stirred with a mixture of lithium sulfide (0.75 g, 15 mmol) and chlorotrimethylsilane (3.15 mL, 25 mmol) in dry acetonitrile (25 mL). The progress of the reactions was monitored by IR, and they were complete in 6–8 h. Pure silyl nitronates were obtained after workup and characterized by their ^{1}H NMR and IR spectra.

Silyl nitronate of **6a**: 1.0 g (98%); bp 37 °C (0.8 torr); IR 1635 cm^{-1} ($\nu_{C=N}$); ^{1}H NMR (CDCl$_3$) δ 0.32 (s, 9 H), 1.74 (m, 6 H), 2.5 (dt, 4 H).

Silyl nitronate of **6b**: 0.85 g (77%); bp 46 °C (0.6 torr); IR 1637 cm^{-1} ($\nu_{C=N}$); ^{1}H NMR (CDCl$_3$) δ 0.46 (s, 9 H), 1.62–3.02 (m, 8 H), 4.52 and 5.3 (br d, 1 H).

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. 1a, 143-08-8; **1b**, 112-42-5; **1c**, 108-93-0; **1d**, 5240-73-3; **1e**, 822-67-3; **1f**, 108-95-2; **1g**, 100-51-6; **1h**, 611-69-8; **1i**, 536-60-7; **2a**, 18388-84-6; **2b**, 17957-64-1; **2c**, 13871-89-1; **2d**, 71700-46-4; **2e**, 54725-71-2; **2f**, 1529-17-5; **2g**, 14642-79-6; **2h**, 71700-47-5; **2i**, 71700-48-6; **3a**, 71733-81-8; **3b**, 67124-67-8; **3c**, 71700-49-7; **3d**, 71700-50-0; **3e**, 53172-91-1; **4a**, 120-92-3; **4b**, 108-94-1; **4c**, 110-43-0; **4d**, 98-86-2; **4e**, 529-34-0; **4f**, 2043-61-0; **4g**, 504-02-9; **4h**, 637-88-7; **5a**, 19980-43-9; **5b**, 6651-36-1; **5c**, 19980-26-8; **5c′**, 19980-27-9; **5c″**, 19980-30-4; **5d**, 13735-81-4; **5e**, 38858-72-9; **5f**, 53282-55-6; **5g**, 61543-59-7; **5h**, 59733-55-0; **5h′**, 59733-56-1; **6a**, 1122-60-7; **6b**, 50998-16-8; **7a**, 71700-51-1; **7b**, 71700-52-2; chlorotrimethylsilane, 75-77-4; *tert*-butyldimethylsilyl chloride, 18162-48-6; cinnamyl alcohol, 104-54-1.

Synthesis of New Acenaphthylene Functional Derivatives. 1. 1-(Trimethylsilyl)- and 1,2- and 1,5-Bis(trimethylsilyl)acenaphthylenes and Related Compounds

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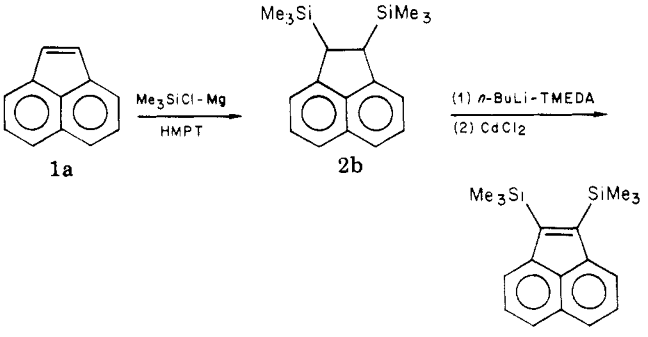
Received August 4, 1978

The title compounds were prepared from acenaphthylene **1a** or acenaphthene **2a** by appropriate silylation reactions followed by oxidation. Of the various reagents used for oxidation, *n*-BuLi–TMEDA–CdCl$_2$ (Harvey's reagent) was found to be the most convenient, as it did not induce partial desilylation. The photoisomerization of 1,3-bis(1-acenaphthylenyl)tetramethyldisiloxane **1g** was also studied.

