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TRICYCLIC HETEROCYCLES WITH BIFUNCTIONAL SILICON CENTERS

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Summary

Condensation of the diorganometallic reagents, $(o\text{-}MC_6H_4)_2X$ (M = Li, MgCl) with $HSiCl_3$ followed by reduction with $LiAlH_4$ provides dibenzosilacycles, I (a, X = —; b, X = NMe; c, X = CH_2; d, X = CH_2CH_2) with two exocyclic H-substituents, $>SiH_2$. Conditions for the stepwise conversion of I to mixed bifunctional systems, $>SiHX$ (II, X = Cl, Br; III, X = OR), and bifunctional derivatives, $>SiX_2$ (IV, X = Cl; V, X = OR) were determined. Controlled halogenation of I to II was accomplished with one molar equivalent of SO_2Cl_2 or NBS although CCl_4 in the presence of $ClRh(PPh_3)_3$ or $PdCl_2$ results in slow monochlorination. The reaction of I with excess $SOCl_2$ or SO_2Cl_2 converts I to III but the latter is faster and provides fewer side reactions. Conversion of I to IV with excess alcohols occurs in high yield with $ClRh(PPh_3)_3$ but in low yield with H_2PtCl_6. Controlled alcoholysis of I to III could not be achieved except with ^tBuOH. The dichlorides, IV, are methylated in high yield to VII, $>SiMe_2$. Reaction of Ib with $ClRh(PPh_3)_3$ results in elimination of H_2 and formation of disilanes as indicated by trapping reactions with alcohols (formation of Vb).

Introduction

We are interested in methods of synthesis of tricyclic derivatives, I, than contain a bifunctional silicon center. Such heterocycles are precursors to silafunctional analogs of psychotropic drugs and possibly to novel cyclo and linear polysilanes. The general approach to these tricycles has already been developed from the condensation of a suitable diorganometallic precursor with a dichlorosilane [1]. Changing the organodichlorosilane to H_2SiCl_2, $HSiCl_3$ and $SiCl_4$ should produce the bifunctional silicon heterocycle with exocyclic bonds $H_2Si<$, $HClSi<$ and $Cl_2Si<$ respectively. However there are disadvantages to all three of these chlorosilanes, H_xSiCl_{4-x} ($x = 0, 1, 2$). Dichlorosilane, a gas, is difficult to handle and ignites or detonates on exposure to air. With $SiCl_4$ or $HSiCl_3$ substitution of a

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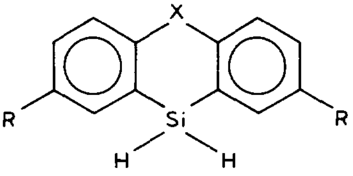
second mole of diorganometallic reagent can occur, especially in the silafluorene case, Ia [2]. When a chlorosilane is obtained from a diorganometallic and H_xSiCl_{4-x} ($x = 0, 1$) aqueous workup is precluded if the chloro-functional group is to be retained. A compromise is to use $HSiCl_3$ for the formation of the heterocycle and reduce the product to the dihydrosilacycle with $LiAlH_4$ before aqueous workup. Since Si–H bonds are readily converted to other silafunctional groups and exhibit a good shelf life the dihydrosilacycle provides a conveniently prepared "storage" unit for other bifunctional silicon heterocycles. In this report we describe the approach as applied to formation of dihydrosilacycles of structural type I and conversions of the SiH bonds to SiCl, SiOR, SiSi and SiOSi containing derivatives.



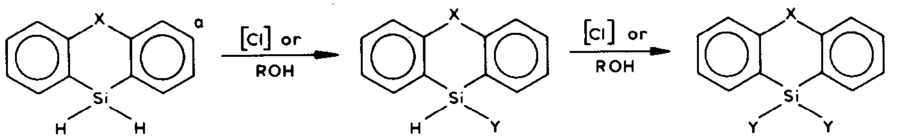
(Ia, X = –, R = H;
Ib, X = NMe, R = Br;
Ic, X = CH_2, R = H;
Id, X = CH_2CH_2, R = H)

Results and discussion

Synthesis of 5,5-dihydrodibenzosilacycles

Our earliest attempt to prepare I involved the reaction of the dilithio reagent prepared from 2,2′,4,4′-tetrabromo-*N*-alkyldiphenylamine with an ether solution of dichlorosilane at −78°C. After workup, only a 23% yield of the product Ib was obtained. However, the yield of Ib is increased when the diorganometallic reagent is added simultaneously with trichlorosilane to a volume of ether cooled to −78°C, followed by warming to room temperature and subsequent reduction with $LiAlH_4$ before workup. In addition, when the lithium–halogen exchange used to generate the diorganometallic is conducted at −78°C yields of Ib up to 67% are realized. In a like manner, Ia was prepared as an oil in up to 62% yield form *o,o*′-dibromobiphenyl. The heterocycles Ic and Id were prepared from bis(*o*-chlorophenyl)methane in 33% yield and *o,o*′-dibromobibenzyl in about 50% yield, respectively. The dihydrosilanes are stable and easily stored. Attempts to remove the bromine groups on the aryl substituents of Ib failed with the published procedures [3,4]. When Ib is treated with the combined reducing agent, $Ni(OAc)_2/NaH$ [3], in THF/EtOH at 63°C decomposition occurred. Likewise, reduction with $LiAlH_4$ under ultrasound conditions (shown to reduce aromatic halides [4]) gave decomposition products after 20 h of sonication although the monobromo derivative is observed after shorter periods.

