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THE SYNTHESIS OF 1-SILAPHENALANES FROM 1,8-DIFUNCTIONAL NAPHTHALENES. CONFIRMATION OF THE STRUCTURES OF THE PYROLYSIS PRODUCTS OF (1-NAPHTHYL)VINYLDICHLOROSILANE

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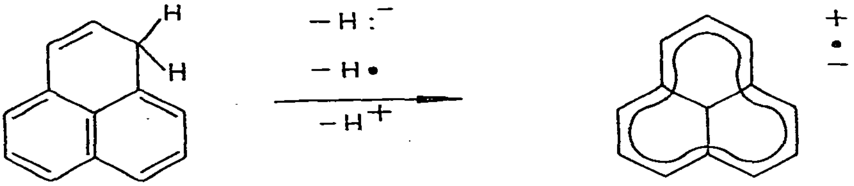
Summary

1-Silaphenalanes have been prepared from 8-bromo-1-(2′-haloethyl)naphthalenes in modest yields. Attempts to dehydrogenate 1-silaphenalanes to 1-silaphenalenes were unsuccessful. Verified is 1,1-dichloro-1-silaphenalene as the major volatile silicon-containing product from the pyrolysis of (1-naphthyl)vinyldichlorosilane. 1,1-Dichlorosilaphenalane was found to be a significant minor product.

Introduction

While carbenium ions are ubiquitous throughout organic chemistry, no reports of silacenium ions in the condensed phase are currently accepted as valid. Our approach to preparing silacenium ions in solution or as a salt has been to try to incorporate Si^+ in an extended π system.

Based on the known chemistry of phenalene, I, [1—3], a unique hydrocarbon that generates a cation (Ia), radical (Ib), and anion (Ic), each of which is aromatic with a resonance energy of approximately 105 kcal/mol, we felt that 1-silaphenalenes (II) were reasonable candidates for producing detectable, or perhaps



(I)

(Ia,b,c)

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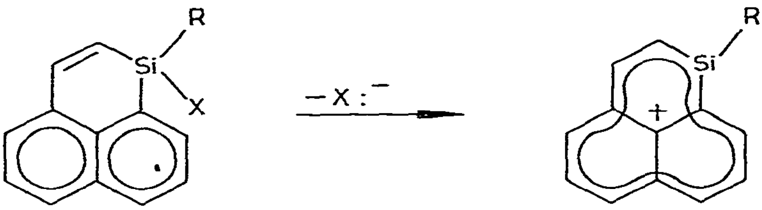
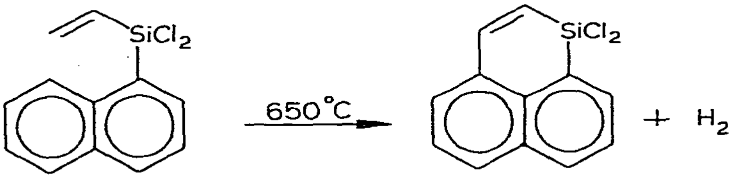
even isolable, silacenium ions of the type IIa. By analogy to I, 1-silaphenalenes



(II) (IIa)

could also lead to aromatic silyl radicals and aromatic silyl anions. A most attractive feature of this system is that these are accessible, in theory at least, by simply removing a leaving group of one's choice from silicon.

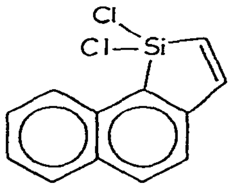
The synthesis of 1-silaphenalene and some of its derivatives has been reported by Chernyshev and coworkers [4]. Several routes to these compounds are described, but in each case the key step is a high temperature dehydrogenative ring closure. The pyrolysis of (1-naphthyl)vinyldichlorosilane, III, is representative of the approach and is particularly relevant to the work described in this paper.



(III) (II, R = X = Cl)

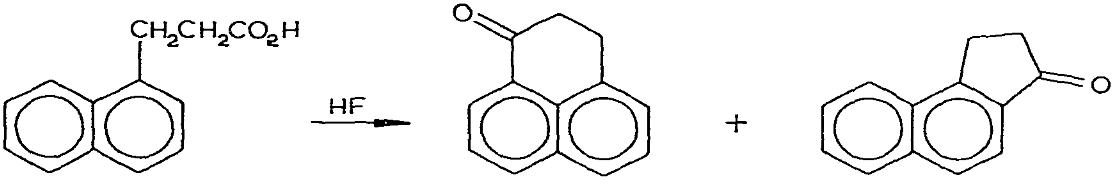
The potential for $d\pi$—$p\pi$ delocalization in the radical anions of several 1-silaphenalenes was investigated by the Russian group using polarography and electron spin resonance spectroscopy [5]. They concluded that, while these compounds show significant electron acceptor properties as evidenced by their low half-wave potentials, the extent of $d\pi$—$p\pi$ delocalization in the radical anions was small compared to the $p\pi$—$p\pi$ interaction in the phenalenyl radical Ib. The narrow spectral width (21—25 G) and small hyperfine coupling constants of the naphthyl hydrogens were cited as supporting evidence for this conclusion.