Within the framework of the utilization of organosilicon compounds for synthetic purposes in organic chemistry,[1] we have earlier reported the varied application of allyl-, vinyl-, and phenylsilanes in the preparation of the functionalized corresponding organic derivatives.[2] We have here focused our interest on the acenaphthylene series because, unlike the acenaphthene series, very few of its functionalized derivatives have been described to date. The work herein involves the synthesis of 1-trimethylsilyl, 1,2- and 1,5-bis(trimethylsilyl)acenaphthylenes, and related compounds. On the basis of the results observed in the silyl benzene series,[3] we believe that these compounds, being newly synthesized via a silylation–desilylation process, can be regarded as convenient precursors of functionalized acenaphthylenes.

Reductive silylation of acenaphthylene **1a** by magnesium in hexamethylphosphortriamide (HMPA) in the presence of trimethylchlorosilane led to the formation of 1,2-bis(trimethylsilyl)acenaphthene (**2b**) in excellent yields.[4] Oxidation of **2b** by Harvey's method[7] gave the desired 1,2-bis(trimethylsilyl)acenaphthylene (**1b**): 1-(trimethylsilyl)acenaphthylene (**1c**) was isolated as a side product (20% yield).[8] When the same oxidation was effected with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) or its corresponding tetrachloro derivative (chloranil),[9] **1c** (contaminated with some **1a**) became the main product.[10]



1a

2b

1b

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(1) See, for instance, E. W. Colvin, *Chem. Soc. Rev.*, 15 (1978).

(2) R. Calas and E. Frainnet, *C. R. Hebd. Seances Acad. Sci., Ser. C* **240**, 203(1955); **243**, 595 (1956); J-P. Pillot, J. Dunoguès, and R. Calas, *Tetrahedron Lett.*, 1871 (1976); G. Dêlêris, J. Dunoguès, and R. Calas, *ibid.*, 2449 (1976); G. Dêlêris, J. Dunoguès, and R. Calas, *J. Organomet. Chem.*, **116**, 645 (1976); J-P. Pillot, J. Dunoguès, and R. Calas, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **278**, 789 (1974); J-P. Pillot, J. Dunoguès, and R. Calas, *Bull. Soc. Chim. Fr.*, 2143 (1975); R. Calas and P. Bourgeois, *J. Organomet. Chem.*, **84**, 165 (1975).

(3) G. Fêlix, J. Dunoguès, F. Pisciotti, and R. Calas, *Angew. Chem., Inter. Ed. Engl.*, **16**, 488 (1977).

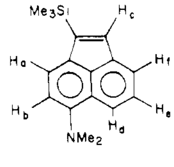
(4) Me$_3$SiCl–Li–THF, a more reactive reagent than Me$_3$SiCl–Mg–HMPT,[5] led to **2b** (21% yield) and polysilylated derivatives resulting from the further reductive silylation of the naphthenic system.[6]

(5) R. Calas and J. Dunoguès, *J. Organomet. Chem. Library*, **2**, 277 (1976).

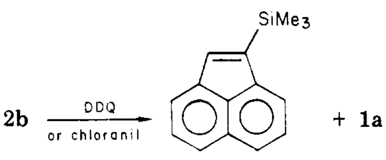
(6) L. Birkofer and N. Ramadan, *Chem. Ber.*, **104**, 138 (1971).

(7) R. G. Harvey and H. Cho, *J. Am. Chem. Soc.*, **96**, 2434 (1974); *J. Org. Chem.*, **40**, 3097 (1976).

(8) In one experiment, the formation of 1-(trimethylsilyl)-6-(dimethylamino)acenaphthylene was observed (20% yield), and the product was isolated and identified (see Experimental Section).

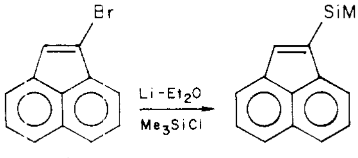


(9) B. Trost, *J. Am. Chem. Soc.*, **89**, 1847 (1967).

