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# 1,8-DIFUNCTIONALIZED NAPHTHALENES AS BUILDING BLOCKS. A CONVENIENT LOW TEMPERATURE SYNTHESIS OF 1-SILAACENAPHTHENES

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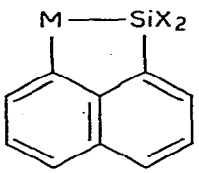
## Summary

The synthesis of 1-silaacenaphthenes by the reaction of chlorosilanes with 8-bromo-1-halomethylnaphthalenes and magnesium is described. The use of dichlorosilanes was found to give better yields of 1-silaacenaphthenes than trichlorosilanes. Halogen—metal exchange between 8-bromo-1-halomethylnaphthalenes and n-butyllithium was also investigated as a method of preparing 1-silaacenaphthenes. 1,1,2,2-Tetramethyl-1-silaacenaphthene was synthesized from 8-bromo-1-iodonaphthalene in good yield.

## Introduction

The work of Sommer and Roark using an optically active 1-silaacenaphthene to demonstrate crossover of mechanism in displacement reactions at strained silicon centers [1] and Ponec's study of the charge-transfer complexes of 1-silaacenaphthenes and tetracyanoethylene [2] are the only reports on the chemistry of 1-silaacenaphthenes. Similarly, the known chemistry of 1,2-disilaacenaphthenes is limited to X-ray [3], ESR, and polarographic [4] studies.

The lack of chemical studies on these systems may be due in part to the limitations inherent in the reported synthesis of 1-silaacenaphthenes (Ia) and 1,2-disilaacenaphthenes (Ib). Currently, the only route to Ia and Ib is from the flow pyrolysis at 680—700°C of 1-methylnaphthalene or 1-(dichlorosilyl)naphthalene with either trichlorosilane or hexachlorodisilane [5]. The necessity of a pyrolysis apparatus and of handling large quantities of chlorosilanes have undoubtedly limited the investigations of these interesting systems. Only 1,1-dichloro-1-silaacenaphthene (Ia, X = Cl) or 1,1,2,2-tetrachloro-1,2-disilaacenaphthene (Ib, X = Cl) are conveniently available from this method. The draw-




(Ia, M = $CH_2$ ;
Ib, M = $SiX_2$ )

backs of this synthesis and our interest in 1,8-disubstituted naphthalenes [6,7] prompted us to consider alternative low temperature routes to these molecules that would allow for more flexibility. This paper details our development of these new syntheses.

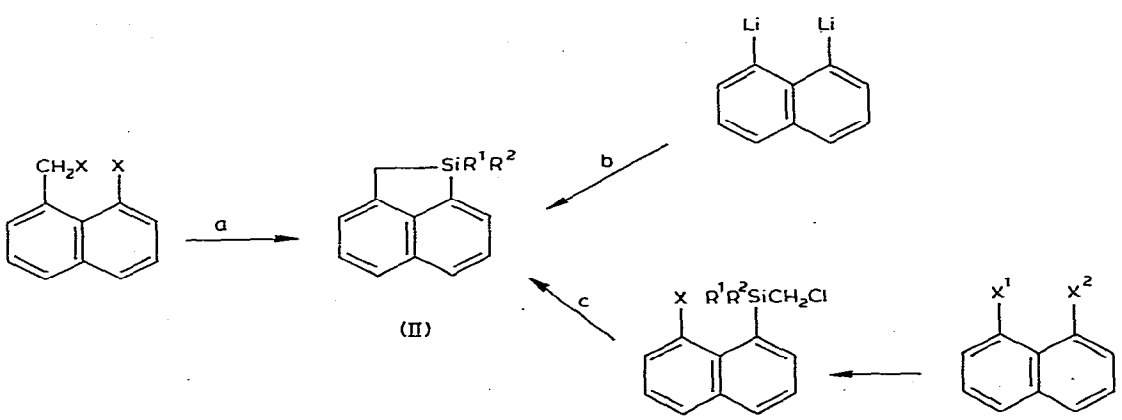
*Synthetic plan*

Three approaches to 1-silaacenaphthenes (II) were considered (Scheme 1). Pathway a is analogous to the cyclizations successful for the formation of benzosilacyclobutane [8] and benzodisilacyclopentane [9] from *o*-bromobenzyl bromide and an appropriate dichlorosilane. The b pathway is similar to the reported uses of 1,8-dilithionaphthalene for the synthesis of 1,1-dimethylnaphtho[1,8-b,c]silete [10a] and 1,8-naphthalene disulfide [10b,c]. The third pathway, c, was viewed as a stepwise modification of b in which there would be greater control of the displacement reactions.