However, careful analysis of the data on 1-silaphenalenes does not lead to an unambiguous structural assignment as reported [4]. Compositional and spectral data support equally well the structure of the isomer, IV.



(IV)

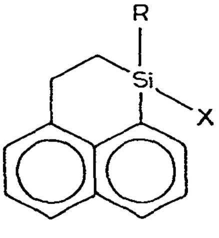
Given that the ring closure reaction to produce a precursor to phenalene, I,



(V) (VI) (VII)

also gives the isomeric benzhydrindone, VII [6] and that II (R = X = Cl) might be unstable at 650°C we felt that the initial structural assignment was questionable. Our fears for the stability of II (R = X = Cl) were based on the failure of our group [7] and others [8] to prepare stable 1-halo derivatives of the carbon analogue, I.

In this paper we describe the details of an unequivocal proof of structure II (R = X = Cl) as the major pyrolysis product of III. We also find, as a significant minor product of the pyrolysis the new compound, 1,1-dichloro-1-silaphenalane (VIII, R = X = Cl). The key to the structural assignments of 1-silaphenalenes and 1-silaphenalanes is the unambiguous synthesis of 1,1-dimethyl-1-silaphenalane (VIII, R = X = Me) from 1-bromo-8-iodonaphthalene.



(VIII)

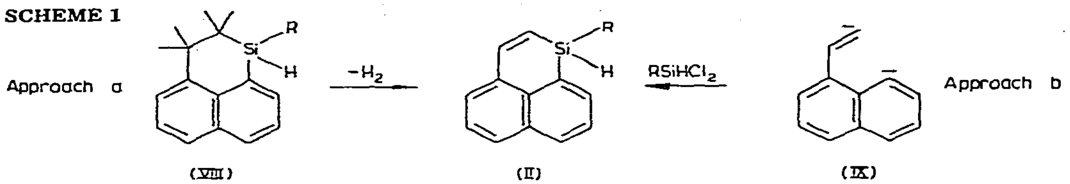
Our efforts were directed primarily at a new general synthesis of 1-silaphenalenes and our synthetic strategy reflects that approach. To our disappointment, we were not able to prepare derivatives of II by conventional methods but, fortunately, our plan included the synthesis of VIII which, ultimately, provided the correct structural assignment of II.

Synthetic plan

The 1-silaphenalene molecule, II is most conveniently viewed as a derivative of naphthalene that contains a three atom bridge across the 1 and 8 positions of naphthalene. Since there are 1,8-difunctional naphthalenes known which can be readily prepared, we focused our attention on routes to II that began with the naphthalene ring intact. Pathways involving construction of all or portions of the naphthalene ring were not investigated.

We envisioned two routes to 1-silaphenalenes. The first was construction of a 1-silaphenalane structure (VIII) followed by introduction of the 2,3-double bond to give II. The second involved double displacement on a dichlorosilane by the dianion of *Z*-1-bromo-2(8'-1'-naphthyl)ethene (IX) to give the silaphenalene directly (Scheme 1).

SCHEME 1

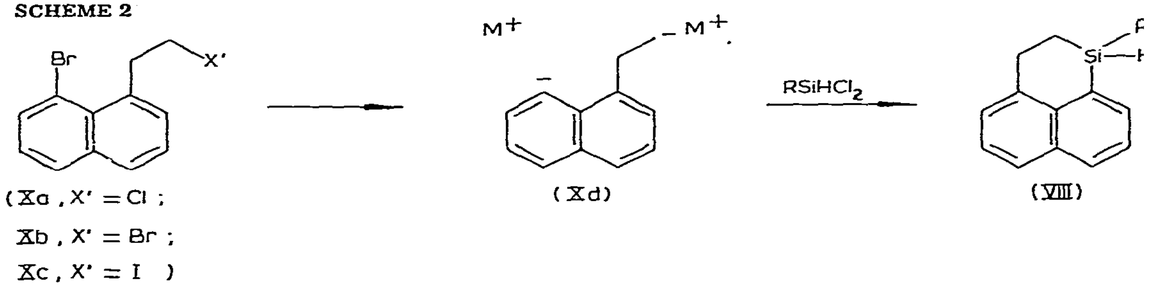


Results and discussion

Approach a

Construction of an 8-bromo-1-(2′-haloethyl)naphthalene (X) and conversion to the dianion, followed by coupling to a dichlorosilane proved to be a straightforward route to VIII (Scheme 2).

