppm) (in part): 4.5—4.3 (q, SiH); 2.6—2.3 (brd m, $SiCH_2Arom$; 0.35—0.28 (d, $SiCH_3$). The $N—CH_2CH_3$ derivative was similarly prepared and characterized by a b.p. 165—185°/0.05 mm Hg.

The distilled silane, IX, was added to *N,N*-dimethylallylamine and two drops H_2PtCl_6 in t-BuOH added. The mixture was heated to reflux for 2.5 h, filtered, stripped and distilled to give the free amine, X, b.p. 195—215°C/0.1 mm Hg, 2.3 g. ^1H NMR δ (ppm): 7.5—6.2 (m, 6.9, Arom); 3.2 (s, 3.6, $N—CH_3$); 2.8—1.9 (s + m, 9.2, $CH_2N(CH_3)_2$ and $SiCH_2Arom$); 1.9—0.5 (m, 3.7, $SiCH_2CH_2CH_2N(CH_3)_2$); 0.17 (s, 2.5, $SiCH_3$). The $N—CH_2CH_3$ derivative was similarly prepared and characterized by a b.p., 190—210°C/0.05 mm Hg.

To the distilled product dissolved in EtOH was added furmaric acid (0.56 g) in i-PrOH and the solvent removed. Xylenes were added to the gum and EtOAc was added until the gum had nearly dissolved. After cooling, the clear solution was decanted from the separated oil and kept at 5°C overnight. The impure, filtered solid, 2.4 g, was recrystallized from EtOH followed by recrystallization from i-PrOH to give the analytical sample, m.p. 168—170°C. (Found: C, 48.18; H, 5.21. $C_{24}H_{30}Br_2N_2O_4Si$ Calcd.: C, 48.16; H, 5.02%.) ^1H NMR δ (ppm) (DMSO; ext. TMS): 7.8—7.0 (m, 5.2, Arom); 6.6 (s, 1.9, $CH=CH$); 3.2 (s, 4.2, $(Arom)_2N—CH_3$); 3.0—2.3; 2.7 (m + s, 11.5, $CH_2N^+(H)(CH_3)_2$ and $SiCH_2Arom$); 1.9—0.35 (brd m, 4.4, $SiCH_2CH_2$); 0.18 (s, 2.7, $SiCH_3$). Similarly prepared was the $N—CH_2CH_3$ derivative as a gum which did not crystallize.

Reaction of bis-(o-bromomethylphenyl)dimethylsilane and primary amines

a) $C_6H_5CH_2NH_2$. A mixture of XI (5.8 g, 0.015 mol), Et_3N (5 ml), $C_6H_5CH_2NH_2$ (1.8 ml) and $CHCl_3$ (75 ml) were heated and stirred at reflux for 4.5 h. The precipitated salt was removed. The solvent was evaporated and the solid residue was recrystallized from EtOH to give XIIa (R = $CH_2C_6H_5$), m.p. 137—138°C, 1.9 g (37%). ^1H NMR δ (ppm): 7.8—6.8 (m, 13.7, Arom); 3.6 and 3.5 (s + s, 5.6, $(CH_2)_2NCH_2$); 0.47 (s, 5.8, $Si(CH_3)_2$). (Found: C, 80.52; H, 7.32. $C_{23}H_{25}NSi$ Calcd.: C, 80.44; H, 7.28%.)

b) t-$BuNH_2$. According to the same procedure, XIIb, m.p. 98.5—99.5°C (20%), was prepared from XI (3.1 g, 0.0078 mol) and t-$BuNH_2$ (0.61 g, 0.0083 mol). ^1H NMR δ (ppm): 7.8—7.0 (m, 7.9, Arom); 3.9 (s, 3.9, $N(CH_2)_2$; 1.07 (s, 9.1, $C(CH_3)_3$); 0.63 (s, 6.1, $Si(CH_3)_2$). The product was characterized by an X-ray crystallographic study [9].