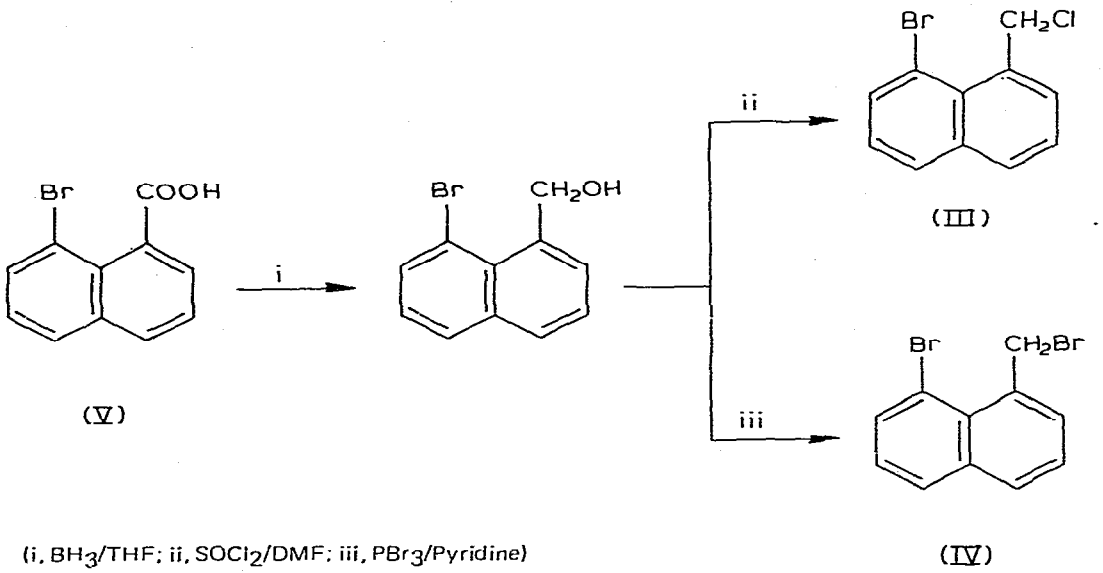
*Approach a.* The necessary starting materials, 8-bromo-1-halomethylnaphthalenes (III and IV), were easily prepared from 8-bromo-1-naphthoic acid (V) [11] by borane reduction followed by halogenation [12] as shown in Scheme 2.

Addition of III and methyldichlorosilane as a tetrahydrofuran (THF) solution to magnesium turnings in refluxing THF gave, after work-up and distillation, 1-methyl-1-silaacenaphthene (VI) in 64% yield (Scheme 3). Use of IV and methyldichlorosilane gives VI in 56% yield after distillation. Since this reaction

SCHEME 1



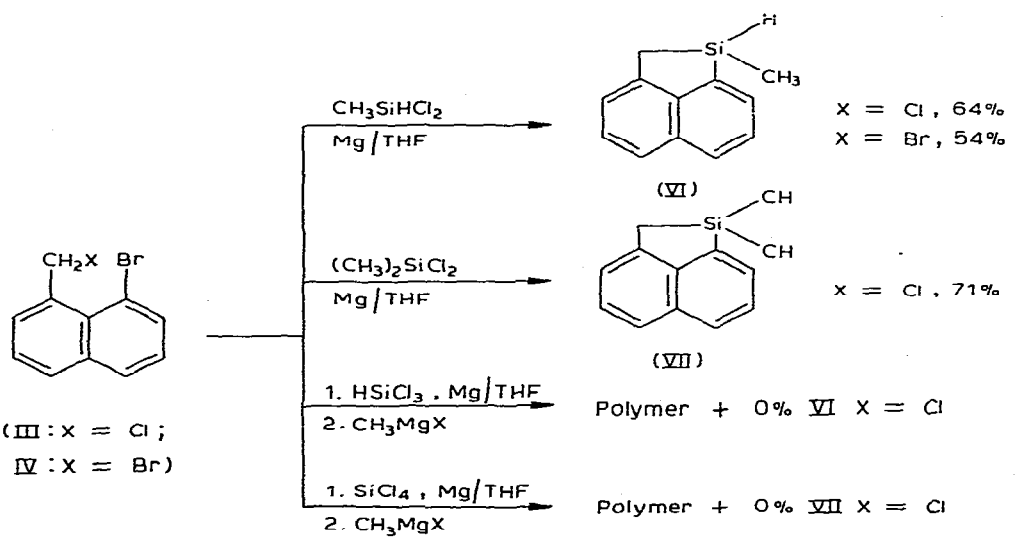
SCHEME 2



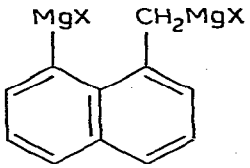

gave good yields of VI, we investigated which other 1-silaacenaphthenes were accessible by this procedure. 1,1-Dimethyl-1-silaacenaphthene (VII) was obtained in 71% yield using III and dimethyldichlorosilane. Use of trichlorisilane and III was expected to give VI after methylation but only polymeric material was found after work-up. When silicon tetrachloride and III were employed, only polymer was isolated.