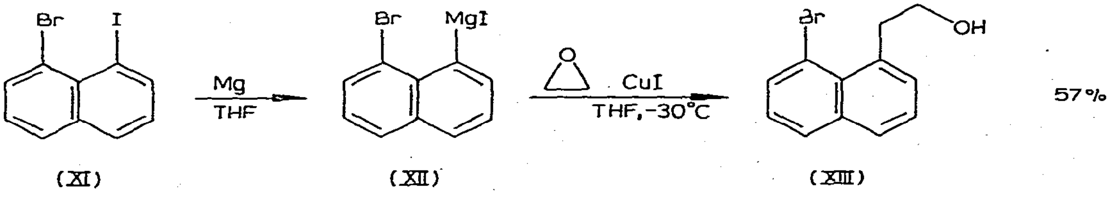
SCHEME 2



The use of oxirane as an electrophilic equivalent of ethanol is widely accepted [9]. Recently, Linstrumelle and coworkers [10] demonstrated that Grignard reagents can open oxirane to the substituted ethanols in high yield when the reaction is carried out in the presence of copper(I) iodide. Since alcohols are

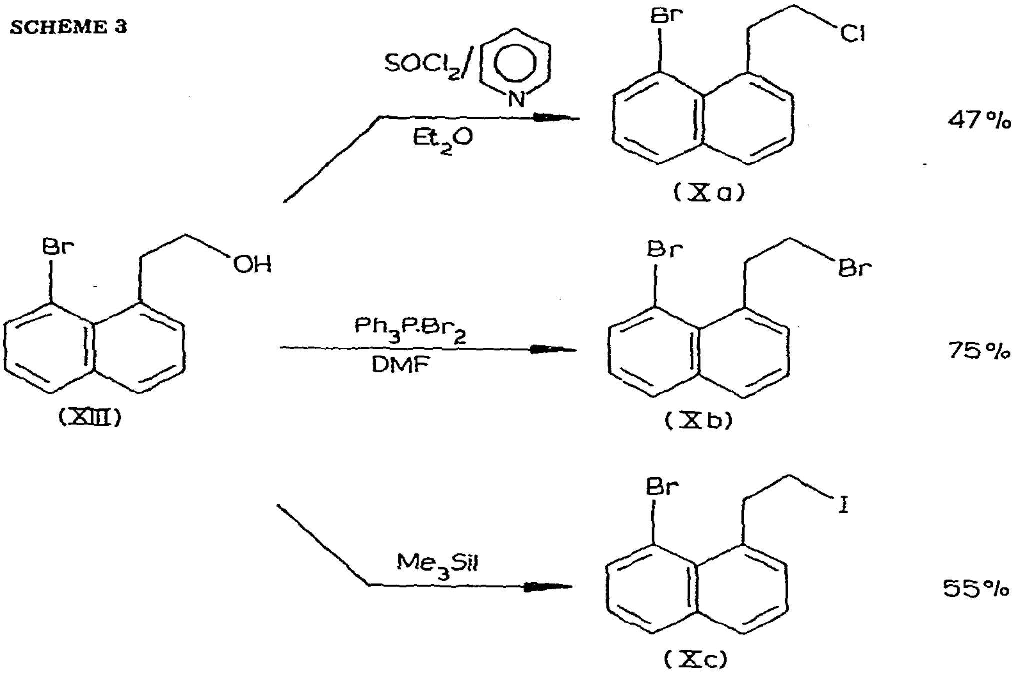
easily converted to halides [11] and the mono-Grignard of 8-bromo-1-iodonaphthalene (XI) can be prepared in high yields [12], the routes to X were obvious. Moreover, earlier work in our laboratories produced a convenient synthesis of XI [13], a reagent we found useful for preparing mono- and disilaacenaphthenes [14], which made this approach still more attractive.

A solution of XI in tetrahydrofuran (THF) was refluxed in the presence of one equivalent of magnesium turnings for 3 h, producing a yellow slurry. Addition of this slurry to a THF solution of oxirane and 10 mole percent CuI produced the desired alcohol (XIII) in good yield:



Conversion of XIII to the halides Xa, Xb and Xc was accomplished as shown

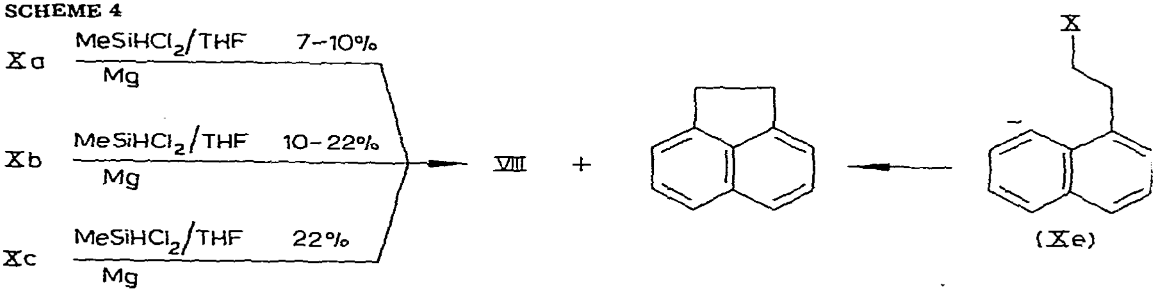
SCHEME 3



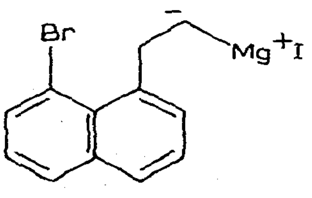
above (Scheme 3). Other halogenation procedures (see Experimental section) did not give yields as high as these. With a synthesis of X in hand we turned to the problem of ring closure to 1-methyl-1-silaphenalane (VIII).