To demonstrate that these dihydrosilanes represent reasonable "storage units" for other silafunctional derivatives the conditions for the stepwise conversion of I to II(III) and IV(V), represented schematically in eq. 1, were explored.



(1)

(I)

(II, Y = Cl;
III, Y = OR)

(IV, Y = Cl;
V, Y = OR)

a. X = NMe; 2,8-dibromo substituents present.

Chlorination studies

Since 9,9-dichlorosilafluorene [2] is a known compound, Ia was used as a model for initial chlorination studies. Both thionyl and sulfuryl chlorides were found to be effective, mild halogenating agents for this system and the results are summarized in Table 1 for Ia–Id. Heating and photolysis is required in the case of $SOCl_2$ to reduce the time required for reaction to occur and halogenation of I to II could not be easily controlled. When Ic reacts with $SOCl_2$ chlorination of the methylene group occurs at a rate almost comparable to introduction of the second halogen at silicon. This secondary reaction is circumvented by using SO_2Cl_2. When Ic reacts with SO_2Cl_2 at room temperature, all of Ic is consumed within 2.5 h and a mixture of IIc/IVc is obtained in about a 2/5 ratio. Heating was required to complete conversion of IIc to IVc but no halogenation of the CH_2 group was evident. When Ib reacts with refluxing $SOCl_2$ a black tar was obtained on removal of excess

TABLE 1

HALOGENATION OF I BY $SOCl_2$ AND SO_2Cl_2

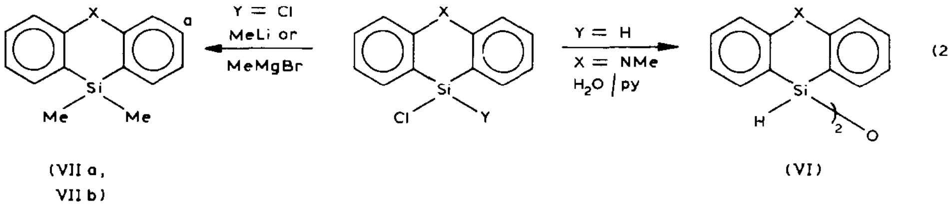
I	$SOCl_2$(A) [a] or SO_2Cl_2(B) [a]	Temperature/h	$h\nu$/h [b]	Ratio [c] I/II/III	Yield of distilled III (%)
Ia	A/–	Reflux/2.5	2.5	1/1/0.5	
Ia	A/–	Reflux/11	11	0/1/2	
Ia	A/–	Reflux/23.5	23.5	0/0/1	85
Ia	A/–	Reflux/88	4.5	0/0/1	88
Ia	A/– [d]	Reflux/97	–	0/0/1	82
Ia	B/CCl_4	Reflux/2	–	0/0/1	89
Ib	A/CCl_4	Reflux/15	–	8/9/0	
Ib	A/CCl_4	Reflux/48	–	1/14/3	
Ib	A/CCl_4	Reflux/72	–	0/8/1	
Ib	B/–	R.t./24	–	0/0/1	91
Ib	B/CCl_4 [e]	R.t./15	–	1/16/3	
Ib	B/CCl_4	Reflux/60	–	0/0/1	90
Ib	B/CCl_4	R.t.	2	0/0/1	93
Ic	B/CCl_4	R.t./2.5	–	0/2/5	
Ic	B/CCl_4	Reflux/4.5 [f]	–	0/0/1	

[a] Excess reagent used unless otherwise specified. [b] Photolysis carried out simultaneously at temperatures indicated. [c] Ratios were determined from integration of ^1H NMR spectra of the SiH_2 and SiHCl regions. The difference in aromatic region was attributed to IV. A 0 entry for I or II implies no detectable resonance. [d] Benzoyl peroxide added. [e] 1 eq. SO_2Cl_2 used. [f] Reflux period followed the 2.5 h at room temperature.

reagent. However, in this case, dilution of $SOCl_2$ with CCl_4 provided reasonable conditions for conversion to the monochloro derivative but reaction is quite slow. Good yields of IVb were achieved with SO_2Cl_2 and the time for the reaction is considerably reduced if photolysis is employed at room temperature.

Controlled halogenation of dihydrosilacycles may be best accomplished with 1 equivalent of NBS (quantitative conversion of Ib to IIb in about 0.5 h as determined by ^1H NMR). Slow chlorination of Ib by CCl_4 occurs with catalytic amounts of $ClRh(PPh_3)_3$ (55% IIb is formed in 60 h at room temperature). Nagai has reported the use of $PdCl_2/CCl_4$ as a halogenating medium for Et_3SiH [5] and 89% monochlorination of $(Me_3SiO)_2SiH_2$ at 0°C has been noted by this reagent combination [6]. However, no chlorination of Ib by $PdCl_2/CCl_4$ occurs at room temperature after 15 h, but when the mixture was heated to 40–50°C about 40% IIb was formed in 2 h. Recently, monohalogenation of dihydrosilanes by $SnCl_4$ (one equivalent) has been reported by Hosmane [7].