To determine if the diGrignard species (VIII) was being generated and then trapped by the dichlorosilane, we added III to a refluxing THF solution containing magnesium. After refluxing 12 h, dimethyldichlorosilane was added.

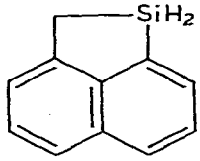
SCHEME 3



Less than 10% yield (by NMR) of the expected VII was found. The remainder of the product is a solid of undetermined structure, containing no silicon (by NMR). Just prior to the addition of the silane, a small aliquot of the reaction mixture was removed and hydrolyzed. Analysis of this GLC showed only a minor amount of 1-methylnaphthalene. It seems reasonable to conclude that very little of VIII is formed in the co-addition reactions. The co-addition reac-



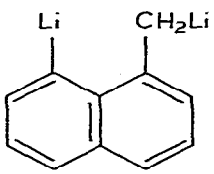

(VIII)




(IX)

tion using trichlorosilane and III was repeated (Scheme 3). However, instead of methylation, the reaction was cooled to 0°C and a second equivalent of trichlorosilane was added. This was followed by reduction with lithium aluminum hydride. This procedure gave an approximately 10% yield of 1-silaacenaphthene (IX). The remainder of the product was polymer. The reaction was repeated using refluxing diethyl ether as solvent. After reduction with $LiAlH_4$ and work-up, only a 17% yield of IX was obtained. When three equivalents of trichlorosilane and III were added to magnesium in refluxing ether, IX was obtained in 37% yield after quenching with $LiAlH_4$.

The work of Parham et al. on the selective halogen—metal exchange of $\omega$-(*o*-bromophenyl)-1-haloalkanes [13] prompted us to explore the possibility of using halogen—metal exchange to generate the dilithio species (X) which is analogous to VII. Only polymeric material was isolated from the reaction of




(X)

two equivalents of n-butyllithium and IV. This result was independent of temperature (—100, —70, 0°C) and the order of addition of the reagents. When two equivalents of n-butyllithium and III were combined at —100°C followed by methyldichlorosilane addition, 8-(butylmethylsilyl)-1-chloromethylnaphthalene was isolated in ~20% yield.

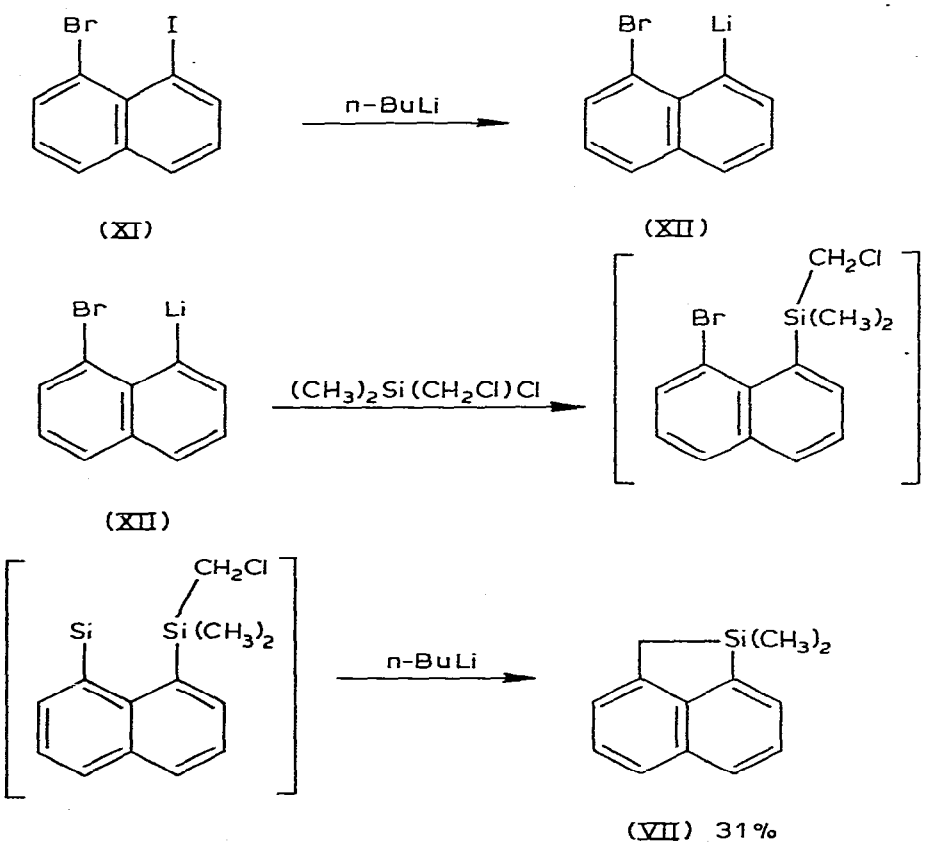
*Approach c.* This pathway involved the stepwise formation of the bonds to the 1 and 8 positions of the naphthalene ring by a lithiation-silation-lithiation-alkylation sequence of reactions. A 1,8-dihalonaphthalene is required as the starting material for this pathway. Three such compounds are readily available, 1,8-diiodonaphthalene [14], 1,8-dibromonaphthalene, and 8-bromo-1-iodonaphthalene. We have recently reported an improved synthesis of the latter two

compounds [6]. We chose to employ 8-bromo-1-iodonaphthalene (XI) since it is the most readily available.

