Journal of Organometallic Chemistry, 210 (1981) 149—161
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SILACARBOCYCLES FROM RING EXPANSION

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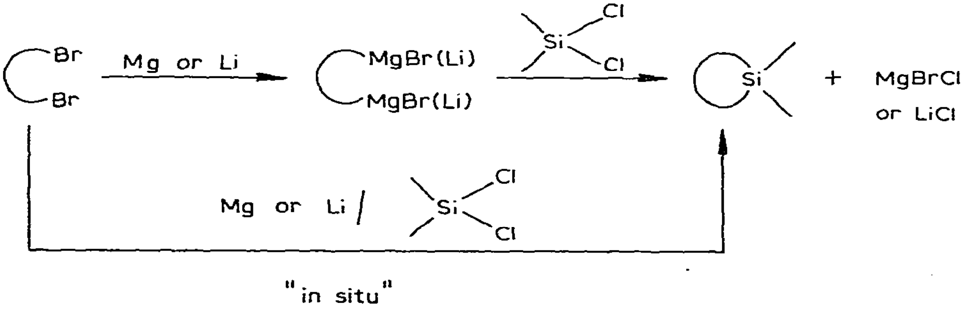
(Received October 8th, 1980)

Summary

Ring enlargement of silicon heterocycles is accomplished from derivatives which contain an exocyclic chloromethyl substituent by reaction with aluminum halide catalyst or with potassium fluoride. Tricyclic derivatives with a silicon atom in a central five-, six-, or seven-membered ring form silins, silepins and silocins, respectively, and are isolated by quenching the product chlorosilanes with H_2O, MeOH, Na/MeOH, $LiAlH_4$, MeMgBr or MeLi. A stoichiometric quantity of fluoride ion also results in conversion of 9-chloromethyl-9-sila-anthracene to 5-fluoro-dibenzo[*b*,*e*]silepin but the percent conversion of the 9-iodomethyl precursor is higher. The limitations of the two methods are discussed briefly.

Introduction

The synthesis of silacarbocycles usually involves the reaction of a diorganometallic reagent with an appropriate dichlorosilane as is shown for the generalized case in eq. 1. The limitations of this approach include the potential diffi-



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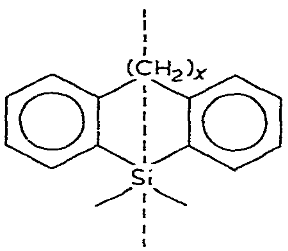
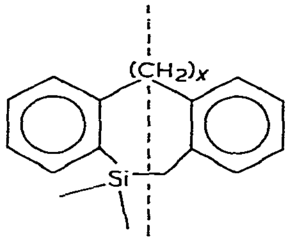
culties in the synthesis of the appropriate organic halide precursor and the problem of forming rings which contain more than seven atoms. In the specific



(I)



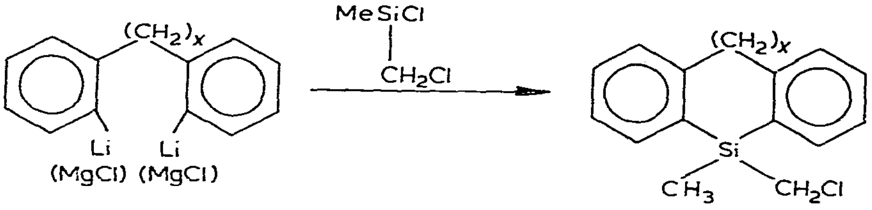
(II)

case of silicon-substituted tricycles, I and II, which differ in that the Si atom occupies a position on a plane which bisects the molecule ("symmetrical" heterocycle) in I and not in II ("unsymmetrical" heterocycle), only the symmetrical framework lends itself readily to the diGrignard(dilithio) reagent approach. Organic precursors to the unsymmetrical systems include, *o*-BrC_6H_4-$C_6H_4CH_2Br$-*o* or *o*-$BrC_6H_4CH_2C_6H_4CH_2Br$-*o*, mixed benzyl/aryl bromides which are prone to cyclization or intermolecular coupling on heating with Mg.

A reasonable alternate route to the synthesis of silacycles such as II would be a ring expansion reaction from I. Two methods both of which incorporate migration of a phenyl group from silicon to the carbon center of an exocyclic chloromethyl substituent have been developed and described briefly [1,2]. The ring enlargement may be induced by addition of a Lewis acid catalyst or by addition of a stoichiometric amount (or excess) of fluoride anion. The details are the concern of this report.

Discussion

The silacycles that are the precursors to the unsymmetrical heterocycles shown as the general formula II are prepared from the reaction of the appropriate diGrignard or dilithio reagents with $Me(ClCH_2)SiCl_2$ (eq. 2), according to the methods reported for the analogous dimethylsilyl derivatives [3,4,5].