Grignard techniques applied to Xa, Xb and Xc accompanied by in situ trapping with methyldichlorosilane produced VIII in modest yields. The major product in all three cases was acenaphthene, indicating that the dominant pathway is formation of carbanion Xe followed by displacement of the alkyl halide (Scheme 4). For each halide, the best yields of VIII were obtained when the

SCHEME 4



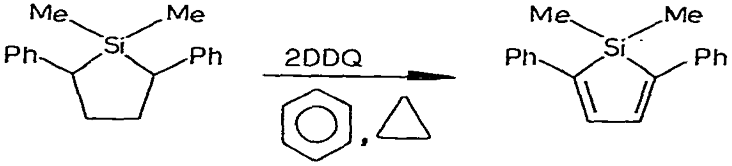
halide and an excess of the chlorosilane were added as a THF solution to a THF/Mg slurry. In the case of Xc, the better yields of VIII are probably because the formation of carbanion Xf is faster than that of the chloro and bromo ana-



(Xf)

logues, thus reducing the internal displacement reaction to form acenaphthene.

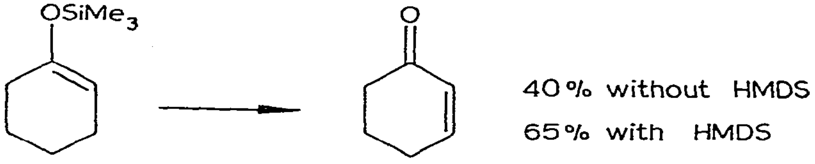
We have not been able to execute the last step in this approach to 1-methyl-1-silaphenalene (II, R = Me, X = H), i.e., introduction of the double bond into the 2,3 position of VIII (R = Me, X = H). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), while useful for introducing two double bonds in the silacyclopentane, XIV, [15] gave only polymer when used in equimolar amounts with



(XIV) (XV)

VIII (R = Me, X = H) using either benzene or dioxane as solvent. *o*-Chloranil (3,4,5,6-tetrachloro-1,2-quinone), a milder oxidizing agent than DDQ, gave polymer and unreacted VIII under similar conditions.

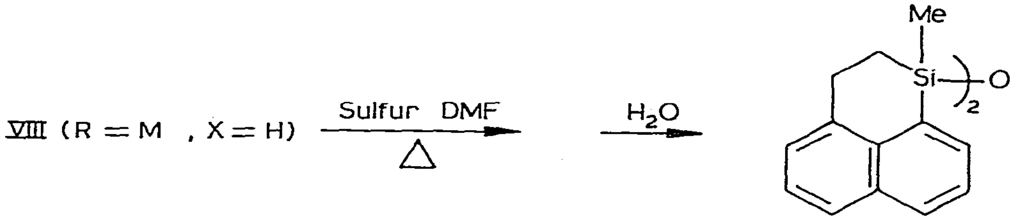
Murai, et al. [16] showed that the yields from DDQ oxidations of silyl enol ethers to enones were increased significantly when carried out in the presence of an equivalent of hexamethyldisilazane (HMDS). When applied to VIII, the



(XVI) (XVII)

reaction was suppressed and VIII was recovered quantitatively. Replacing HMDS with trimethylchlorosilane gave the same results.

Dehydrogenation by elemental sulfur at high temperatures has been used extensively to introduce double bonds [17]. Refluxing VIII in dimethylformamide (DMF) in the presence of one equivalent of sulfur gave no silaphenalene as evidenced by the absence of absorptions in the vinyl region in the NMR spectrum. Following water work-up, a solid was isolated and tentatively identified as the siloxane XVIII.



(XVIII)

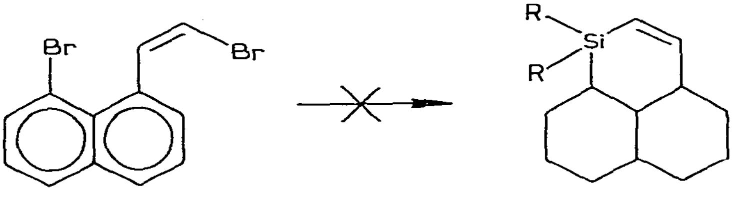
The presence of Si—H and Si—naphthyl bonds clearly increases the difficulty of oxidizing carbon—carbon bonds adjacent to silicon. Our failure to generate II (R = Me, X = H) from VIII (R = Me, X = H), and the absence of reports in the literature of successful dehydrogenations of alkylsilanes containing Si—H or

Si—naphthyl bonds suggest that such a transformation may be a formidable challenge.

Approach b

Unable to dehydrogenate VIII (R = Me, X = H), we investigated a cyclization reaction similar to Approach a using a substrate that contained the necessary double bond. *Z*-1-Bromo-2-(8′-bromo-1′-naphthyl)ethene XXII was chosen as the precursor to the desired dianion, IX.

A number of stereoselective syntheses of *E* or *Z* vinyl halides from terminal acetylenes have been developed [18—20]. By modifying the method developed by Miller and Reichenbach [20] we were able to prepare XXII relatively free of the *E* isomer from 1-bromo-8-ethynylnaphthalene [21]. However, attempts to prepare derivatives of 1-silaphenalene using Mg or Li—halide exchange and a dichlorosilane failed. Details of these efforts are presented elsewhere [22].