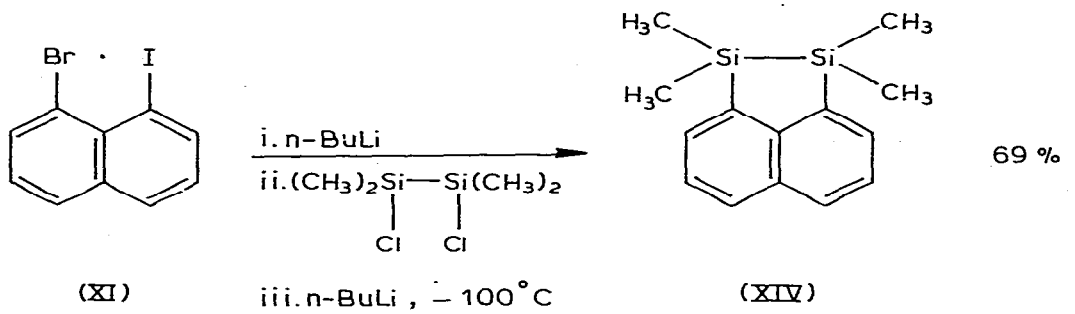
At —70°C, 8-bromo-1-lithionaphthalene (XII) was generated in THF from XI and 1 equivalent of n-butyllithium and chloromethyldimethylsilane was added. After allowing the solution to warm to —40°C, it was cooled to —100°C and one equivalent of n-butyllithium was added. At —100°C, displacement reactions by alkyllithium reagents are slow [15] while halogen—metal exchange occurs rapidly [13]. Work-up of this reaction gave VII in 31% yield (Scheme 4). In a separate experiment we have shown that XI can be quantitatively monolithiated at —70°C to give XII. Silylation of XII proceeds smoothly as demonstrated by the isolation of 8-bromo-1-(dimethylsilyl)naphthalene in 77% yield. A small amount of 1-bromonaphthalene was also present but no unreacted XI could be found.

*Approach b.* 1,8-Dilithionaphthalene, the required starting material for pathway b, was generated from XI via procedures previously reported [10]. To a solution of 1,8-dilithionaphthalene (XIII) at —70°C was added dimethylchloromethyl chlorosilane. Following warming and work-up, less than 17% yield of VII was obtained (by NMR). This result prompted us to abandon this procedure as a practical synthesis of 1-silaacenaphthenes.

SCHEME 4



SCHEME 5




(XI) (XIV)

*1,2-Disilaacenaphthenes*

While the yields of 1-silaacenaphthenes from pathways b and c are low, we reasoned that if both steps involved displacement of a silicon chloride the yield of cyclized material would be higher. This would provide a low temperature synthesis of 1,2-disilaacenaphthenes.

Using the procedure described in Approach c, XI and 1,2-dichlorotetramethyldisilane gave 1,1,2,2-tetramethyl-1,2-disilaacenaphthene (XIV) in 67% yield (Scheme 5). Pathway b gave 18% yield of XIV.

## Conclusion

Of the three methods investigated for constructing 1-silaacenaphthenes, pathway a is clearly the method of choice. It offers higher yields and greater flexibility than the other two routes.

Since a large number of dichlorosilanes are available, our procedure provides a direct route to a variety of 1-silaacenaphthenes. In other work, the benzyl alcohol precursor of III was prepared from the mono-anion of XI, i.e. XII, and formaldehyde *. This may open the way to 1-silaacenaphthenes with substitutents on the benzyl carbon.

## Experimental

NMR spectra were taken on a Varian EM 390 spectrometer using tetramethylsilane as internal standard. Spectra were obtained using $CDCl_3$ as solvent. Infrared spectra were taken on a Perkin—Elmer 137 spectrometer using polystyrene film for calibration. Mass spectra were taken on a Finnigan 1015 D GC-MS mass spectrometer at 70 eV. Microanalyses were performed by Chemalytics, Inc. Melting and boiling points are uncorrected. 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. Before use, all glassware was oven dried, assembled hot, and cooled under a stream of dry nitrogen.

* Unpublished results

All reactions were run under a nitrogen atmosphere and were continuously stirred by means of a magnetic stirrer. 8-Bromo-1-iodonaphthalene was prepared as described, m.p. 96—97°C not 92—93°C as previously reported [6].

*8-Bromo-1-hydroxymethylnaphthalene*

The procedure described by Gay and Hauser [12] was employed using THF as solvent in place of diglyme. No change in yield was noted.