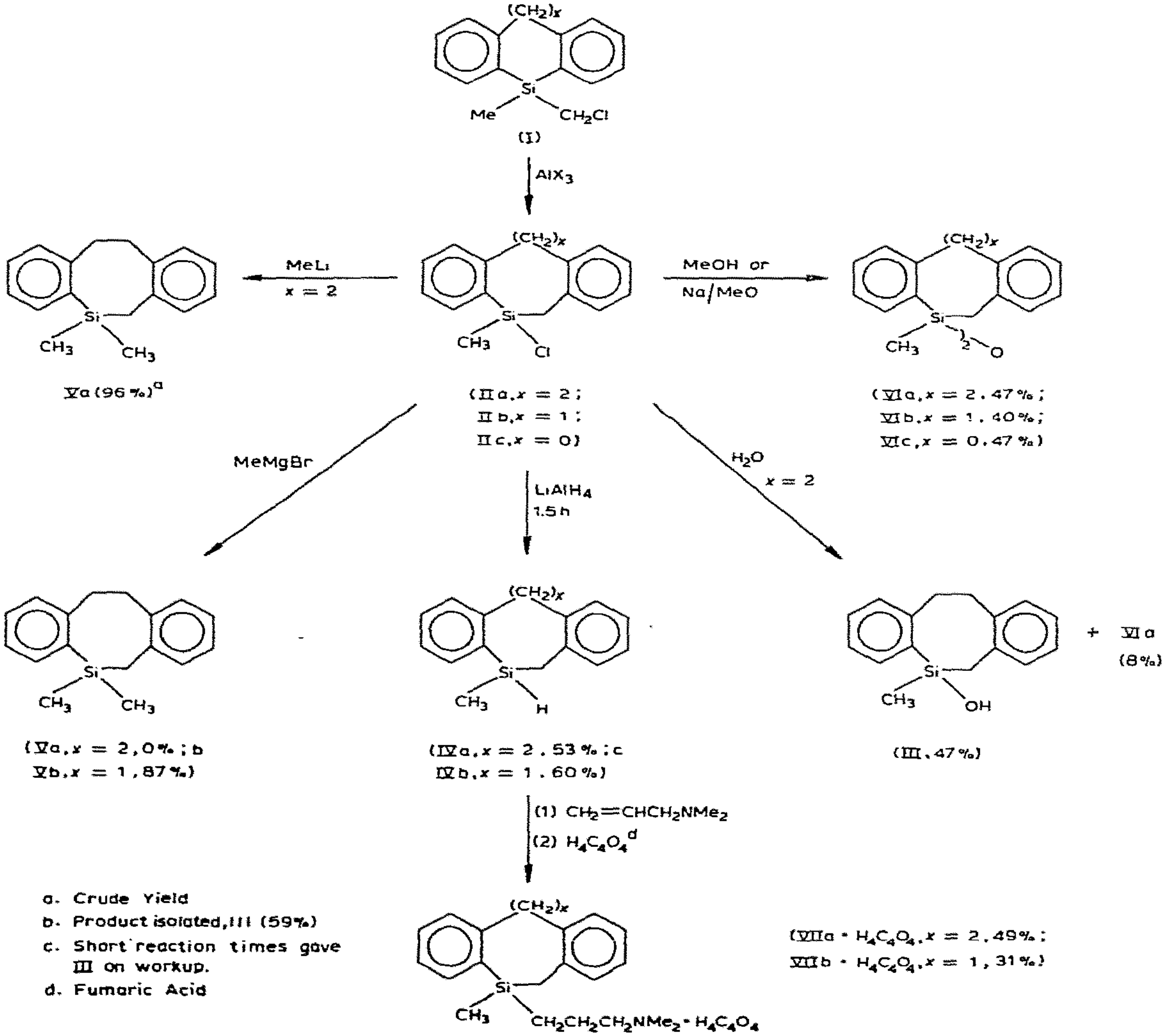


(2)

(Ia, X = 2, 46%
Ib, X = 1, ~37%
Ic, X = 0, 46%)

When pure, Ia and Ic are recrystallizable solids, however, efforts to remove the impurities from the silaanthracene, Ib, by a sequence of distillation/elution chromatography/redistillation were not successful, although these purified samples were suitable for ring expansion studies. On long standing (about 8 months) purified samples of Ib deposited a solid, m.p. 170—176°C, whose ^1H NMR spectrum does not contain the characteristic AromCH_2Arom AB quartet of Ib. The solid was not characterized further.

The Lewis acid-catalyzed reactions were carried out in benzene in oven-dried glassware in an inert atmosphere chamber. Although rigorously purified samples of I were not required for successful runs, any siloxane impurities must be removed prior to reaction with the Lewis acid. Normally this could be effected by elution of crude, distilled samples of I over silica gel. Purified sublimed samples of aluminum chloride or freshly prepared, distilled samples of aluminum bromide were normally used. The direct ring expansion product, the halosilane, II, was not isolated but reaction mixtures were quenched with H_2O, Na/MeOH,



a. Crude Yield
b. Product isolated, III (59%)
c. Short reaction times gave III on workup.
d. Fumaric Acid

SCHEME 1

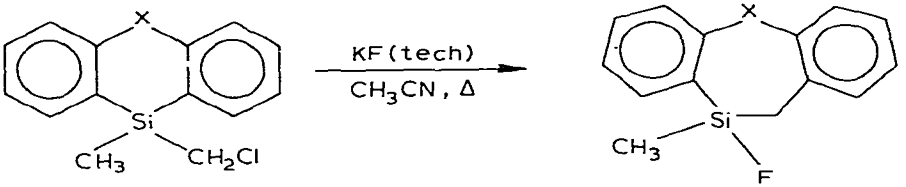
$LiAlH_4$, MeLi or MeMgBr. In earlier studies quenching of IIc with MeOH provided a mixture of the methoxy and hydroxy derivatives which could not be separated [1]. Attempts were thus made to form methoxy derivatives by quenching reaction mixtures of IIc with solutions prepared by dissolving a stoichiometric equivalent of sodium in methanol. Under these conditions only siloxanes, VI, were formed by IIa—c. It is probable that water impurities resulted in the formation of silanol or silanolate which condensed to form the isolated VI. Although, for the most part, the expected products IV and V were obtained from reduction or methylation of II with $LiAlH_4$ or MeM (M = MgBr, Li), respectively, the reactions of the eight-membered ring, IIa, required more rigorous conditions. When solutions which contained IIa were reacted for short time periods with $LiAlH_4$ or with MeMgBr under reflux only silanol, III, was eventually isolated. Clearly, in these experiments, unreacted chlorosilane, IIa, was converted to III during aqueous workup. The more reactive organometallic, MeLi, will convert IIa to Va. Although substitution at silicon in IIa does not readily occur, hydride addition of IVa (and IVb) to *N*,*N*-dimethylallylamine occurs to form VII which was purified by conversion to the fumarate salt. The results are summarized in Scheme 1. Unless specified otherwise, the yields quoted are for isolated, purified products. It is probable that conversion of I to II is quite high (>80%) but that purification and separation procedures for the quenched products diminish the actual yield.