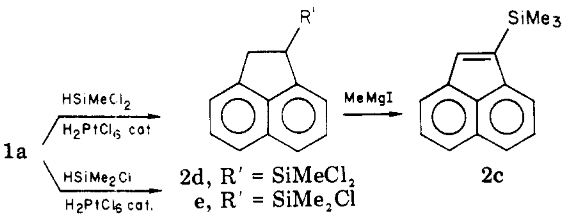


1c (50-60%)

The synthesis of **1c** was also achieved by two other convenient and newly-developed routes. One of these routes consisted of the silylation of 1-bromoacenaphthylene (**1h**) by lithium in diethyl ether in the presence of trimethylchlorosilane; the second involved hydrosilylation of acenaphthylene (**1a**) to the silylacenaphthene followed by oxidation. From **1a**, silylating agents methyldichloro- and dimethylchlorosilane gave the adducts **2d** and **2e**, which were methylated to the trimethylsilyl derivative **2c** in excellent yield (80 and 85% respectively). Treatment of **2c** with *n*-BuLi–TMEDA–CdCl$_2$ as oxidant resulted in a 90% yield of **1c**, whereas treatment with DDQ or chloranil gave maximum yields of only 50%.

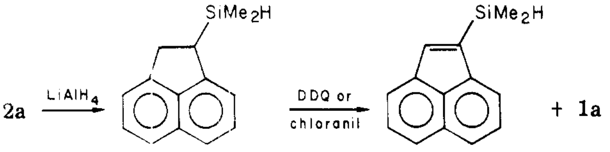


1h 1c (85%)



2d, R' = SiMeCl$_2$
e, R' = SiMe$_2$Cl
2c

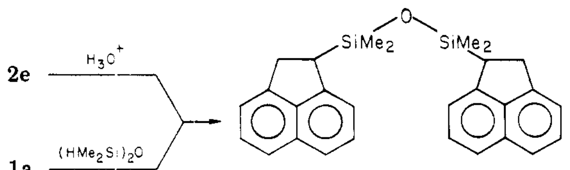
Reduction of the silicon–chlorine bond by lithium aluminum hydride converted **2e** into the silane **2f** (86%). Oxidation of this compound either by DDQ or chloranil afforded 1-(dimethylsilyl)acenaphthylene (**1f**) in moderate yields only (40–50%), because desilylation was found to be a competing side-reaction.



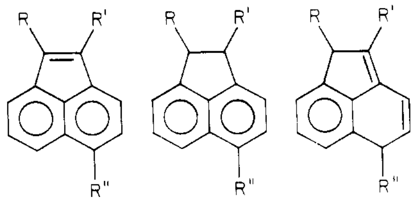
2f 1f

Harvey's reagent could not be used in this case because of the reactivity of *n*-butyllithium toward the Si–H bond.[11]

When hydrolyzed under acidic conditions,[12] the chlorosilane **2e** afforded the siloxane **2g** quantitatively. The same siloxane resulted from the catalyzed hydrosilylation of acenaphthylene (**1a**) in the presence of 1,1,3,3-tetramethyldisiloxane (60–70% yield).



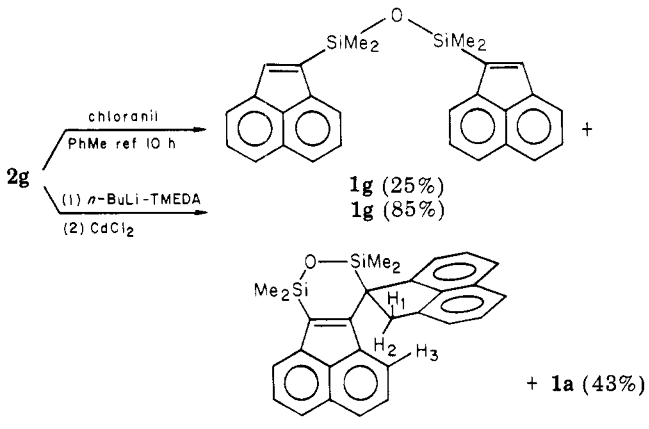
2g



1 2 3

a, R = H; R' = H; R'' = H
b, R = SiMe$_3$; R' = SiMe$_3$; R'' = H
c, R = H; R' = SiMe$_3$; R'' = H
d, R = H; R' = SiMeCl$_2$; R'' = H
e, R = H; R' = SiMe$_2$Cl; R'' = H
f, R = H; R' = SiMe$_2$H; R'' = H
g, R = H; R' = (SiMe$_2$)$_2$O; R'' = H
h, R = Br; R' = H; R'' = H
i, R = SiMe$_3$; R' = H; R'' = SiMe$_3$

Oxidation of **2g** with Harvey's reagent gave the corresponding diacenaphthylenyldisiloxane (**1g**) (85% yield), whereas treatment with DDQ led to partial desilylation (formation of **1a**), and treatment with chloranil led to an unexpected product **4** (30% yield) along with acenaphthylene (**1a**) (43% yield).