*8-Bromo-1-chloromethylnaphthalene (III) [16]*

In a 250 ml single necked round bottomed flask equipped with a pressure-equalizing addition funnel was placed 20 ml of reagent grade chloroform and 2.0 ml (26 mmol) of dry dimethylformamide. To this was added 1.9 ml (26 mmol) of thionyl chloride, producing a pale yellow solution. This solution was stirred for 30 min and then a solution of 6.24 g (26 mmol) of 8-bromo-1-hydroxymethylnaphthalene in 50 ml of chloroform was added dropwise. The solution was stirred overnight, after which time the $CHCl_3$ solution was washed with water, sodium bicarbonate solution, and saturated NaCl solution. After drying with $MgSO_4$ and filtration, the $CHCl_3$ was removed in vacuo by roto-evaporator to give, after crystallization from 3/1 pentane/ether, 5.0 g (75%) of a white solid III (m.p. 67.5—69.5°C). (lit. [16] m.p. 64—66°C). Removal of the solvent from the mother liquor and recrystallization of the crude solid gave an additional 0.6 g of III as a yellow solid (m.p. 67—70°C). NMR: $\delta$ 5.48 (s, 2 H, $CH_2Cl$), 7.13—8.00 ppm (m, 6 H, ArH). IR ($cm^{-1}$, $CCl_4$): 3030 (C—H), 1495, 1450 (C=C).

*8-Bromo-1-bromomethylnaphthalene (IV) [12]*

The apparatus described above for preparing III was used for this experiment. The flask was charged with 3.50 g (14.7 mmol) of 8-bromo-1-hydroxymethylnaphthalene, 100 ml of ether, and 1.20 ml (14.7 mmol) of dry pyridine. To this solution was added dropwise 1.40 ml (14.7 mmol) of phosphorus tribromide. This addition caused a white precipitate to form, and it remained over the 2.5 days the solution was stirred. The ether solution was washed with water and dilute sodium bicarbonate solution, then dried ($MgSO_4$), filtered, and the ether removed in vacuo to give 3.55 g (80%) of a white solid, IV (m.p. 71—73°C). This solid was greater than 92% pure by NMR. The product was found to be sufficiently pure for further utilization. Pure IV was obtained by two recrystallizations from 3/1 pentane/ether (m.p. 76—77°C). NMR: $\delta$ 5.51 (s, 2 H, $CH_2Br$), 7.13—8.00 ppm (m, 6 H, ArH). IR ($cm^{-1}$, $CDCl_3$): 3030 (C—H), 1500, 1450 (C=C). Mass spectrum: *m/e* 302, 300, 298 (parent), 221, 219 (base peak), 140.

*Pathway a: Standard method*

*1-Methyl-1-silaacenaphthene (VI) from III.* In a 3 necked 50 ml round bottomed flask equipped with condenser and a pressure-equalizing addition funnel was placed 5 ml of THF, 0.60 g (25 mmol) of magnesium turnings, and 0.10 ml (1.2 mmol) of 1,2-dibromoethane. The reaction mixture was refluxed for 10 minutes. A solution of 1.28 g (5 mmol) of III and 0.44 ml (5 mmol) of methyldichlorosilane in 7 ml of THF was added dropwise to the refluxing

THF/magnesium slurry. The mixture was refluxed for 20 h, then was cooled and diluted with 75 ml of ether. This solution was washed successively with saturated $NH_4Cl$ solution and saturated NaCl. The solution was dried ($MgSO_4$), filtered, and the ether/THF was removed under vacuum. The residue was chromatographed on alumina (activity 3, column 6 × 2 cm) with 150 ml of pentane. Removal of the pentane gave 0.68 g of a cloudy oil which was distilled at 0.1 Torr using a Kontes short path microstill at 125—130°C to give 0.59 g (64%) of VI as a clear, colorless oil. NMR: $\delta$ 0.50 (d, 3 H, $SiCH_3$), 2.43 (center of AB quartet, 2 H, $CH_2Si$), 4.90 (m, 1 H, Si—H), 7.26—7.90 ppm (m, 6 H, ArH). Coupling constants: $J$(Si—H, $CH_2$—Si) 3 Hz, $J(N_pCH_AH_B)$ 19.5 Hz, $J$(Si—H, $SiCH_3$) 3 Hz.

The AB quartet at 2.43 ppm has an upfield proton centered at 2.23 ppm and a downfield proton centered at 2.60 ppm. Assignments were confirmed by spin decoupling experiments.

IR ($cm^{-1}$, neat film): 3000, 2910, 2860 (C—H), 2125 (Si—H), 1480, 1445 (C=C), 1240 (Si—$CH_3$), 820 and 775 (1,8-disubstituted naphthalene). Mass spectrum: *m/e* 184 (parent and base peak), 183, 169 ($P-15$), 167, 155, 141; Analysis. Found: C, 77.93; H, 6.28. $C_{12}H_{12}Si$ calcd.: C, 78.20; H, 6.57%.