Several other Lewis acids including BCl_3, $SnCl_4$ and $TiCl_4$ were examined as possible catalysts for the ring expansion reaction but were ineffective. The $TiCl_4$ caused extensive silicon—carbon bond cleavage. Aluminum bromide may be generated "in situ" from aluminum foil and bromine in benzene [6]. When Ib was added to such solutions a reaction took place but the products did not correspond to those from isolated, distilled samples of aluminum bromide and this alternative catalyst preparation was abandoned.

Although the Lewis acid-catalyzed rearrangement is an effective method for formation of "unsymmetrical" heterocyclic derivatives such as II and for generation of medium sized rings, there are certain disadvantages. Siloxane impurities must be removed prior to reaction with the Lewis acid. In certain cases this may be tedious as is particularly the case with Ib or the purification procedures may be applicable to only small quantities of the desired halomethyl compound. The Lewis acid must be of reasonable purity and although commercial samples of $AlCl_3$ could be used as a catalyst, aged samples that contain HCl cause cleavage of the silicon—phenyl bond. Water must therefore be rigorously excluded to avoid hydrolysis of the catalyst. The approach to ring expansion through Lewis acid catalysts could not be extended to systems which contain heteroatoms with lone pairs, even when a stoichiometric excess of Lewis acid was added. The NMR spectrum of 2,8-dibromo-5,10-dimethyl-10-chloromethyl-5,10-dihydrophenazasilin and $AlCl_3$ in C_6D_6 clearly shows line broadening of the N—Me absorption which indicates coordination/exchange of the Lewis acid Lewis base. The phanazasilin was recovered unchanged after hydrolysis.

Since the direct products of the AlX_3-catalyzed ring expansion are chlorosilanes which are, in general, more difficult to handle and purify in addition to the disadvantages outlined in the previous paragraph, an alternative ring expansion reaction was developed which was more convenient, amenable to aqueous workup and where it was possible to monitor the course of the reaction by spectroscopic techniques. When dibenzosilicon heterocycles with halomethyl substituents at silicon are heated with potassium fluoride in acetonitrile phenyl group migration occurs and silyl fluorides are isolated in 60—70% yield as is illustrated in eq. 3 [2,8,7].

When Ib was reacted with KF the yield of ring expanded product, VIII, was not only disappointingly low (<20%) but VIII could not be separated from unreacted starting material [2]. In an effort to improve formation of VIII, the chloromethyl group of Ib was converted to iodomethyl prior to reaction with KF. Such a tactic proved successful and VIII was formed in approximately 70% isolated yield. Attempts to prepare an analytical sample of VIII were unsuccessful as was the case for all products generated from Ib that are oils. A solid derivative of Ib was prepared by oxidation to the ketone, X. The ketone, X,



(3)

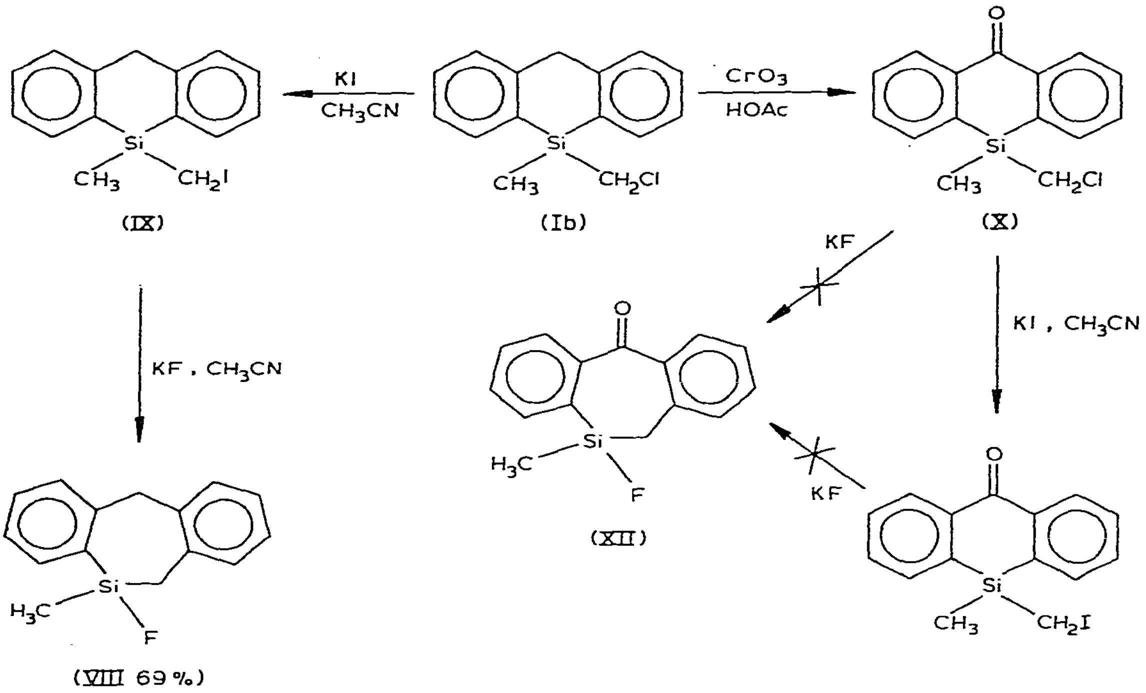
X = NMe [7]*, O [8], SO$_2$ [2]

*2,8-dibromo-substituents

could be converted also to the iodomethyl derivative, XI, with KI. All attempts to ring expand the ketone from either X or XI and KF or KF · HF in CH_3CN have been unsuccessful, although starting material is consumed during the reaction. After removal of a small quantity of volatile forerun the residue does not distill up to 260°C/0.06 mmHg and forms a glass on cooling. These results are summarized in Scheme 2.