To demonstrate the presence of the monochlorinated derivative, IIb, a sample was hydrolyzed with water/pyridine to the disiloxane, VI. The dichlorinated derivatives, IVa and IVb, were treated with MeLi or MeMgBr to give the known compounds, 2,8-dibromo-5,10,10-trimethylphenazasiline [1b] and 9,9-dimethylsilafluorene [1a]. These two reactions are summarized in eq. 2.



a. X = NMe; 2,8-dibromo substituents present

Alcoholysis

Conversion of hydrosilanes to alkoxysilanes requires some form of catalyst, usually a transition metal. The reactions of dihydrosilanes with various alcohols are summarized in Table 2. To determine if alcoholysis can be controlled, Ib and one equivalent of EtOH were treated in the presence of $ClRhL_3$ ($L = PPh_3$). A mixture of Ib, IIb and IVb resulted. When the bulkier alcohol, ^{t}BuOH was added only IIIb ($R = Bu^t$) was obtained. An attempt to force conversion of IIIb ($R = Bu^t$) to Vb with excess ^{t}BuOH at reflux resulted in decomposition through ring cleavage. In the presence of an excess of ROH (R = Me, Et), Ib is smoothly converted at room temperature to Vb in high isolated yield (about 80%) [with $ClRhL_3$]. Alcoholysis also occurs with the catalyst H_2PtCl_6 but yields are low (20–25%).

No systematic study of the effectiveness of different catalysts for conversion of SiH to SiOR as a function of structural features of a silane has been published. It is probable that steric bulk of the alcohol or of the silicon center as well as temperature influences the extent of conversion of a dihydrosilane, R_2SiH_2 to $R_2Si(OR')H$ and/or $R_2Si(OR')_2$. In our system, IIIb could not be converted to Vb with ^{t}BuOH (rhodium catalyst). Steric bulk at silicon also influences the extent of alcoholysis in a dihydrosilane since $^tBu_2SiH_2$ reacts with only one mole of MeOH even in the presence of a large excess of alcohol (Rh catalyst; the dialkoxide was

TABLE 2

REACTION OF HYDROSILANES WITH ALCOHOLS AND METAL CATALYSTS

Silane (g)	Alcohol (ml)	Catalyst (mg) ^{a}	Addition order ^{b}	Temperature/h	Product (%) m.p.
Ib(1.0)	MeOH(2) ^{c}	Rh(25)	A	R.t./3 h	Vb(79) ^{c} 173–174.5°C
Ib(1.0)	MeOH(10)	Pt(15)	A	R.t./4 h	Vb(22)
Ib(0.3)	MeOH(3) ^{c}	Rh(25)	B	R.t./0.5 h	IVb + VI (~1/1) ^{d,e}
Ib(1.0)	EtOH(2) ^{c}	Rh(25)	A	R.t./3 h	Vb(86) ^{f} 128–129.5°C
Ib(1.0)	EtOH(10)	Pt(15)	A	R.t./4 h	Vb(29) ^{f}
Ib(1.0)	^{t}BuOH(1) ^{c}	Rh(25)	A	R.t./3 h	IIIb(67) 163–164°C
				Reflux/6 h	IIIb(27) Ar_2NMe(21) ^{g}
Ib(1.0)	^{t}BuOH(1) ^{c}	Rh(20)	B	R.t./0.75 h	IIIb(53) VI(31)
Ph_2SiH_2(0.60)	EtOH(2)	Rh(25)	A	R.t./3 h 40°C/0.5 h^{h} R.t./h	$Ph_2Si(OEt)_2$(90)
Ph_2SiH_2(0.60)	^{t}BuOH(2) ^{c}	Rh(25)	A	R.t./3 h	$Ph_2Si(OBu^t)$(88)
Ph_2SiH_2(0.60)	^{t}BuOH(2) ^{c}	Rh(25)	A	R.t./3 h and Reflux/14 h^{h}	Decomposition

[a] Rh = $(Ph_3P)_3RhCl$; Pt = H_2PtCl_6. [b] A = alcohol and catalyst mixed before silane added. B = silane and catalyst mixed before alcohol added. [c] Toluene solvent. [d] Elution over silica gel resulted in decomposition of IV. [e] Workup in air. [f] R = OEt. [g] Ar = p-$BrC_6H_4^-$. [h] Additional catalyst added after initial 3 h.

formed from $^{t}Bu_2SiCl_2$/NaOMe) [9]. In contrast to the reaction of Ib, we observed that even when an excess of alcohol is added to Ph_2SiH_2 (Rh catalyst) only Ph_2SiHOR is detected. Addition of a second portion of catalyst to the reaction mixture and heating to 60°C was required to form $Ph_2Si(OR)_2$ (with MeOH but not ^{t}BuOH).

Our major focus in this study has been to explore conversions of the hydrosilanes, I. However, chlorosilanes are also starting points for other functional groups. Alkoxysilanes are often prepared from the reaction of an alcohol with a chlorosilane. An alternative to the bifunctional silane III could result, in principle by addition of alcohol instead of $LiAlH_4$ to the direct product from the dilithio reagent and $HSiCl_3$. When the reaction mixture produced from (2,4-$LiBrC_6H_4)_2NMe$ and $HSiCl_3$ was quenched with ROH/py at 0°C the only isolated product was Ib (14%) and no IIIb was detected. A similar observation has been reported in an ammonolysis of chlorosilane [8]. Since the reaction of I with ^{t}BuOH did not provide V, an attempt was made to determine whether the chlorosilane, IIa, would react with excess ^{t}BuOH to give Va (in the presence of 4-dimethylaminopyridine, DMAP). The only product that was obtained was tentatively assigned to the siloxane that would be formed from the equivalent of hydrolysis of 9-chloro-9-t-butoxysilafluorene. Successful conversion of Ph_2SiCl_2 to $Ph_2Si(OBu^t)_2$ in ^{t}BuOH with DMAP catalyst has been claimed [10].