*1-Methyl-1-silaacenaphthene (VI) from IV.* The following amounts were used: IV, 1.28 g (4.3 mmol) and $CH_3SiHCl_2$, 0.44 ml (5 mmol) in 7 ml of THF, Mg, 0.60 g (25 mmol) and 1,2-dibromoethane, 0.10 ml (1.2 mmol) in 5 ml of THF. After work-up and distillation, 0.44 g (56%) of VI was obtained.

*1,1-Dimethyl-1-silaacenaphthene (VII) from III [5a].* The following amounts were used: III, 1.00 g (3.9 mmol) and $(CH_3)_2SiCl_2$, 0.47 ml (3.9 mmol) in 7 ml of THF, Mg, 0.60 g (25 mmol) and 1,2-dibromoethane, 0.10 ml (1.2 mmol) in 5 ml of THF. Work-up and distillation (b.p. 95—100°C at 0.05 Torr) gave 0.55 g (71%) of VII as a clear, colorless oil. NMR: $\delta$ 0.33 (s, 6 H, $SiCH_3$), 2.23 (s, 2 H, $CH_2Si$), 7.20—7.80 ppm (m, 6 H, ArH). IR ($cm^{-1}$, neat film): 3030, 2930, 2860, (C—H), 1465, 1450 (C=C), 1275 ($SiCH_3$) Mass spectrum: *m/e* 198 (parent), 183 ($P-15$, base peak). Analysis. Found: C, 79.02; H, 7.17. $C_{13}H_{14}Si$ calcd.: C, 78.72; H, 7.11%.

*Attempted synthesis of VII from III and $SiCl_4$.* The following amounts were used: III, 1.00 g (3.9 mmol) and $SiCl_4$, 0.45 ml (3.9 mmol) in 7 ml of THF, Mg, 0.60 g (25 mmol) and 1,2-dibromoethane, 0.10 ml (1.2 mmol) in 5 ml of THF. After 20 h at reflux, the reaction mixture was cooled to 0°C and a 10-fold excess of methyl Grignard in THF was added. The resulting mixture was stirred for 1 h and was worked up in the usual manner. After chromatography and removal of the solvent, a foam-like, white solid was obtained. No VII could be detected by NMR. The solid appeared to be polymeric (b.p. > 220°C at 0.1 Torr).

*Attempted synthesis of 1-silaacenaphthene (IX) from III and $HSiCl_3$(-THF solvent) [5a].* The following amounts were used: III, 1.38 g (5 mmol) and $HSiCl_3$, 0.50 ml (5 mmol) in 7 ml of THF, Mg, 0.60 g (25 mmol) and 1,2-dibromoethane, 0.10 ml (1.2 mmol) in 5 ml of THF. After 20 h at reflux, the reaction mixture was cooled to 0°C and a three-fold excess of $LiAlH_4$ was added. After chromatography and removal of the solvent, a foam-like, white solid was obtained. There was no evidence of IX in the NMR. This solid also appeared to be polymeric (b.p. > 250°C at 0.1 Torr).

This reaction was repeated with the following modifications after the reaction was cooled to 0°C, a second equivalent of $HSiCl_3$ was added prior to the $LiAlH_4$ reduction. The polymer obtained contained 10% of IX by NMR integration. Distillation from the polymer gave an oil which contained IX (approximately 70%) and unknown aromatic impurities (by NMR analysis). The overall yield of IX was estimated at 6%.

*1-Silaacenaphthene (IX) from III and $HSiCl_3$ (ether solvent).* The following amounts were used: III, 0.52 g (2 mmol) and $HSiCl_3$, 0.20 ml (2 mmol) in 7 ml of ether, Mg, 0.60 g (25 mmol) and 1,2-dibromoethane, 0.10 ml (1.2 mmol) in 5 ml of ether. After refluxing for 20 h, the reaction mixture was cooled to 0°C and an excess of $LiAlH_4$ was added. NMR showed that 17% of IX was present after work-up and chromatography.

This reaction was repeated on the same scale but three equivalents of $HSiCl_3$ (0.60 ml, 6 mmol) was used. From this reaction 37% of IX was obtained as a clear colorless oil after distillation (b.p. 90—95°C at 0.05 Torr). NMR: $\delta$ 2.57 (t, 2 H, $CH_2Si$), 4.75 (t, 2 H, $SiH_2$), 7.20—8.00 ppm (m, 6 H, ArH). Coupling constants: $J(CH_2Si, SiH)$ 3 Hz. IR ($cm^{-1}$, $CDCl_3$): 3000 (C—H), 2130 (Si—H), 1480, 1440 (C=C). Mass spectrum: *m/e* 170 (parent and base peak), 160, 168, 167, 141. Analysis. Found: C, 77.40; H, 6.00. $C_{11}H_{10}Si$ calcd.: C, 77.59; H, 5.92%.