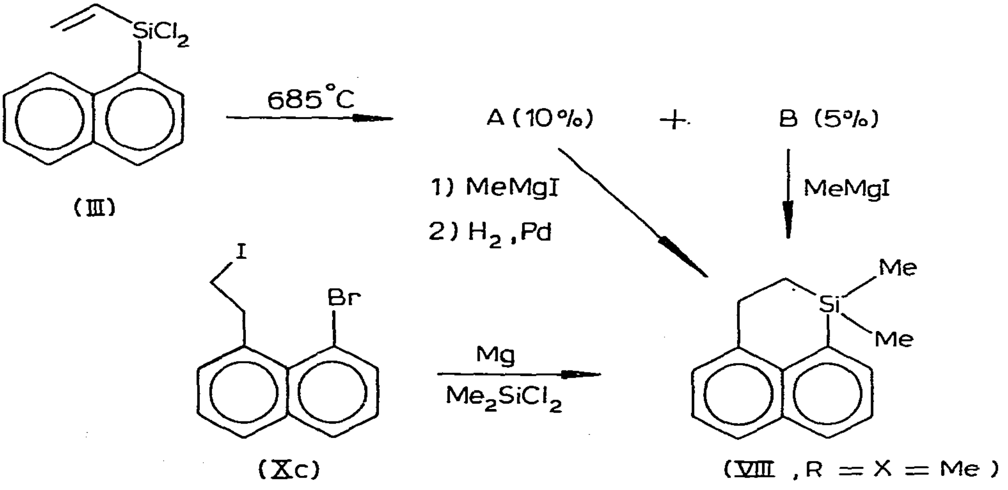
(XXII) (II)

Confirmation of the structures of the pyrolysis products of (1-naphthyl)vinyldichlorosilane(III)

Unable to prepare the 1-silaphenalene skeleton by the routes described above, we investigated the pyrolysis products of III. In view of our failure to make II, this was our best chance of obtaining useful quantities of these compounds if, in fact, the structural assignments [4] were correct.

In our hands, the pyrolysis of III led to two products. The structures were proven by the following sequence of reactions (Scheme 5):

SCHEME 5



When pure A, obtained by crystallization from hexane, was treated with excess MeMgI followed by hydrogenation, a colorless liquid was obtained which was confirmed as 1,1-dimethylsilaphenalane (VIII, R = X = Me) by comparing its GC retention time and spectra (IR and NMR) with those of an authentic sample prepared as described above (Approach a). A 2 : 1 mixture of A and B was also treated with excess MeMgI. Analysis by NMR showed that II (R = X = Me) and VIII (R = X = Me) were present. Hydrogenation of the mixture gave a single product which was identified as VIII (R = X = Me). These results lead to the assignment of the structure II (R = X = Cl) to compound A and the assignment of the structure VIII (R = X = Cl) to compound B.

Thus pyrolysis of III is the best route to II (R = X = Cl) and, having verified that, we have begun a study of 1-silaphenalenes to investigate their potential as precursors to aromatic silicon-containing cations, radicals and anions. We will report on these studies in due course.

Experimental

NMR spectra were taken on a Varian A60-A, T-60, or EM390 spectrometer using $CDCl_3$ or CCl_4 as solvent with TMS or cyclohexane as internal standard. Infrared spectra were taken on a Perkin-Elmer 137 spectrometer using polystyrene film for calibration. Mass spectra were taken on a Finnigan 1015D GC-MS mass spectrometer at 70 eV. Elemental analyses were done by Galbraith Laboratories, Inc.

THF was distilled as needed from benzophenone-sodium ketyl under nitrogen. Ether was obtained from freshly opened cans of absolute ether (MC/B). n-Butyllithium was used as a 1.6 *M* hexane solution (Aldrich). Chlorosilanes were from the Dow Corning Co. or Petrarch Systems, Inc. and were used as obtained. Me_3SiI was from Aldrich and used without further purification. CuI was used as purchased from Alfa. 8-Bromo-1-iodonaphthalene was prepared and purified as described in the literature [13].

Before use, all glassware was oven dried, assembled hot, and cooled under a stream of dry nitrogen. All reactions were run under a nitrogen atmosphere. Stirring of solutions was done with a magnetic stirrer and all reactions were continuously stirred unless otherwise specified. All additions were dropwise from a pressure-equalizing addition funnel unless stated otherwise.

The statement "worked-up in the usual manner" refers to removal of solvent by a rotary evaporator under aspirator vacuum followed by dissolving the residue in ether. The ether was washed with saturated sodium chloride solution. All Grignard reactions were first washed with saturated ammonium chloride solution, then dried with Na_2SO_4 or $MgSO_4$, filtered by gravity, and the ether removed under aspirator vacuum using a rotary evaporator.