Reaction of dihydrosilanes with $ClRh(PPh_3)_3$

In transition metal catalyzed alcoholysis of hydrosilanes the silane is added to a mixture of catalyst and alcohol. The order of addition is important since when the catalyst is mixed with a solution of the silane before the alcohol (or other reactant) is added, a different product distribution is obtained. If the rhodium catalyst is added to a solution of Ib in toluene and then the alcohol added, followed by workup in air the major product observed is IIIb (up to 53% isolated and purified yield with ^{t}BuOH). In addition, varying amounts of isolated disiloxane, VI, are observed (see Table 2). If no alcohol is added to the mixture and workup is conducted in the same manner, only VI is obtained. Since siloxanes are not observed when the reactions are conducted as described in the previous section, and only V is obtained with excess alcohol, these results suggest that a reaction of I occurs in the presence of the rhodium catalyst. The formation of silicon–silicon bonds by dehydrogenative coupling with transition metal catalysts has been reported in at least three cases, but with very little detail. Examples include, $Ph_2SiHSiHPh_2$ from Ph_2SiH_2 and $ClRhL_3$ [(L = PPh_3 [11,12] or RhCl(COD)L] (L = $:\overline{\mathrm{CN(Me)CH_2CH_2N}}\mathrm{Me}$) [12]; $Et_2SiHSiHEt_2$ and $HSiEt_2SiEt_2SiEt_2H$ from Et_2SiH_2 and $ClRhL_3$ [11]; $(PhSiH)_x$ from $PhSiH_3$ and $Cp_2TiR'_2$(R′ = Me, $PhCH_2$) [13] and $ClMe_2SiSiEt_2H$ from $Et_2SiH_2/ClMe_2SiH$ and $L_2PtC_2H_4$ or $ClRhL_3$ [14]. Cleavage of silicon–silicon bonds by alcohols occurs in a matter of minutes in the presence of $ClRhL_3$ [15]. When mixtures of $Ph_2SiHSiHPh_2$ are exposed to air in the presence of $ClRhL_3$ or RhCl(COD)L′ (L′ = $:\overline{\mathrm{CN(Me)CH_2CH_2N}}\mathrm{Me}$), Ph_2SiHO-$SiHPh_2$ is produced (rate not specified) [12]. Therefore our observations on the reaction of Ib with $ClRhL_3$ followed by alcohols and workup in air are consistent with formation of a disilane followed by cleavage of this bond in the presence of alcohol and/or oxygen.

Isolation of $Ph_2SiHSiHPh_2$ from Ph_2SiH_2 and *trans*-[$ClRh(PPh_3)_2L'$] (L′ = $:\overline{\mathrm{CN(Me)CH_2CH_2N}}\mathrm{Me}$) is claimed by direct recrystallization but details are not provided [12]. Our efforts to isolate a disilane from Ib have thus far failed. The molecular weight (> 736) of both disilane or disiloxane have precluded distillation or even analysis by gas chromatographic methods. Attempts to remove the catalyst before exposure to air have also failed. The properties of the solution species formed from Ib and $ClRhL_3$ have been explored in a preliminary way. When the reaction of Ib with $ClRhL_3$ is conducted in degassed C_6D_6 and monitored by NMR, the ratio of arom/SiH_x decreases from 6/2 to 7/1 within 30 min at room temperature. No further change is observed over 24 h. A similar NMR experiment with Ph_2SiH_2 shows the presence of at least 5 SiH resonances consistent with the previously reported condensation/disproportionation [11]. These results suggest that a slight excess of one SiH bond per mole of Ib has been lost. An ESR spectrum of Ib with added rhodium (I) showed the absence of radicals. It has been speculated that silenoid intermediates are formed from R_2SiH_2 and transition metals [11,14] but we have failed to detect such intermediates from Ib/Rh either on addition of Et_3SiH or isoprene. Support for the formation of disilanes by dehydrogenative coupling will require independent synthesis of 1,2-dihydrodisilanes and a study of the reactions of these disilanes with air and alcohols when metal catalysts are present. Such work is now in progress.

Experimental

All reactions were performed in an atmosphere of dry N_2 or argon in flame dried glassware. The commercial reagents, n-BuLi, H_2SiCl_2, $ClRh(PPh_3)_3$, $SOCl_2$, SO_2Cl_2, NBS, $PdCl_2$ were used as supplied.

The following compounds were prepared by literature methods: *o,o*′-dibromobiphenyl [16]; 2,2,′4,4′-tetrabromo-*N*-methyldiphenylamine [17]; bis(*o*-chlorophenyl)methane [18]; *o,o*′-dibromobibenzyl [19].

Ethanol and methanol were distilled from Mg and stored over charged molecular sieves. ^{t}BuOH was dried over sodium or charged molecular sieves for several days. Trichlorosilane was distilled over anhydrous K_2CO_3. Tetrahydrofuran, dimethoxyethane, ether and toluene were distilled over sodium/benzophenone. Pyridine was distilled over CaH_2.

^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian T-60 spectrophotometer or a JEOL FX 100 MHz multinuclear spectrometer (internal TMS as reference, δ(ppm), in $CDCl_3$ with internal TMS, unless otherwise specified. Mass spectral data were recorded at 70 eV on an AEIMS-1201B mass spectrophotometer. Infrared spectra were determined on a Perkin–Elmer Model 783 as KBr discs. Kugelrohr distillation was employed in all vacuum distillations.