*Attempted generation of VIII.* The following amounts were used: III, 1.00 g (3.9 mmol) in 7 ml of THF, Mg, 0.60 g (25 mmol) and 1,2-dibromoethane, 0.20 ml (1.2 mmol) in 5 ml of THF. After the reaction mixture had refluxed for 20 h, 0.47 ml (3.9 mmol) of dimethyldichlorosilane was added and the reflux continued for 1 h. Following work-up, a white solid was isolated which contained less than 10% of VII and less than 5% of 1-methylnaphthalene by NMR analysis.

Prior to the addition of the dimethyldichlorosilane, a small aliquot was removed and hydrolyzed. GLC analysis showed only solvent and 1-methylnaphthalene which was identified by comparison of its retention time with that of an authentic sample. The peak area of the 1-methylnaphthalene indicated approximately 5% yield by comparison to a standard solution.

*Attempted synthesis of 1,1-dimethyl-1-silaacenaphthene (VII) from IV and n-butyllithium.* In a 3 necked 100 ml round bottomed flask equipped with pressure-equalizing addition funnel and internal thermometer was placed 50 ml of THF and 4.00 ml (6.4 mmol) of n-butyllithium. This solution was cooled to —100°C and a solution of 0.75 g (2.5 mmol) of IV in 20 ml of THF was added slowly enough to keep the n-butyllithium solution at or below —100°C. This addition gave a dark green solution. To this green solution was added 0.30 ml (2.5 mmol) of dimethyldichlorosilane. The solution was allowed to warm slowly to room temperature. The green color discharged to yellow at approximately —40°C. The THF was removed under vacuum and the residue was taken up in ether. This ether solution was washed with NaCl solution, dried ($MgSO_4$), filtered, and the ether removed in vacuo to give a yellow oil. The oil was chromatographed on alumina (activity 3, 6 × 2 cm) with pentane. After removal of the pentane, the residual oil did not contain any VII (absence of benzyl signal at $\delta$ 2.23 ppm).

Repetition of this reaction at —70°C and 0°C also gave no VII. Reversing

the addition order, so that the n-butyllithium was added to the solution of IV at —100°C and —70°C, gave the same results.

*Attempted synthesis of 1-methyl-1-silaacenaphthene (VI) from III and n-butyllithium.* The procedure described for the attempted synthesis of VII from IV and n-butyllithium (Pathway a) was as follows. The following amounts were used: III, 1.00 g (3.9 mmol), n-butyllithium, 5.40 ml (8.6 mmol), and $CH_3SiHCl_2$, 0.40 ml (3.9 mmol).

Addition of the $CH_3SiHCl_2$ immediately discharged the green color. Standard work-up and chromatography gave a light yellow oil which was found to contain predominately 8-(n-butylmethylsilyl)-1-chloromethylnaphthalene. The remainder of the product appeared to be aromatic polymer. NMR: δ 0.47 (d, 3 H, $SiCH_3$), 0.67—1.50 (m, 9 H, butyl protons), 4.96 (m, 1 H, Si-H), 5.30 (s, 2 H, $ArCH_2$), 7.20—8.00 ppm (m, 11 H, ArH).

*Pathway c: Standard method*

*1,1-Dimethyl-1-silaacenaphthene (VII) from XI and $(CH_3)_2SiCl(CH_2Cl)$.* In a 3 necked 100 ml round bottomed flask equipped with pressure-equalizing addition funnel and internal thermometer was placed 2.00 g (6 mmol) of XI and 50 ml of THF. This solution was cooled to —70°C and 3.8 ml (6 mmol) of n-butyllithium was added dropwise to give an orange solution. After 5 minutes at —70°C, 0.8 ml (6 mmol) of dimethylchloromethylchlorosilane was added and the orange color discharged to yellow. The solution was allowed to warm to —40°C, then it was cooled to —90°C. Rapid stirring was necessary to prevent freezing of the solution to the flask walls. With the temperature maintained below —90°C, anonther 3.8 ml (6 mmol) of n-butyllithium was added to give an orange solution. The reaction mixture was warmed slowly to room temperature. After 30 minutes, the reaction was worked-up and purified as described in the previous synthesis of VII (see Pathway a). This procedure gave 0.37 g (31%) of VII.

*1,1,2,2-Tetramethyl-1,2-disilaacenaphthene (XIV) from XI and $(CH_3)_2SiClSiCl(CH_3)_2$ [17].* The following amounts were used: XI, 2.00 g (6 mmol), n-butyllithium, 2 × 3.8 ml (6 mmol) each), and 1,2-dichlorotetramethyldisilane [18], 1.12 g (6 mmol). After the reaction mixture had stood at room temperature for 30 minutes, the THF was removed in vacuo and the residue chromatographed on alumina (activity 1, 6 × 2 cm.) using pentane as elutant. Removal of the solvent gave 1.44 g (99% crude yield) of a white solid. This solid was recrystallized from methanol to give 1.00 g (69%) of XIV (m.p. 89°C) (lit. [17] m.p. 89°C). GLC analysis indicated greater than 99% purity. NMR: δ 0.38 (s, 12 H, $SiCH_3$), 7.26—7.83 ppm (m, 6 H, ArH). IR ($cm^{-1}$, $CDCl_3$): 3030, 2940 (C—H), 1240 ($SiCH_3$), 1475 (C=C). Mass spectrum: *m/e* 242 (parent), 227 (*P* - 15 base peak).