2-(8'-bromo-1'-naphthyl)ethanol, XIII

In a 100 ml single necked flask were placed 30 ml of THF, 0.42 g (17 mmol) of magnesium turnings, and 0.2 ml (2 mmol) of 1,2-dibromoethane and the slurry was reluxed for 10 minutes. To this slurry of THF and magnesium was added 5.00 g (15 mmol) of 8-bromo-1-iodonaphthalene XI [13] and the solution was reluxed for 3 hours. The yellow slurry was cooled to room temperature and diluted with 30 ml of THF. This solution was added to a slurry of 40 ml of THF, 0.20 g (1.5 mmol) of dry copper (I) iodide, and 0.74 ml (15 mmol) of oxirane at —30°C. After the addition of the Grignard was complete, the reaction mixture was maintained at —30°C for 1 h, then allowed to warm to room temperature and stir overnight. The reaction mixture was quenched with saturated NH_4Cl solution, then worked-up in the usual manner to give a brown oil, which was dissolved in 180 ml of boiling hexane and treated with activated charcoal. After gravity filtration, the solution was stored in the freezer overnight producing 1.82 g (48%) of white crystals. The mother liquor was concentrated to give a brown oil, from which no more of the desired product could be obtained. The crystals had a melting point of 75—76.5°C. NMR (ppm $CDCl_3$), δ 7.97—7.13 (m, 6 H, NpH), 4.17—3.70 (m, 4 H, CH_2CH_2), 1.55 (broad singlet, 1 H, OH). IR (cm^{-1}, $CDCl_3$), 3575 (broad, OH), 3000, 2900, 2850, (C—H), 1555 (C=C) Analysis. Found: C, 57.48; H, 4.49. $C_{12}H_{11}OBr$ calcd.: C, 57.40; H, 4.41%.

1-Chloro-1-(8'-bromo-1'-naphthyl)ethane, Xa

In a 50 ml single necked flask were placed 0.50 g (2 mmol) of XIII, 20 ml of dry ether, and 0.16 ml (2 mmol) of pyridine. To this solution was added 0.15 ml (2 mmol) of thionyl chloride to give a white precipitate. This slurry was stirred for 72 hours, then washed with saturated ammonium chloride, H_2O, dried with $MgSO_4$, filtered, and the ether removed under aspirator vacuum to give a yellow oil. This oil was chromatographed on alumina (activity 3, 7 × 2 cm) using pentane as eluent. Removal of the pentane gave 0.25 g (47%) of a clear oil, Xa. NMR (ppm $CDCl_3$), δ 7.83—6.98 (multiplet, 6, NpH), 4.00—3.60 (multiplet, 4, CH_2CH_2). IR (cm^{-1}, $CDCl_3$), 3080, 2960, (C—H), 1570, 1500 (C=C), 1240, 1180, 1075, 1025.

When XIII was refluxed in $CCl_4/CHCl_3$ containing 1.75 equivalents of triphenylphosphine a 24% yield of Xa was obtained after work-up [23].

1-Bromo-2-(8'-bromo-1'-naphthyl)ethane, Xb

In 100 ml three necked flask equipped with rubber septum covered inlet and internal thermometer was placed 70 ml of dry dimethylformamide (DMF), 4.02 g (15.3 mmol) of triphenylphosphine, and 3.50 g (13.9 mmol) of XIII and the solution cooled to 0°C. To this solution was added via syringe 0.76 ml (15 mmol) of bromine. During the bromine addition the temperature of the DMF solution was kept below 5°C. Once all the bromine had been added, the solution was allowed to warm to room temperature and stirred for 16 hours. The DMF was removed under aspirator pressure to give an orange oil which was stirred with pentane (4 × 100 ml) to extract the product from the triphenylphosphine oxide. The pentane fractions were combined and the pentane removed to give a brown oil. This oil was chromatographed on alumina (activity 3, 6 × 2 cm) using pentane as eluent. After removal of the pentane, 3.38 g (79% yield) of a clear oil was obtained. In the freezer this oil would solidify, however, warming to room temperature again gave a semisolid. No melting point could be obtained. NMR (ppm $CDCl_3$), δ 7.96—7.00 (m, 6 H, NpH), 4.13—3.83, (m, 2 H, NpCH), 3.73—3.47 (m, 2 H, CH_2Br). M.S. (*m/e*), 314 (P^+) 316, 312, 288, 286, 284, 208, 206, 126 (base peak).

When XIII was treated with 1 molar equivalent of PBr_3 in ether containing pyridine 21% yield of Xb was obtained [24].

1-Iodo-2-(8'bromo-1'-naphthyl)ethane, Xc

In a 100 ml single necked flask covered with aluminum foil to block out light was placed 0.75 g (3 mmol) of XIII, 30 ml of CH_2Cl_2, and 0.60 ml (4.5 mmol) of trimethylsilyl iodide (Aldrich). The brown solution was stirred for two days. The methylene chloride solution was washed with H_2O, saturated sodium thiosulfate solution, dried with Na_2SO_4, filtered, and the solvent removed at aspirator vacuum to give a brown solid. This solid was chromatographed on alumina (activity 3, 6 × 2 cm) with pentane as eluent. Removal of the pentane gave 0.75 g (70% yield of a white solid, m.p. 68—71°C). Over a period of 24 h this solid would turn yellow-brown even when protected from the light. NMR (ppm $CDCl_3$), δ 8.00—7.16 (m, 6 H, NpH), 4.20—4.00 (5 line multiplet, 2 H, $NpCH_2$), 3.60—3.33 (5 line multiplet, 2 H, CH_2I). IR (cm^{-1}, $CDCl_3$), 3000 (C—H), 1540, 1480 (C=C), 1160. M.S. (m/e), 362, 360 (P^+), 235, 233, 154 (base peak).