The failure to isolate XII from ring expansion of X or XI is unfortunate since a carbonyl group in XII provides a point in the central ring where additional substituents may be incorporated by standard organic reactions [9]. We speculate that the failure to isolate ring-expanded product is due to interaction of the fluoride ion at the carbonyl group of X or XI followed by attack of this newly formed anionic center with the halomethyl silyl group either in an inter- or intramolecular fashion. Support for this hypothesis is obtained from the observation that the tricyclic ketone, 5H-dibenzo[*a,d*]cyclohepten-5-one, interacts with $n\text{-}Bu_4N^+F^-$ in THF to form red-colored solutions whose color persists at room temperature whereas slow addition of $n\text{-}Bu_4N^+F^-$ to X produces an intense blue-red coloration which disappears almost immediately. Treatment of 10-oxo-9,9-dimethyl-9,10-dihydro-9-silaanthracene (methyl replaces chloromethyl of X) with KF/CH_3CN followed by hydrolysis gives the starting material unchanged. Interaction of ketones with fluoride ion has been observed [10].

The expansion of silicon heterocycles by one methylene unit has been demonstrated with two types of reaction approaches. Although the Lewis acid catalyzed rearrangement of chloromethylsilacycles requires careful purification



SCHEME 2

of starting materials and exclusion of moisture, good yields of products are obtained. This reaction approach could not be extended to systems which contain heteroatoms with lone pairs. In this latter case the more convenient fluoride ion-induced ring expansion is the preferred route to the increase of ring size although it in turn is limited by the presence of organic substituents in the starting ring system which may interact with fluoride ion or may necessitate conversion of the chloromethylsilacycle to the iodomethylsilacycle with the more readily displaced iodo substituent.

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. Ring expansion reactions with Lewis acids were carried out in an inert atmosphere box under N_2 in glassware that had been dried at 110°C for a minimum of 24 h.

The commercial reagents, $MeSi(CH_2Cl)Cl_2$, CrO_3, KI, KF(tech), $LiAlH_4$, MeLi, MeMgBr, BuLi, $CH_2{=}CHCH_2NMe_2$, H_2PtCl_6, and *trans*-$HOOCCH{=}CHCO_2H$, were used as supplied. Commercial samples of $AlCl_3$ were sublimed and stored in ampules and $AlBr_3$ was distilled from aluminum foil and stored in ampules. Samples of $AlBr_3$ which developed a brown coloration were redistilled prior to use as a catalyst. The organic halides, $(o\text{-}ClC_6H_4)_2CH_2$, $o\text{-}BrC_6H_4CH_2$-

$CH_2C_6H_4Br$-*o*, and *o*-$BrC_6H_4C_6H_4Br$-*o*, were prepared according to the literature methods [11—13].

Tetrahydrofuran was dried by treatment with n-BuLi (*o*-phenanthroline indicator) followed by distillation [14] and benzene was dried by azeotropic distillation and stored over molecular sieves. Acetonitrile was dried over molecular sieves a minimum of two days prior to use.

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 AEI MS-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.

5-Chloromethyl-5-methyl-10,11-dihydro-5H-dibenzo[b,f]silepin, Ia

The silepin was prepared according to the published procedure for the related dimethylsilepin derivative [3] by addition of chloromethylmethyldichlorosilane (10.3 g, 0.0632 mol) to a solution of *o,o'*-dilithiobibenzyl prepared from *o,o'*-dibromobibenzyl (21.5 g, 0.0632 mol) and n-BuLi (80 ml, 1.6 *M* BuLi). After hydrolysis and workup, distillation of the residue afforded Ia, 7.6 g, b.p. 140—160°C/0.2 mmHg. Recrystallization from heptane gave a sample of pure Ia, m.p. 77—79°C. ^1H NMR δ (ppm): 7.8—6.9 (m, 8.1, Arom); 3.1, 3.08 (s + s, 5.8, CH_2CH_2 + $SiCH_2Cl$); 0.73 (s, 3.1, $SiCH_3$). (Found: C, 70.50; H, 6.55. $C_{16}H_{17}SiCl$ calcd.: C, 70.43; H, 6.28%).

9-Chloromethyl-9-methyl-9-silaanthracene, Ib

The silaanthracene was prepared according to the procedure published for the 5,5-dimethylsilaanthracene derivative [11] by simultaneous addition of a solution of chloromethylmethyldichlorosilane (21 ml, 0.17 mol) in THF and the Grignard reagent prepared from bis-*o*chlorophenylmethane (40 g, 0.17 mol) and Mg (16 g mesh, 0.67 mol) in THF (both solutions adjusted to a volume of 200 ml) to 100 ml of THF. After hydrolysis with saturated NH_4Cl solution and the usual workup, distillation provided impure Ib, b.p. 140—190°C/0.1 mmHg, 26 g (approximately 70% Ib). Redistillation of 20 g provided purified Ib, 120—140°C/0.05 mmHg, 14 g, which was suitable for oxidation to X.