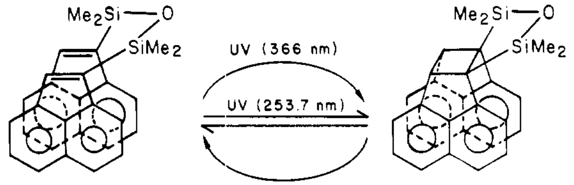


1g (25%)
1g (85%)

4 (30%)

+ 1a (43%)

The photochemical behavior of **1g**, a yellow crystalline solid, proved to be very interesting. Upon irradiation (366 nm) in cyclohexane solution, even in low concentration (10^{-4} m/L), it underwent an intramolecular cyclization leading to the cyclobutane derivative **5**, which regenerated **1g** on warming to its melting point (265 °C). Irradiation of either **1g** or **5** at 253.7 nm for approximately 15 h resulted in a photostationary equilibrium in which **1g** was the predominant product (**1g**–**5** 72:28).



1g 5

The same silylation–oxidation process as in the case of **1b** was utilized to prepare, in excellent yield, 1,5-bis(trimethylsilyl)acenaphthylene (**1i**) from acenaphthylene (**1a**). The quenching of the acenaphthylene dianion[13] with tri-

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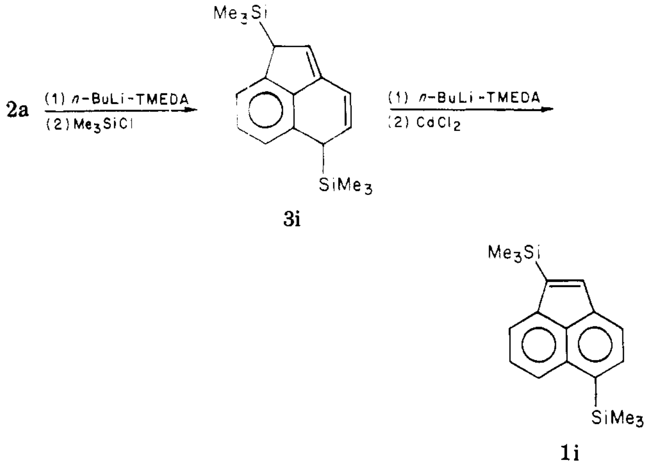
(10) According to Trost,[9] the hydrogen abstraction from silylated acenaphthene led to the phenoxy anion of DDQ or chloranil which easily cleaved the Si–C (aromatic) bond.

(11) See, for instance, H. Gilman and S. P. Massie, *J. Am. Chem. Soc.*, **68**, 1128 (1946), or R. N. Meals, *ibid.*, 1880 (1946).

(12) Careful hydrolysis of **2e** in neutral conditions afforded the corresponding silanol (ν_{OH} 3300).

(13) (a) R. G. Lawler and C. V. Ristagno, *J. Am. Chem. Soc.*, **91**, 1534 (1969); (b) L. D. Kershner, J. M. Gaidis, and H. H. Freedman, *ibid.*, **94**, 935 (1972); (c) C. V. Ristagno and R. G. Laroler, *Tetrahedron Lett.*, 159 (1973); (d) T. S. Cantrell, *ibid.*, 1803 (1973); (e) W. E. Rhine, J. H. David, and G. Study, *J. Organomet. Chem.*, **134**, 139 (1977).



methylchlorosilane gave **3i** quantitatively and was followed by Harvey's oxidation (92% crude; 55% after recrystallization).

1,5-Bis(trimethylsilyl)-1,5-dihydroacenaphthylene (**3i**) was unstable: on standing under nitrogen atmosphere in a carbon tetrachloride solution, it completely decomposed into **2i** (70%), **2c** (15%) and **1i**. The formation of compounds **2i** and **2b** clearly indicated that a 1–5 migration of the proton and silyl group occurred, with the migration of the former being the predominant. Such silyl migrations have already been recognized and reviewed.[14] This silyl migration provided initial proof of a 1–5 migration occurring in a 1,5-disubstituted 1,5-dihydroacenaphthylene.