When XIII was treated with two equivalents of $(CH_3)_3SiCl$ and two equivalents of sodium iodide in acetonitrile [25] no Xc was isolated. Use of 2,5-bis-(trimethylsilyl)-1,4-cyclohexadiene and iodine [11] to generate trimethylsilyl iodide in the presence of XIII also gave no isolated Xc.

1-Methyl-1-silaphenalane, VIII (R = Me, X = H)

In a three necked 50 ml flask were placed 0.60 g (25 mmol) of magnesium turnings, 2 ml of THF, and 0.10 ml (1.2 mmol) of 1,2-dibromoethane. This slurry was refluxed for 10 minutes and then a THF solution (3 ml) of 0.82 g (2.3 mmol) of Xc and 0.41 ml (4.6 mmol) of methyldichlorosilane was added over 10 minutes. The reaction mixture was refluxed for 20 h then worked-up in the usual manner to give a yellow oil. Isolation by preparative GLC (10' × 1/4", 25% SE-30 on Chromosorb W column at 180°C) gave 0.1 g of a clear oil. Overall yield was 22%. When Xa or Xb were used in this procedure, yields were in the 7—12% range. Use of Rieke's activated magnesium [26] produced no detectable VIII.

NMR (ppm, $CDCl_3$), 7.90—7.13 (m, 6 H, NpH), 4.65 (m, 1 H, Si—H), 3.27 (t, 2 H, $NpCH_2$), 1.13 (m, 2 H, CH_2Si), 0.38 (d, 3 H, $SiCH_3$)..

Spin decoupling experiments provided the following coupling constants. $J(N_pCH_2Si)$ = 7 Hz, $J(SiH—SiCH_3)$ = 4 Hz, IR (cm^{-1}, CCl_4), 3020, 2900 (C—H), 2100 (Si—H), 1480, 1430, (C=C), 1245 ($SiCH_3$), M.S. (m/e), 198 (P^+ and base peak), 197, 196, 195 (P — 3 H), 183 (P — 15), 181 (P — 17), 153, 152. Analysis. Found: C, 78.51; H, 6.97, $C_{13}H_{14}Si$ calcd.: C, 78.77; H, 7.06%.

Oxidation of VIII (R = Me, X = H) with benzoquinones [15]

In a 5 ml single necked flask were placed 2 ml of benzene-d_6 and 0.10 g (0.5 mmol) of VIII (R = Me, H). To this was added 0.126 g (0.55 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to give a dark green solution. This solution refluxed for 20 h. The reaction mixture was cooled, washed with pH 7 buffer, dried with Na_2SO_4, filtered, and the solvent removed under vacuum to give a dark green semi-solid. By NMR, only polymer is present (broad, featureless band at 8.3—7.3 ppm). Use of *o*-chloranil in place of DDQ resulted in formation of polymer and approximately 50% recovered silane. When dry dioxane was substituted for benzene in this reaction, polymeric materials were obtained after work-up.

Oxidation of VII (R = Me, X = H) with DDQ in the presence of silating agents [16]

In a dry NMR tube were placed 0.014 g (0.07 mmol) of VIII (R = Me, X = H) in 100 μl of benzene and 0.6 ml of benzene-d_6. To this were added 60 μl of a solution of 0.2 g (0.9 mmol) of DDQ and 0.3 ml (2.4 mmol) of HMDS in 2.0 ml of benzene-d_6 (this is 0.33 equivalents of DDQ) to give a dark green solution. This solution was monitored by NMR for 1 h, after which time the solution was orange colored with a red precipitate on the tube walls. A second 0.33 equivalent of DDQ was added giving a green solution. No change in the spectrum was noted. After one additional hour, the solution was red with more precipitate noted, and a third 0.33 equivalent of DDQ was added. After three more hours the solution was red with a precipitate on the tube walls. No spectrum change was observed. The NMR tube was heated at 50°C for one hour. No spectrum change was noted.

Use of trimethylchlorosilane in place of HMDS also gave a precipitate and no change in the spectrum of VIII (R = Me, X = H) even after 12 hours at 80°C.

Reaction of VIII (R = Me, X = H) with sulfur

In 10 ml single necked flask were placed 0.042 g (0.2 mmol) of VIII (R = Me, X = H), 5 ml of dry DMF, and 0.01 g (0.3 mmol) of sublimed sulfur. The solution was refluxed for 16 hours after which time it contained a black precipitate. This reaction mixture was cooled to 0°C, diluted with 20 ml of ether, washed with pH 7 buffer, dried with Na_2SO_4, filtered, and the solvents removed under vacuum to give a brown solid. By NMR, there are no vinyl protons and no silicon hydride. An infrared spectrum of this solid also shows no Si—H but does show a siloxane stretch at 1050 cm^{-1}. These data suggest that the siloxane XVIII is produced.