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

Preparation of Ia, Ib and Id

The dilithio reagent was prepared by dropwise addition of n-BuLi to a a solution or slurry of the appropriate dibromide in ether which had been cooled in a dry ice/acetone bath. After completion of the addition the solution was allowed to come to room temperature and stirred for 3 to 5 h. The lithium reagent was cannulated into a pressure addition funnel and a solution of the chlorosilane in the same volume of solvent was added to a second addition funnel. The two solutions were added simultaneously to 300 ml of ether and the resultant mixture stirred from 3 h to overnight. A charge of $LiAlH_4$ was added and the mixture heated to reflux for 1 to 3 h or stirred overnight. After hydrolysis with saturated ammonium chloride the ether layer was removed, dried over sodium sulfate and the volatiles removed. Distillation provided I.

a. 9,9-Dihydro-5-silafluorene (Ia). The lithium reagent was prepared from n-BuLi (48 ml, 1.47 *M*) and *o,o*′-dibromobiphenyl (10 g, 32 mmol) in 200 ml ether and reacted with $HSiCl_3$ (6 ml, 59 mmol). Distillation provided Ia, b.p. 60–80°C/0.01 mm/Hg (3.62 g, 62%). ^{1}H NMR δ(ppm): 4.73 (s, 1.8, SiH); 7.07–7.63 (m, 8.2, arom). A GC trace showed the presence of a minor impurity which could not be removed. $m/e = 182$ (M^+).

b. 2,8-Dibromo-5-methyl-10,10-dihydrophenazasiline (Ib) from H_2SiCl_2. The lithium reagent was prepared from n-BuLi (16 ml, 42 mmol) 2,2′,4,4′-tetrabromo-*N*-methyldiphenylamine (10 g, 20 mmol) in dry ether (75 ml) and reacted with H_2SiCl_2 (40 mmol) dissolved at −78°C in anhydrous ether (*caution*: extreme care must be taken in handling of dichlorosilane; for details of handling and hazards see ref. 20). Distillation provided Ib as a dark brown oil, b.p. 170–190°C/0.01 mmHg (1.7 g, 23%). An analytical sample was prepared by crystallization with hexane/CH_2Cl_2 70/30, m.p. 164.5–165.5°C. ^{1}H NMR δ (ppm): 3.5 (s, 2.8H, NCH_3); 4.8 (s, 1.7H, SiH_2); 6.9–7.8 (m, 6.4H, arom). $m/e = 367$ (M^+) (based on ^{79}Br). Anal. Found: C, 42.14; H, 3.12. $C_{13}H_{11}Br_2NSi$ calcd.: C, 42.27; H, 2.98%.

c. Ib from $HSiCl_3$. The lithium reagent was prepared from 2,2′,4,4′-tetrabromo-*N*-methyldiphenylamine (20 g, 40 mmol) and reacted with $HSiCl_3$ (5.4 g, 40 mmol). After removal of the volatiles the solid residue was distilled, b.p. 180–200°C/0.1

mmHg, to give a white solid. Recrystallization from hexane/methylene chloride, 70/30, gave Ib, m.p. 164.5–165.5°C (8.6 g, 58%).

d. 2,8-Dibromo-5-ethyl-10,10-dihydrophenazasiline. The *N*-ethyl derivative was prepared from 2,2′,4,4′-tetrabromo-*N*-ethyldiphenylamine (20 g, 39 mmol) and trichlorosilane (5.3 g, 39 mmol) as described for Ib. The product distilled at 140–160°C/0.05 mmHg. Recrystallization from hexane/methylene chloride, 70/30, gave a solid (8.1 g, 54%), m.p. 141–142°C, ^{1}H NMR δ(ppm): 1.3–1.6 (t, 3.2H, NCH_2CH_3); 3.9–4.2 (q, 1.8H, NCH_2CH_3); 4.9 (s, 1.8H, SiH_2); 6.9–7.8 (m, 6.2H, arom). $m/e = 383$ (M^+) (based on ^{79}Br). Anal. Found: C, 43.86; H, 3.85. $C_{14}H_{13}Br_2NSi$ calcd.: C, 43.86; H, 3.39%.

e. 10,11-Dihydro-5H-dibenzo[b,f]silepin (Id). The lithium reagent was prepared from *o,o*′-dibromobibenzyl (10 g, 29 mmol) and reacted with $HSiCl_3$ (4.0 g, 30 mmol). Distillation provided slightly impure Id, b.p. 140–160°C/0.1 mmHg (3.3 g, 53%). ^{1}H NMR δ(ppm): 3.3 (s, 4H, CH_2CH_2); 5.0 (s, 2H, SiH_2); 7.0–7.8 (m, 8H, arom). $m/e = 210$ (M^+). Attempts to prepare an analytical sample by redistillation or by elution over silica gel failed (decomposition on the column occurred).

9,10-Dihydro-9-silaanthracene (Ic)

The Grignard reagent was prepared from bis-*o*-chlorophenylmethane (22 g, 92 mmol) and magnesium (100 mesh, 4.6 g, 190 mmol) in THF (75 ml) [18] and cannulated into a pressure addition funnel. A second addition funnel was charged with $HSiCl_3$ (12 ml, 0.12 mol) in the same volume of THF and the two solutions were added simultaneously to THF (100 ml). After completion of the addition the mixture was heated at reflux for 1.5 h, cooled and $LiAlH_4$ (3.7 g) added in two portions. After stirring overnight, the slurry was heated at reflux for an hour, hydrolyzed with saturated NH_4Cl and the organic layer dried over $MgSO_4$. The oil that remained after removal of the volatiles was distilled to give slightly impure Ic, b.p. 105–130°C/0.3 mmHg (5.8 g, 32%) which solidified on standing. Recrystallization from hexane/CH_2Cl_2 gave Ic, m.p. 74–76°C. ^{1}H NMR δ(ppm): 4.0 (s, 1.9, CH_2); 4.8 (s, 1.6, SiH_2); 6.7–7.8 (m, 8.4, arom).