For successful ring expansion reactions with $AlCl_3$ distilled samples of Ib were purified further by elution over silica gel. Typical results are as follows: from elution of Ib (3.0 g of once distilled) over silica gel (60 g) was obtained 1.7 g in the fraction which eluted in 30% benzene in heptane or from elution of Ib (2.3 g twice distilled) over silica gel (55 g) was obtained 2.1 g in the fraction which eluted in 30% benzene in heptane. ^1H NMR δ (ppm): 7.7—6.8 (m, 8.4, Arom); 4.4—3.4 (q, 2.1, AromCH_2Arom); 3.0 (s, 1.9, $SiCH_2Cl$); 0.68 (s, 2.6, $SiCH_3$). $m/e = 258$ (M^+ based on ^{35}Cl).

Further purification of eluted samples was attempted by distillation. Analysis of the fraction, b.p. 117—120°C/0.05 mmHg, indicated that minor impurities are still present. (Found: C, 67.58; H, 5.78. $C_{15}H_{15}SiCl$ calcd.: C, 69.81; H, 5.84%.) On standing for approximately 8 months, this sample deposited a white solid which melts with bubbling from 170—176°C. In addition to the aromatic region the ^{1}H NMR spectrum exhibits singlets at 0.6, 2.4 and a broad singlet at 5.6 ppm (Arom/CH = 1.5).

9-Chloromethyl-9-methyl-9-silafluorene, Ic

The silafluorene was prepared according to the procedure published for 5,5-dimethyl-5-silafluorene [5] from addition of chloromethylmethyldichlorosilane (7.1 ml, 0.056 mol) to the organolithium reagent prepared from *o,o'*-dibromobiphenyl (19 g, 0.062 mol) and n-BuLi (85 ml, 1.5 *M*). After hydrolytic workup and evaporation of ether, 5.0 g portions of the residual oil were eluted over silica gel (70 g) to give crude Ic, 1.7 g, in the fractions with 30 and 40% benzene in hexanes. Eluted samples were of sufficient purity for ring expansion reactions.

Distillation of 1.45 g of crude, eluted Ic gave purified product, b.p. 120—130°C/0.02 mm Hg, 0.78 g, which partially solidified. Recrystallization from absolute ethanol provided an analytical sample of Ic, m.p. 41.5—42.5°C. ^{1}H NMR δ (ppm): 7.0—7.9 (m, 8.5, Arom); 3.0 (s, 1.6, $SiCH_2Cl$); 0.61 (s, 2.9, $SiCH_3$). (Found: C, 68.72; H, 5.55. $C_{14}H_{13}SiCl$ calcd.: C, 68.97; H, 5.37%.) m/e = 244 (M^+ based on ^{35}Cl).

General conditions for $AlCl_3$ catalyzed ring expansion reactions

All operations were carried out in an inert atmosphere chamber under an atmosphere of N_2. To a solution of purified chloromethylsilane (0.5 to 2.0 g of Ia, Ib or Ic) dissolved in anhydrous benzene (25 ml to 50 ml) was added solid $AlCl_3$ or $AlBr_3$ (about 0.1 molar equivalent) and the mixture stirred for 1 to 3 h during which time the solutions developed a deep orange-brown color. After removal from the drybox reaction mixtures were added all at once to the appropriate quenching agent.

Quenching of ring expansion reaction of Ia with H_2O

A mixture of purified Ia (0.91 g, 0.0034 mol) and $AlBr_3$ (0.45 g, 0.0016 mol) in C_6H_6 (~25 ml) was stirred for 1 h and poured into distilled water (~50 ml). After extraction with ether and drying the organic layer over $CaCl_2$, evaporation of the ether gave 0.70 g oil. Elution of the oil over silica gel (70 g) gave siloxane, VIa (0.13 g) in the portion eluting in 20% heptane in benzene and in benzene, as well as silanol, III (0.40 g), which eluted with EtOAc. The oil slowly solidified over a period of months. Both samples were identified by comparison to authentic VIa and III isolated from reactions which were quenched with MeOH and $LiAlH_4$ (short reaction times) respectively.

Quenching of ring expansion reactions with $LiAlH_4$

a. Reaction of Ia to form IVa. After stirring for 1.25 h, a solution prepared by the addition of $AlCl_3$ (0.12 g) to Ia (2.8 g) in benzene was poured into a slurry of $LiAlH_4$ (1.0 g) in anhydrous ether and the mixture stirred for 1.5 h. After workup, stripping the ether gave IVa as an oil which was of suitable purity for addition reactions to *N,N*-dimethylallylamine (formation of VIIa).

Elution of crude IVa (0.1 g) over silica gel (70 g) provided purified silocin (0.06 g) from the benzene/heptane = 1/1 fraction. ^{1}H NMR δ (ppm, CCl_4, ext. TMS): 7.3—6.7 (m, 8.1, Arom); 4.7—4.5 (m, 0.9, SiH); 3.1 (s, 3.6, CH_2CH_2);

2.8—2.1 (doublet of apparent AB quartet, 2.5, Si(H)C*H*$_2$Arom); 0.47—0.40 (d, 3.0, SiC*H*$_3$). (Found: C, 79.85; H, 7.76. $C_{16}H_{18}Si$ calcd.: C, 80.61; H, 7.60%.) *m*/*e* = 238 (*M*$^+$). No attempt was made to further purify IVa.