*Pathway b: Standard method*

*1,1-Dimethyl-1-silaacenaphthene (VII) from 1,8-Dilithionaphthalene (XIII).* In a 3 necked round bottomed flask equipped with pressure-equalizing addition funnel and internal thermometer was placed 1.25 g (3.8 mmol) of XI and 30 ml of THF and the solution cooled to —70°C. To this was added 4.70 ml (7.5 mmol) of n-butyllithium dropwise to give an orange solution. After 10 minutes,

0.50 ml (3.8 mmol) of dimethylchloromethylchlorosilane was added to the solution, discharging the color. The reaction mixture was slowly warmed to room temperature and worked up as described in the preparations of VII. A clear oil (0.46 g) was obtained which by NMR contained ~17% of VII (integration of benzyl protons vs. aromatics).

*1,1,2,2-Tetramethyl-1,2-disilaacenaphthene (XIV) from XIII.* The following amounts were used: XI, 1.25 g (3.8 mmol), n-butyllithium, 4.70 ml (7.5 mmol), 1,1,2,2-tetramethyl-1,2-dichlorosilane [18], 0.70 g (3.8 mmol). After work-up and chromatography as described previously, 0.51 g of a clear oil was obtained. This oil contained ~18% of XIV by NMR analysis.

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## References

1 D.N. Roark and L.H. Sommer, J. Amer. Chem. Soc., 95 (1973) 969.
2 R. Ponec, E.A. Chernyshev, N.G. Tolstikova, and V. Chvalovsky, Collect. Czech. Chem. Commun., 41 (1976) 2714.
3 S.V. Soboleva, O.A. D'yachenko, L.O. Atovmyan, N.G. Komalenkova, and E.A. Chernyshev, Izv. Akad. Nauk. SSSR, Ser. Khim., (1974) 2156.
4 I.G. Makarov, V.M. Kazakova, N.G. Tolstikova, and E.A. Chernyshev, Zh. Strukt. Khim., 10 (1969) 595.
5 (a) E.A. Chernyshev and N.G. Tolstikova, Zh. Obshch, Khim., 40 (1970) 1052;
(b) E.A. Chernyshev, N.G. Komalenkova, T.A. Klochkova and T.M. Kuz'mina, ibid., 45 (1975) 2223;
(c) E.A. Chernyshev, N.G. Komalenkova, S.A. Bashkirova, and T.A. Zhavovonkova, ibid., 46 (1976) 1278.
6 J.S. Kiely, L.L. Nelson and P. Boudjouk, J. Org. Chem., 42 (1977) 1480.
7 J.S. Kiely, P. Boudjouk and L.L. Nelson, J. Org. Chem., 42 (1977) 2626.
8 C. Eaborn, D.R.M. Walton, and M. Chan, J. Organometal. Chem., 9 (1967) 251; see also K. Tamao, M. Kumada, and M. Ishikawa, ibid., 31 (1971) 17, and L. Birkofer and W. Weniger, Chem. Ber., 106 (1973) 3595.
9 F.P. Tsui and G. Zon, J. Organometal. Chem., 70 (1974) C3.
10 (a) L.S. Yang and H. Shechter, J. Chem. Soc. Chem. Commun., (1976) 775;
(b) J. Meinwald, D. Dauplaise, F. Wudl, and J.J. Hanser, J. Amer. Chem. Soc., 99 (1977) 255;
(c) J. Meinwald, D. Dauplaise, and J. Clardy, ibid., 99 (1977) 7743.
11 H. Rule and E. Purcell, J. Chem. Soc., (1934) 168.
12 R.L. Gay and C.R. Hauser, J. Amer. Chem. Soc., 89 (1967) 2297.
13 W.E. Parham, L.D. Jones, and Y.A. Sayed, J. Org. Chem., 41 (1976) 1184.
14 H.O. House, D.G. Koepsell, and W.J. Campbell, J. Org. Chem., 37 (1972) 1003.
15 A.E. Bey and D.R. Weyenberg, J. Org. Chem., 31 (1966) 2036. D. Seyferth and S.C. Vick, J. Organometal. Chem., 144 (1978) 1.
16 D.C. Kleinfelter and P.H. Chen., J. Org. Chem., 34 (1969) 1741.
17 E.A. Chernyshev, N.G. Komalenkova, T.A. Klochova, S.A. Shchepinov, and A.M. Mosin, Zh. Obshch. Khim., 41 (1971) 122.
18 H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, Tetrahedron Lett., (1966) 5493.