Pyrolysis of dichloro-1-naphthylvinylsilane (III)

Forty grams of III was added dropwise under nitrogen down the side of an empty 25 × 500 mm quartz tube at 685°C over a period of 60 min. Thirty-five grams of brown-black condensate was collected. Two fractions were isolated by distillation: A, 13 g, 105—135°C/0.2 torr, consisting mostly of III and naphthalene; B, 10.90 g, 135—165°C/0.2 torr, which showed two components of similar retention times when analyzed by gas chromatography (6′ × 1/4″, 10% SE-30 on Chromosorb W). The compound with longer retention time was twice as abundant as the more volatile product.

Cooling this mixture in the refrigerator produced white crystals. These were recrystallized from hexane followed by vacuum sublimation to give 2.0 g of a white solid (m.p. 92°C). The filtrate was separated into its components by preparative gas chromatography giving 2 g of the white solid previously obtained from crystallization and 2 g of a clear colorless liquid. The white solid was identified as 1,1-dichloro-1-silaphenalene (II, R = X = Cl) and the liquid as 1,1-

dichloro-1-silaphenalane (VIII, R = X = Cl) via the reaction sequence in Scheme 5.

1,1-Dichloro-1-silaphenalene (II, R = X = Cl): yield, 4 g (10%), m.p. 92°C (lit. [4] m.p. 93°C). NMR (ppm, $CDCl_3$), δ 7.26—8.30 (m, 7 H, NpH and NpCH), 6.33—6.50, (d, 1 H, Si—C—H).

1,1-Dichloro-1-silaphenalane (VIII, R = X = Cl): yield, 2 g (5%). NMR (ppm, $CDCl_3$), δ 7.20—8.20 (m, 6 H, NpH), 3.20—3.56 (m, 2 H, $NpCH_2$), 1.76—1.53 (m, 2 H, $SiCH_2$).

Preparation of 1,1-dimethyl-1-silaphenalane (VIII, R = X = Me) from 1-iodo-2-(8′-bromo-1′-naphthyl)ethane (Xc)

In a three necked flask fitted with a water condenser, nitrogen inlet and a magnetic stir bar were placed magnesium turnings (0.60 g, 25 mmol), THF (2 ml) and 1,2-dibromoethane (0.10 ml, 1.2 mmol). This slurry was refluxed for 10 min followed by the addition of a THF solution (3 ml) of Xc (0.45 g, 2.3 mmol) and Me_2SiCl_2 (0.50 ml, 4.6 mmol) over a 10 min period. The reaction mixture was refluxed for 20 h and then worked up in the usual manner to give 0.1 g (20%) of a pale yellow oil. A pure sample was obtained by preparative gas chromatography.

NMR (ppm, $CDCl_3$), δ 7.23—7.93 (m, 6 H, NpH), 3.33 (t, 2 H, $NpCH_2$) 1.13 (t, 2 H, Si—CH_2—C), 0.37 (s, 6 H, $SiCH_3$). MS (*m/e*) 212 (P^+), 197 (base peak), 195, 169. Analysis. Found: C, 79.02; H, 7.67, $C_{14}H_{16}Si$ calcd.: C, 79.19; H, 7.59%.

Preparation of VIII (R = X = Me) from the pyrolysate of 1-naphthylvinyldichlorosilane (III)

A 2 : 1 mixture of II (R = X = Cl) and VIII (R = X = Cl) was methylated and hydrogenated as described below to give only VIII (R = X = Me). A pure sample was obtained by preparative gas chromatography and was identical to the sample of VIII (R = X = Me) obtained from above experiment.

Preparation of 1,1-dimethyl-1-silaphenalene, II (R = X = Me) from II (R = X = Cl).

To a 15 ml ethereal solution of II (R = X = Cl) (0.63 g, 2.5 mmol) was added 3.0 ml (6 mmol) of a 2 *M* solution of MeMgI in ether (Alfa). This was refluxed for 1 h, cooled to r.t. and worked up in the usual manner. Using preparative gas chromatography 0.28 g (52%) of II (R = X = Me) was isolated as a viscous liquid.

NMR (ppm, $CDCl_3$), δ 7.16—7.83 (m, 7 H, NpH and NpCH), 6.1 (d, 1 H, $SiCH_A{=}CH_B$), 0.23 (s, 6 H, $SiCH_3$). Coupling constant, J_{AB} = 15 Hz. MS (*m/e*), 210 (P^+), 195 (base peak), 167. Analysis. Found: C, 79.79; H, 6.89. $C_{14}H_{14}Si$ calcd.: C, 79.94; H, 6.70%.

Preparation of 1,1-dimethyl-1-silaphenalane, VIII (R = X = Me), from 1,1-dimethylsilaphenalene, II (R = X = Me)

A hexane (10 ml) solution of 0.28 g (1.3 mmol) II (R = X = Me) was hydrogenated at 100 psi using 10% Pd on charcoal as the catalyst. Quantitative conversion was achieved after 6 h as shown by NMR analysis of the filtrate of the product mixture. The product was purified by preparative gas chromatography and identified by comparison to other samples of VIII (R = X = Me).

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