In a run where the ring expansion reaction was quenched with $LiAlH_4$ and allowed to react for only 0.5 h before hydrolysis, silanol, III, was isolated from the fraction which eluted over silica gel in EtOAc/C_6H_6 = 2/5. The fraction crystallized slowly to give III, m.p. 80—82° C (37%). ^{1}H NMR δ (ppm, CCl_4): 7.2—6.4 (m, 7.8, Arom); 3.2—2.7 (m, 5.1 C*H*$_2$C*H*$_2$ + SiO*H*); 2.3 (brd s, 2.1, SiC*H*$_2$); 0.33 (s, 3.0, SiC*H*$_3$). Recrystallization from hexane provided the analytical sample, m.p. 95—97° C. (Found: C, 76.12; H, 7.37. $C_{16}H_{18}OSi$ calcd.: C, 76.19; H, 7.09%.) *m*/*e* = 254 (*M*$^+$).

b. Reaction of Ib to give IVb. After stirring for 2 h, a solution prepared by the addition of $AlCl_3$ (0.10 g) to Ib (1.99 g) in benzene was poured into a slurry of $LiAlH_4$ (1.0 g) in ether and the mixture stirred for 1 h. The solution was filtered and the filtrate hydrolyzed with saturated NH_4Cl. The organic layer was dried over Na_2SO_4 and stripped to give 1.28 g oil. Samples were of suitable purity for addition to *N*,*N*-dimethylallylamine (formation of VIIb).

Elution of the reaction product over silica gel gave IVb in the fraction which eluted with C_6H_6/heptane = 1/1. ^{1}H NMR δ (ppm, CCl_4, ext. TMS): 7.5—7.0 (m, 8.5, Arom); 4.6—4.3 (m, 0.7, Si*H*); 4.1—3.6 (AB q, 2.1, AromC*H*$_2$Arom); 2.8—2.1 (doublet of apparent AB quartet, 1.9, Si(H)C*H*$_2$Arom); 0.23—0.20 (d, 2.8, Si(H)C*H*$_3$). Analysis of eluted samples indicated that minor impurities were still present. (Found: C, 79.37; H, 7.16. $C_{15}H_{16}Si$ calcd.: C, 80.36; H, 7.14%.) *m*/*e* = 224 (*M*$^+$).

Quenching of ring expansion reactions with MeMgBr and MeLi

a. Reaction of Ia and MeMgBr. A sample of Ia (0.83 g, recrystallized) and $AlCl_3$ (0.10 g) in benzene (20 ml) was stirred for 1.8 h before addition of ether (20 ml) and MeMgBr (5 ml, 2.5 *M*). The mixture was heated at reflux for 3 h and stirred at room temperature overnight before hydrolysis with saturated NH_4Cl. The ether layer was stripped to give an oil which was dissolved in hexanes. A solid slowly precipitated, m.p. 95—97° C, 0.43 g (59%), which was identical to a sample of the silanol, III, described previously.

b. Reaction of Ia to give Va. A sample of Ia (2.8 g, recrystallized) and $AlCl_3$ (0.20 g) in benzene (50 ml) was stirred for 1.8 h before addition of MeLi (5.7 ml, 2.4 *M*). After 1 h at room temperature the reaction mixture was hydrolyzed. The organic layer was stripped to give an oil (2.5 g) which slowly deposited solid. Two recrystallizations from EtOH provided Va, m.p. 72—74° C. ^{1}H NMR δ (ppm): 7.0—6.2 (m, 8.4, Arom); 3.1—2.7 (m, 3.4, C*H*$_2$C*H*$_2$); 2.2 (s, 1.9, SiC*H*$_2$Arom); 0.33 (s, 6.2, Si(C*H*$_3$)$_2$). (Found: C, 81.21; H, 8.23. $C_{17}H_{20}Si$ calcd.: C, 80.95; H, 7.94%.) *m*/*e* = 252 (*M*$^+$).

c. Reaction of Ib to give Vb. A sample of Ib (2.5 g, purified by passing over silica gel and the appropriate fractions distilled) and $AlCl_3$ (0.22 g) in benzene (50 ml) was stirred for 1.5 h and then added to a solution of MeMgBr (10 ml, 2.0 *M*) in additional ether (50 ml). The mixture was heated at reflux for 2 h. After hydrolysis with saturated NH_4Cl the residual oil was distilled to give Vb, b.p. 118—122°C/0.05 mm Hg, 2.0 g. ^{1}H NMR δ (ppm): 7.5—6.7 (m, 8.0, Arom); 4.0 (s, 1.8, AromC*H*$_2$Arom); 2.5 (s, 1.8, SiC*H*$_2$Arom); 0.22 (s, 6.4,

$Si(CH_3)_2$). m/e = 238 (M^+). Minor impurities are still present as indicated by analysis. (Found: C, 79.95; H, 7.88. $C_{16}H_{18}Si$ calcd.: C, 80.61; H, 7.61%.) No effort was made to purify the sample further.