Attempted debromination of Ib

a. A slurry of Ib (1.5 g, 4.1 mmol), and $LiAlH_4$ (0.50 g, 13 mmol) in freshly distilled DME (20 ml) was sonicated for 5 h. The reaction mixture was poured into CH_2Cl_2 (100 ml) and ice (100 g), the organic layer was dried over Na_2SO_4 and the volatiles were removed. Distillation provided a volatile fraction, b.p. 130–160°C/0.01 mmHg (400 mg) which contained at least 3 products. The major product (about 70%) appears to be the monobromo derivative based on comparison of the ^{1}H NMR spectrum to that of the related derivative, 2-bromo-5,10,10-trimethyl-5,10-dihydrophenazasiline [1b]. Sonication of mixtures of Ib and $LiAlH_4$ in DME for longer periods resulted in decomposition.

b. To NaH (1.4 g, 58 mmol) in DME (20 ml) was added $Ni(OAc)_2$ (0.90 g, 5.1 mmol; prepared by drying $Ni(OAc)_2 \cdot H_2O$ at 100–110°C for 18 h) and the slurry heated to reflux before addition of MeOH (3.0 g, 94 mmol). The reflux was continued for 1 h and a solution of Ib (1.0 g, 2.7 mmol) in DME (6 ml) added and heating continued for 30 min. An ether/water mixture, 30/20, was added to the cooled solution slowly. After filtration the ether layer was dried over Na_2SO_4 and the volatiles removed. No material was obtained on distillation up to 230°C/0.02 mmHg.

Chlorination of I with $SOCl_2$ and SO_2Cl_2 and isolation of dichlorinated derivatives, IV

Mixtures of I (0.5 to 6 g) and $SOCl_2$ or SO_2Cl_2 either neat or in CCl_4 were allowed to react under a N_2 atmosphere and the conditions and times are given in Table 1. The course of the reaction was monitored by removal of an aliquot and addition of CCl_4 if required. The proton resonances associated with I and the monochlorinated derivative, II, are clearly separated. The dichlorinated material was estimated on the basis of the residual aromatics after subtraction of I and monochlorinated derivative.

IVa. To Ia (1.12 g, 6.1 mmol) in CCl_4 (5 ml) was added SO_2Cl_2 (8.3 g, 61 mmol). The solution was refluxed and stirred for 2 h. The solvents were removed to give a solid (1.33 g, 89%). The NMR spectrum of the solid showed the absence of resonances attributable to SiH_2 and SiHCl.

Alternatively the residue obtained from chlorination with either $SOCl_2$ or SO_2Cl_2 were distilled at 90–110°C/0.1 mmHg (Lit. [2], 108–110°C/mmHg).

IVb. To Ib (1.0 g, 2.7 mmol) in CCl_4 (15 ml) was added SO_2Cl_2 (4 ml). The solution was irradiated with a sunlamp for 2 h. After the solvents were removed, the resulting oil was distilled to give a liquid, b.p. 190–210°C/0.5 mmHg, which solidified (1.1 g, 93%). Recrystallization from hexane/CH_2Cl_2, 70/30, gave IVb, m.p. 166–167°C (decomp). ^1H NMR δ(ppm): 3.6 (s, 2.9H, NMe); 6.9–7.9 (m, 6.1H, arom).

Bromination of Ib with N-bromosuccinimide (NBS)

To Ib (1.0 g, 2.7 mmol) was added freshly recrystallized NBS (0.48 g, 2.7 mmol) in CCl_4 (25 ml). After 30 min photolysis with a sunlamp the reaction mixture was cooled to room temperature and the succinimide removed. ^1H NMR δ(ppm): 3.6 (s, 2.9H, NMe); 5.8 (s, 0.9H, SiH); 6.9–7.8 (m, 6.2H, arom).

The reaction was repeated on the same scale with two equivalents of NBS. After filtering the succinimide and removal of the solvent, the solid residue was crystallized from hexane/methylene chloride 60/40 to give IVb, m.p. 175–178°C (decomp) (1.3 g, 89%). ^1H NMR δ(ppm): 3.6 (s, 2.9H, NMe); 7.0–8.0 (m, 6.1 H, arom).

Chlorination of Ib with CCl_4 catalyzed by $ClRh(PPh_3)_3$

A mixture of Ib (40 mg, 0.57 mmol) and $ClRh(PPh_3)_3$ (5 mg) in CCl_4 (5 ml) was stirred under N_2 for 60 h. The NMR spectrum of an aliquot showed the presence of Ib in approximately 55% yield.

Chlorination of Ib with CCl_4 catalyzed by $PdCl_2$

A mixture of Ib (200 mg, 0.54 mmol) and $PdCl_2$ (10 mg) in CCl_4 (5 ml) was stirred at room temperature for 15 h under N_2. The ^1H NMR spectrum indicated only starting material was present. The solution was heated at 40–50°C for 2 h after which IIb was present in 43% yield as indicated by the NMR spectrum.

Hydrolysis of IIb

To 1.0 g (2.7 mmol) of Ib in CCl_4 (10 ml) was added SO_2Cl_2 (0.22 ml, 2.7 mmol) and the solution stirred for 15 h. The NMR spectrum of an aliquot indicated that the major species present was the monochlorinated product, IIb. A mixture of pyridine/water, 2ml/2ml, was added and the solution stirred overnight. The resultant slurry was filtered to give 0.60 g (59%) of a solid which was washed with 5 ml water and recrystallized from CH_2Cl_2/hexane, 80/20, m.p. 215–217°C. ^1H NMR δ(ppm): 3.4 (s, 2.8H, NMe); 5.4 (s, 1H, SiH); 6.8–7.7 (m, 6.2H, arom). IR (KBr disc): 2180 cm^{-1} (SiH); 1020–1135 cm^{-1} (Si–O–Si). Anal. Found: C, 41.24; H, 2.48. $C_{26}H_{20}Br_4N_2Si_2O$ calcd.: C, 41.48; H, 2.65%.