c) c-$C_6H_{11}NH_2$. According to the same procedure, XIIc, m.p. 128.5—130°C (48%), was prepared from XI (5.2 g, 0.013 mol) and c-$C_6H_{11}NH_2$ (1.55 ml). ^1H NMR δ (ppm): 7.8—7.0 (m, 7.8, Arom); 3.83 (s, 3.9, $N(CH_2)_2$); 1.9—0.83 (brd. m, 10.9, $N—C_6H_{11}$); 0.55 (s, 6.3, $Si(CH_3)_2$).

d) $MeNH_2$. $MeNH_2$ was bubbled into $CHCl_3$ (75 ml) until there was a weight gain of 2 g. XI (5.1 g, 0.013 mol) and Et_3N (5 ml) were added and the mixture heated as described in the previous paragraph except that a dry-ice condenser

replaced the usual reflux condenser. After workup a yellow oil which slowly solidified was obtained. Recrystallization from EtOH gave XIId (R = CH_3), m.p. 52—53°C, 1.7 g (50%). ^{1}H NMR δ (ppm): 7.8—7.0 (m, 7.9, Arom); 3.6 (s, 4.1, $N(CH_2)_2$); 2.3 (s, 3.1, NCH_3); 0.43 (s, 5.8, $Si(CH_3)_2$). (Found: C, 76.23; H, 7.81. $C_{17}H_{21}NSi$ Calcd.: C, 76.40; H, 7.87%.)

e) $H_2NCH_2CH_2CH_2\overline{N(CH_2)_3CO}$. XI (4.8 g, 0.012 mol), $H_2N(CH_2)_3\overline{N(CH_2)_3CO}$ (4.3 g, 0.032 mol) and $CHCl_3$ (75 ml) were refluxed for 4 h and the solvent was then removed. The residue was treated with 6 *M* NaOH (100 ml) and extracted with ether. After removal of ether the oil was distilled and the product obtained in the fraction, b.p. 190—215°C/0.4 mm Hg, 2.7 g. After recrystallization from cyclohexane, XIIf (R = $CH_2CH_2CH_2\overline{N(CH_2)_3CO}$), m.p. 95—96°C, was obtained. ^{1}H NMR δ (ppm): 7.8—7.0 (m, 7.6, Arom); 3.8 (s, 4.0, $N(CH_2)_2$); 3.4—1.6 (m, 12.7, $NCH_2CH_2CH_2\overline{NCH_2CH_2CH_2CO}$); 0.50 (s, 5.6, $Si(CH_3)_2$). (Found: C, 73.22; H, 7.95. $C_{23}H_{30}N_2OSi$ Calcd.: C, 73.01; H, 7.93%.)

f) $H_2NCH_2CH_2CH_2NMe_2$. In like manner, reaction of XI (3.9 g, 0.010 mol) and $Me_2NCH_2CH_2CH_2NH_2$ (3.3 g, 0.030 mol) gave the desired product in the fraction, b.p. 160—188°C/0.55 mm Hg, 2.0 g. ^{1}H NMR δ (ppm): 7.8—7.2 (m, 8.2, arom); 3.7 (s, 3.8, $N(CH_2)_2$); 2.6—1.5 (m, 12.1, $NCH_2CH_2CH_2N(CH_3)_2$); 0.4 (s, 5.9, $Si(CH_3)_2$). The product was reacted with fumaric acid (0.69 g, 0.0059 mol) to give two solids of m.p. 56—58°C and 105—106°C. After several recrystallizations of the higher melting derivative from i-PrOH, an analysis consistent with XII · 2 H_2Fm (R = $CH_2CH_2CH_2NMe_2$), m.p. 174—176°C, was obtained. (Found: C, 60.61; H, 7.30. $C_{21}H_{32}N_2Si(C_4O_4H_4)_2$ Calcd.: C, 61.05; H, 6.67%.)

Acknowledgement

We gratefully acknowledge the partial support of this work by NIH research grant number R01NS10903 from the National Institute of Neurological Diseases and Stroke. We also wish to thank M. Lowhorn for technical assistance during the early stages of this work.

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