Quenching of ring expansion reactions with Na/MeOH or MeOH

a. Reaction of Ia to give VIa. A sample of Ia (0.90 g) and $AlBr_3$ (0.09 g) in benzene (30 ml) was stirred for 3.5 h and then poured into MeOH. After removal of the solvents the residue was eluted over silica gel to give VIa in the benzene/heptane = 4/1 and benzene fractions (0.59 g). Recrystallization of the combined, eluted fractions from heptane provided a purified sample, m.p. 143—145° C. (Found: C, 78.93; H, 7.09. $C_{32}H_{34}Si_2O$ calcd.: C, 78.31; H, 6.98.) m/e = 475 ($M^+ - 15$).

b. Reaction of Ib to give VIb. A sample of Ib (0.43 g, purified by passage over silica gel) and $AlBr_3$ (0.06 g) in benzene (25 ml) was stirred for 2 h and poured into a solution prepared by the addition of Na (0.04 g) in MeOH (30 ml). After 1 h the MeOH was evaporated and water (50 ml) added. The mixture was extracted with ether and the oil obtained from the ether was eluted over silica gel (70 g). The fraction which eluted with 15% heptane in benzene contained product consistent with VIb. ^1H NMR δ (ppm, ext. TMS): 7.3—6.8 (m, 8.0, Arom); 3.5 (brd s, 1.9, AromCH_2Arom); 2.5—2.0 (m, 2.2, $SiCH_2$-Arom); 0.18 (s, 3.0, $SiCH_3$). m/e = 462 (M^+). Attempts to obtain an analytical sample by distillation failed.

c. Reaction of Ic to give VIc. A sample of Ic (1.0 g) and $AlBr_3$ (0.15 g) in benzene (30 ml) was stirred for 2 h and then poured into a solution prepared by the addition of Na (0.1 g) to MeOH (40 ml). After 1 h the MeOH was removed and H_2O added (50 ml). After extraction with ether and stripping the volatiles, an oil, 0.9 g, was obtained. Elution of the oil over silica gel (70 g) gave VIc (0.42 g) in the fractions which eluted with benzene/heptane = 3/2 and 7/3. Recrystallization from heptane provided an analytical sample, m.p. 115—117° C. ^1H NMR δ (ppm, CCl_4, ext. TMS): 7.6—6.7 (m, 8.0, Arom); 2.2—1.5 (AB q, 2.1, $SiCH_2$); 0 (s, 2.9, $SiCH_3$). (Found: C, 77.13; H, 6.11. $C_{28}H_{26}Si_2O$ calcd.: C, 77.36; H, 6.03%.) m/e = 434 (M^+).

5-Methyl-5-(γ-dimethylaminopropyl)-5,6,11,12-tetrahydro-dibenzo[b,f]silocin, VIIa and VIIa · H_2Fm

The ring expansion product from Ia (2.8 g) and $AlCl_3$ (0.12 g) was quenched with $LiAlH_4$. After hydrolysis with saturated NH_4Cl and the usual workup the residual oil was added directly to *N,N*-dimethylallylamine (3 ml). The catalyst, H_2PtCl_6 in t-BuOH (2 drops), was added (exothermic reaction) and the mixture heated at reflux for 2 h. Methylene chloride was added, the solution filtered to remove the Pt residue, the volatiles removed and the oil distilled to give VIIa, b.p. 154—160° C/0.15 mm Hg (2.0 g). ^1H NMR δ (ppm): 7.3—6.6 (m, 7.9, Arom); 3.4—2.8 (brd m, 4.2, $SiCH_2CH_2$); 2.4—1.9, 2.0 (overlapping m + s, 9.4, $SiCH_2$Arom and $CH_2N(CH_3)_2$); 1.8—0.5 (brd m, 4.6, $SiCH_2CH_2CH_2N(CH_3)_2$); 0.25 (s, 2.9, $SiCH_3$).

A solution of fumaric acid (0.72 g) in EtOH was added to the free amine (2.0 g) in EtOH and on cooling, VIIa · H_2FM precipitated (2.23 g). Recrystallization of 1.0 g from EtOH/EtOAc provided an analytical sample, m.p. 146.5—

148°C (0.73 g). (Found: C, 68.35; H, 8.00. $C_{25}H_{33}NO_4Si$ calcd.: C, 68.30; H, 7.57%.)

5-Methyl-5-(γ-dimethylaminopropyl)-6,11-dihydro-5H-dibenzo[b,e]silepin, VIIb, and VIIb · H_2Fm

A mixture of silane, IVb (1.3 g crude material), *N,N*-dimethylallylamine and H_2PtCl_6 · t-BuOH catalyst were stirred at room temperature for 0.5 h and the volatiles removed. The residue was dissolved in CH_2Cl_2, filtered, stripped and distilled to give VIIb, b.p. 165—175°C/0.05 mmHg, 0.66 g. ^1H NMR δ (ppm): 7.5—6.7 (m, 7.9, Arom); 4.2—3.6 (apparent ABq, 2.0, AromCH_2Arom); 3.2—1.8, 2.2 (overlapping ABq, t + s, 9.3, SiCH_2Arom + $CH_2N(CH_3)_2$); 1.8—0.3 (brd m, 4.9, SiCH_2CH_2); 0.20 (s, 2.8, SiCH_3). $m/e = 309$ (M^+).

To the free amine (0.66 g) dissolved in EtOH was added a solution of fumaric acid (0.52 g) in EtOH. Ether was added just to the point of cloudiness and the solution was left to stand at 5°C. The solid salt, VIIb · H_2Fm, precipitated very slowly, m.p. 140—142°C (0.74 g). ^1H NMR δ (ppm, ext. TMS) (in part): 4.2 (brd s, 1.5, AromCH_2Arom); 2.9—2.4, 2.6 (overlapping m + s, 9.4, SiCH_2Arom and $CH_2NH^+(CH_3)_2$); 1.9—0.5 (brd m, 4.6, SiCH_2CH_2); 0.3 (s, 2.5, SiCH_3). (Found: C, 67.98; H, 8.02. $C_{24}H_{31}NO_4Si$ calcd.: C, 67.73; H, 7.34%.)