Reaction of IVa with methylmagnesium bromide

To Ia (2.3 g, 12.6 mmol) in CCl_4 (10 ml) was added SO_2Cl_2 (11.2 ml, 126 mmol). The solution was refluxed and stirred for 2 h. The solvent was removed to give solid IVa. To IVa dissolved in anhydrous ether (35 ml) at 0°C was added dropwise MeMgBr (8 ml, 3.2 *M*, 25 mmol). The solution mixture was stirred overnight followed by hydrolysis with water (6.5 ml). The water layer was extracted with two portions of ether and the combined organic layers dried over Na_2SO_4. After removal of the volatiles, distillation provided an oil, b.p. 125–160°C/0.9 mmHg (2.6 g, > 90%) which solidified, to give VIIa, m.p. 48–54°C (Lit. [2], 58–59°C). A GC trace showed that the sample contained an 8% impurity of biphenyl by comparison to authentic samples.

Reaction of IVb with methylmagnesium bromide

To IVb (2.0 g, 5.4 mmol) in anhydrous ether (30 ml) was added methylmagnesium bromide (2.9 ml, 3.2 *M*) in ether. The solution was refluxed overnight. After hydrolysis and extraction with ether the organic layer was washed with water and then dried over Na_2SO_4. After removal of the volatiles the resulting oil was distilled to give an oil, b.p. 140–160°C/0.2 mmHg, which solidified to give Ib, m.p. 127–128°C (1.3 g, 72%) (Lit. [1b], 128–129°C). Spectroscopic properties were identical to those of an authentic sample.

Reaction of Ib with alcohols in the presence of metal catalysts and isolation of the products

To a N_2 filled single necked flask with a side arm fitted with a rubber septum were added the catalyst, solvent (when used) and alcohol. A solution of Ib was syringed into the flask and the solution stirred at room temperature. After removal of the volatiles the resultant solid was dissolved in hexane/methylene chloride, 70/30, and cooled to 0°C. The solution was decanted from the small amount of gum that had formed and the decantate recooled to 0°C to provide the product. The various runs are summarized in Table 2.

a. 2,8-Dibromo-5-methyl-10,10-dimethoxyphenazasiline (Vb: R = Me). From Ib and methanol in toluene (10 ml) was obtained Vb (R = Me), m.p. 173–174.5°C (0.91 g, 79%). ^1H NMR δ(ppm): 3.4–3.6 (overlapping singlets, 8.7H, NMe and $Si(OMe)_2$); 6.9–7.8 (m, 6.3H, arom). $m/e = 427$ (M^+) (based on ^{79}Br). Found: C, 43.61; H, 3.62. $C_{15}H_{15}Br_2NO_2Si$ calcd.: C, 43.34; H, 3.84%.

b. 2,8-Dibromo-5-methyl-10,10-diethoxyphenazasiline (Vb: R = Et). From Ib and ethanol in toluene (10 ml) was obtained Vb (R = Et), m.p. 128–129.5°C (1.1 g, 86%). ^1H NMR δ (ppm): 1.0–1.4 (t, 6H, OCH_2CH_3); 3.5–3.9 (q, 3.7H, OCH_2CH_3); 3.4 (s, 2.9H, NMe); 6.8–7.7 (m, 6.3H, arom). $m/e = 455$ (M^+) (Based on ^{79}Br). Found: C, 44.49; H, 4.33. $C_{17}H_{19}Br_2NO_2Si$ calcd.: C, 44.64; H, 4.15%.

Addition of H_2PtCl_6 to Ib dissolved in MeOH or EtOH provided IVb but the yields ranged from 22–29%.

c. 2,8-Dibromo-5-methyl-10-hydro-10-t-butoxyphenazasiline (IIIb). From Ib and ^{t}BuOH in toluene (15 ml) was obtained IIIb (R =^{t} BuO) (0.79 g, 67%). An analytical sample, m.p. 163–164°C, was prepared by recrystallization from the same hexane/methylene chloride, 60/40, mixture. ^{1}H NMR δ(ppm): 1.3 (s, 8.8H, O^{t}Bu); 3.6 (s, 2.7H, NMe); 5.6 (s, 0.9H, SiH); 6.9–7.8 (m, 6.6H, arom). IR(KBr disc): 2080 cm^{-1} (SiH). Found: C, 45.87; H, 4.32. $C_{17}H_{19}Br_2NOSi$ calcd.: C, 46.25; H, 4.31%.

In another run on the same scale, the solution was refluxed for 6 h. Using the same workup as above, the ring cleavage product, 4,4′-dibromo-*N*-methyldiphenylamine (220 mg, 21%) and IIIb (R =^{t} Bu) (320 mg, 27%) were obtained.

d. Diphenyldiethoxysilane. From diphenylsilane and ethanol stirred for 3 h before an additional portion of catalyst was added and heating to 40°C for 0.5 h and room temperature for 1 h was obtained diphenyldiethoxysilane, b.p. 110–130°C/0.2 mmHg (Lit. [21], 130°C/2 mmHg) (800 mg, 90%). ^{1}H NMR δ(ppm): 1.0–1.3 (t, 6H, OCH_2CH_3), 3.5–3.9 (q, 4H, OCH_2CH_3); 7.0–7.6 (m, 10H, arom).

e. Diphenyl-t-butoxysilane. From diphenylsilane and ^{t}BuOH in toluene (10 ml) was obtained diphenyl-t-butoxysilane, b.p. 110–130°C/0.1 mmHg (Lit. [11], 110–115°C/0.1 mmHg) (0.74 g, 88%). ^{1}H NMR δ(ppm): 1.2 (s, 8.8H, O^{t}Bu); 5.5 (s, 0.9H, SiH); 6.8–7.6 (m, 10.3H, arom). Heating caused decomposition as indicated by loss of intensity of the resonance attributed to ^{t}Bu at 1.3 ppm).