9-Methyl-9-iodomethyl-9,10-dihydro-9-silaanthracene, IX

A solution of Ib (2.48 g, purified by elution over silica gel), and KI (1.73 g) in CH_3CN (50 ml) was heated at reflux for 8.5 h. The solvent was stripped and the residue dissolved in ether and the solution filtered to remove the salts. After removal of the ether the oil was distilled to give IX in the fraction, b.p. 135—145°C/0.05 mm Hg, 2.19 g. Elution of 1.04 g of distilled oil over silica gel (50 g) gave 0.65 g of oil in the fraction which eluted with benzene/heptane = 3/10. An attempt to obtain an analytical sample by redistillation of the eluted sample (0.56 g, b.p. 140—142°C/0.05 mmHg) failed. ^1H NMR δ (ppm): 7.8—6.7 (m, arom); 4.5—3.7 (AB q, AromCH_2Arom); 2.2 (s, SiCH_2I); 0.77 (s, SiCH_3). $m/e = 350$ (M^+).

10-Oxo-9-methyl-9-chloromethyl-9,10-dihydro-9-silaanthracene, X

A solution of redistilled Ib (2.3 g) and CrO_3 (1.4 g) in glacial acetic acid (75 ml) was heated at reflux for 2 h and stirred at room temperature overnight. The reaction mixture was poured into 150 ml water, extracted with ether and the ether layer dried over Na_2SO_4. After stripping the ether the product was obtained in the fraction, b.p. 130—140°C/0.04 mmHg, 2.1 g. The distilled oil slowly crystallizes. Recrystallization (twice) from EtOH provided the analytical sample, m.p. 78—78.5°C. ^1H NMR δ (ppm): 8.5—8.2 (m, 2.5, Arom); 7.9—7.0 (m, 5.5, Arom); 2.9 (s, 2.0, SiCH_2Cl); 0.63 (s, 3.0, Si—CH_3). $m/e = 272$ (M^+ based on ^{35}Cl. (Found: C, 66.45; H, 4.77. $C_{15}H_{13}ClOSi$ calcd.: C, 66.05; H, 4.77%.)

10-Oxo-9-methyl-9-iodomethyl-9,10-dihydro-9-silaanthrene, XI

A solution of X (1.2 g, 0.0043 mol) and KI (1.4 g, 0.0086 mol) in CH_3CN (50 ml) was heated at reflux for 18 h. The cooled solution was filtered and stripped to give a solid. Two recrystallizations from ethanol provided an analytical sample of XI, m.p. 110—111.5°C, 1.5 g. ^{1}H NMR δ (ppm): 8.6—8.1 (m, 1.8, Arom). 7.9—7.1 (m, 6.7, Arom); 2.2 (s, 1.8, $SiCH_2I$); 0.75 (s, 2.7, $SiCH_3$). $m/e = 364$ (M^+). (Found: C, 49.32; H, 3.76. $C_{15}H_{13}IOSi$ calcd.: C, 49.46; H, 3.69%.)

5-Fluoro-5-methyl-6,11-dihydro-5H-dibenzo[b,e]silepin, VIIId

A solution of IX (1.15 g, 0.00329 mol) and KF (0.23 g, technical grade) in CH_3CN (50 ml) was heated at reflux for 5 h. The CH_3CN was stripped, the residue dissolved in ether and the solution filtered to remove the inorganic salts. After removal of the ether, distillation of the oil gave slightly impure VIIId, b.p. 110—120°C/0.04 mm Hg, 0.55 g (69%). ^{1}H NMR δ (ppm): 7.6—6.6 (m, 8.1, Arom); 4.3—3.7 (q, 1.9, AromCH_2Arom); 3.0—2.1 (m, 1.9, $SiCH_2$Arom); 0.47—0.35 (d, 3.0, $SiCH_3$). $m/e = 242$ (M^+). (Found: C, 72.74; H, 6.20. $C_{15}H_{15}FSi$ calcd.: C, 74.33; H, 6.24%.) No effort was made to further purify VIIId.

Reaction of X with KF

A slurry of X (5.7 g, approximately 85% X) and KF (1.2 g technical grade) in CH_3CN (100 ml) was heated at reflux for 25 h. After filtration of the salts and removal of the volatile material the residual oil was distilled to give a distillable component, b.p. 135—180°C/0.1 mm Hg, 1.7 g which contained a mixture of products including the original impurity but none identifiable with that expected for XII. The residue, 2.6 g, does not distill up to 260°C/0.1 mm Hg and forms a glass on cooling. Several Si—CH_3 absorptions were observed in the ^{1}H NMR spectrum of the glass.

Reaction of XI with KF

A slurry of recrystallized XI (1.30 g) and KF (0.41 g, technical grade) in CH_3CN (50 ml) was heated at reflux for 5 h. After removal of the solvent ether was added, the inorganic salts removed, and the ether layer stripped to give an oil. Distillation of the residue gave a small forerun which distills up to 180°C/0.2 mm, 0.12 g. The residue did not distill up to 260°C/0.10 mm Hg and formed a glass on cooling, 0.50 g.

Reaction of 10-Oxo-9,9-dimethyl-9,10-dihydro-9-silaanthracene and KF

A mixture of 10-oxo-9,9-dimethyl-9,10-dihydro-9-silaanthracene (0.235 g) and KF (0.064 g technical grade) in CH_3CN was heated at reflux for 10 h. After quenching with water and extraction with ether the organic layer was dried over Na_2SO_4. After removal of the volatile material, the NMR spectrum of the solid residue was identical to that of the starting ketone.

Acknowledgement

We gratefully acknowledge the partial support of NIH research grant number R01NS10903 from the National Institute of Neurological Diseases and Stroke and the University of Missouri-St. Louis Summer Research Fund. We wish to thank Dr. R.E.K. Winter and Dr. C. Maryanoff for helpful discussions and W. Knubley for technical assistance in the early stages of the silocin work.

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