Attempt to prepare IIIb by alcohol workup from reaction of 2,2′-dilithio-4,4′-dibromo-N-methyldiphenylamine with $HSiCl_3$

The reaction mixture prepared from the dilithium reagent (generated from 10 g of tetrabromodiphenylamine) and trichlorosilane (2.71 g, 20 mmol) was quenched with a solution of methanol (3 ml) and pyridine (2 ml) and refluxed for 3 h. After the usual workup the only identifiable product was Ib (1.0 g, 14%).

Reaction of IVa with ^{t}BuOH

A mixture of IVa (5.3 mmol), ^{t}BuOH (18 g, 25 mmol), pyridine (1.5 ml, 14 mmol) and 4-dimethylaminopyridine (DMAP) (0.26 g, 2.1 mmol) was refluxed with stirring for 24 h. An NMR spectrum indicated that no more than one equivalent of the alcohol had reacted and that a mixture of products was generated.

Reaction of Ib with $ClRh(PPh_3)_3$

A single necked flask was charged with Ib (500 mg, 1.4 mmol), $ClRh(PPh_3)_3$ and toluene (15 ml). Gas evolution was spontaneous on stirring and the color of the solution changed to dark orange within five minutes. After stirring for 8 h the solvents were stripped with no attempt to exclude air to give a solid (450 mg) which was recrystallized from hexane/CH_2Cl_2, 50/50. The spectroscopic properties of this product are identical to the disiloxane, VI. The mixed melting point with an authentic sample of disiloxane was not depressed.

In a separate run, an ESR spectrum taken within 30 min of mixing showed that no detectable radicals were present.

The same results were obtained from reactions performed in degassed solvents with normal workup conditions.

A sample was prepared for an NMR spectrum by adding Ib (150 mg) to an NMR tube that had been purged with Ar and degassed C_6D_6 (1 ml) was added followed by a second purging of Ar. The catalyst (5 mg) was added and the sample purged again. The contents of the tube were shaken for 2 min whereupon the orange color develops. The ^1H NMR spectrum, compared to that taken before addition of the catalyst shows that the integration of the arom/SiH_2 changes from 6/2 to 7/1 (a broad impurity peak appears upfield of the NMe resonance). A spectrum taken after 48 h shows no change.

Reaction of Ib with $ClRh(PPh_3)_3$ followed by ^tBuOH

A single-necked flask with a side arm fitted with a rubber septum was charged with a magnetic stirrer, Ib (1.0 g, 2.7 mmol), the catalyst (20 mg) and deoxygenated toluene (15 ml). The solution was stirred for about 10 min under N_2 then ^tBuOH (1 ml) was syringed into the flask and the solution stirred for another 45 min. Removal of the solvent gave a solid which was dried under vacuum. The NMR spectrum indicated the presence of at least two products (two resonances in the NMe region). The product mixture was eluted over silica gel (heated in an oven for several hours at 110°C) with hexane/CH_2Cl_2, 70/30, to give IIIb (R =^{t} Bu) (630 mg, 53%). The disiloxane (VI, 350 mg, 31%), was eluted with hexane/CH_2Cl_2 50/50. The spectroscopic properties of both products were identical to those of authentic samples.

Reaction of Ib with $ClRh(PPh_3)_3$ followed by MeOH

In a round bottom flask under N_2 a mixture of Ib (300 mg), toluene (30 ml) and catalyst (10 mg) was stirred for 10 min before addition of methanol (3 ml). The solution was stirred for another 30 min and the solvents removed to give a solid (280 mg). The NMR spectrum shows the presence of two components (2 NMe singlets and one OMe singlet of equal intensity) which are equivalent to those observed for IIIb (R = Me) and disiloxane. When the reaction mixture was passed through a silica gel column only the siloxane eluted with CH_2Cl_2/hexane 60/40 (180 mg, 58%).

Reaction of Ib with triethylsilane in the presence of $ClRh(PPh_3)_3$

A round bottom flask was charged with a magnetic stirrer, Ib (1.0 g, 2.7 mmol), Et_3SiH (4.4 ml, 27 mmol), toluene (10 ml) and $ClRh(PPh_3)_3$ (25 mg) and the solution stirred under reflux for 20 h. The solvents were removed from the resultant purple solution to give a solid (0.64 g). Recrystallization from hexanes/CH_2Cl_2, 60/40, gave a solid, m.p. 214–216°C (0.53 g, 52%) whose spectroscopic properties were identical to that of the disiloxane.

Reaction of Ib with isoprene is the presence of $ClRh(PPh_3)_3$

To a 50 ml single necked round bottom flask equipped with a magnetic stir-bar and reflux condenser was added Ib (1.0 g, 2.7 mmol), isoprene (4 ml) and $ClRh(PPh_3)_3$ (25 mg) and toluene (15 ml) under N_2. The solution was refluxed for 20 h and the solvents removed to give a solid (0.52 g). Recrystallization from hexane/CH_2Cl_2, 40/60, gave a solid, m.p. 214–216°C (0.40 g, 38%). The spectroscopic properties are identical to the disiloxane.

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