Conclusion

We have shown the synthesis of various 1-, 1,2-, and 1,5-silylated acenaphthylenes from acenaphthylene by a silylation–oxidation process. Harvey's reagent was found to be the efficient oxidation reagent for silylated acenaphthene derivatives, DDQ and chloranil inducing partial desilylation.

Currently we are investigating the synthesis of functionalized acenaphthylenes via electrophilic substitutions of the silicon moiety. The results are forthcoming in a future publication.

Experimental Section

IR spectra were recorded on a Perkin-Elmer Model 457. NMR spectra were recorded on Perkin-Elmer R-12 and R-24B (60 MHz) and on a Brüker WH-270 (270 MHz).

UV spectra were recorded on a Unicam SP-1800 and mass spectra on an AEI MS 12. All VPC analyses were effected on an Intersmat IGC 15 with SE-30 column (1.5 m, 10% on Chromosorb P).

Preparative high-pressure LC was carried out on a JOBIN-YVON model Chromatospact Prep 10 (reverse phase Lichroprep RP 8). Melting points are not corrected.

Unless otherwise specified, CCl_4 with Me_4Si as internal standard was used for all NMR spectra, and results are given in δ. Wavelengths of maximum absorbance of UV spectra are reported in nanometers followed by the logarithm of the extinction coefficient in parentheses.

New compounds **1b**, **1c**, **1f**, **1g**, **2b**, **2c**, **2f**, **2g**, and **2i** gave satisfactory elemental analyses which were submitted for review. Unstable products **2e**, **2d**, **3i**, and **6** as well as **4** were all identified by means of physicochemical data.

Synthesis of 1,2-Bis(trimethylsilyl)acenaphthene (2b). **1a** (5.4 g, 0.05 mol) dissolved in HMPA (40 mL) was added dropwise over 1.5 h to a stirred suspension of Mg (1.6 g, 0.05 mol + excess) in Me_3SiCl (18 g, 0.1 mol + excess) and HMPA (100 mL) and maintained at 80 °C under nitrogen. The reaction mixture was heated for 3 h after completion of addition and then cooled. This was followed by acid hydrolysis at 0 °C, extraction with ether (3 × 50 mL), washing and neutralization of the ethereal layer, drying over $MgSO_4$, and removal of ether in vacuo, leaving product **2b**. Recrystallization from ethanol gave white crystals, mp 115 °C, in 81% global yield (crops of 10.6 g and 1.4 g): NMR δ 0.1 (s, 18 H, 2 $SiMe_3$), 2.84 (s, 2 H, 2 CHSi), 6.78–7.37 (m, 6 H, aromatic), including peaks at 7.03, 7.16, 7.21, and 7.25.

Oxidation of 1,2-Bis(trimethylsilyl)acenaphthene (2b). (i) With DDQ. **2b** (1 g) was dissolved in benzene (20 mL), DDQ (1.6 g, 2 molar equiv) added, and the solution refluxed for 20 h. The benzene was removed, and the crude product was eluted with cyclohexane through a Merck 50 silica gel column (70–230 mesh ASTM, activity 2–3, pH 7). Products **1a**–**1c** (1/1) were quantitatively isolated by high-pressure LC (H_2O–MeOH 80:20 as eluant, packing pressure = 10 bars, elution rate = 20 mL/min). Repetition under identical conditions yielded **1a** and **1c** weight ratios between 40:60 and 50:50.

(ii) With Chloranil. **2b** (1 g) and chloranil (1.7 g, 2 molar equiv) were refluxed in toluene (20 mL) for 20 h. Once cooled, the reaction mixture was treated as in the case of DDQ. **1a** (15%) and **1c** (35%) were obtained, and 50% of **2b** was recovered.

1c: IR $\nu_{C=C}$ 1620 cm^{-1}; NMR (C_6H_{12} 1.44 ppm as internal standard), δ 0.42 (s, 9 H, 1 $SiMe_3$), 7.14 (s, 1 H, ethylenic H), 7.28–7.74 (m, 6 H, aromatic H); UV 5.98 × 10^{-5} mol L^{-1} in cyclohexane, 232.5 (4.51), and 329 (3.95).

(iii) Harvey's Method. A mixture of **2b** (6 g, 0.02 mol) and 50 mL of 1.6 N *n*-BuLi[22] (0.08 mol) in TMEDA (50 mL) (treated overnight by refluxing with KOH pellets and distilled before use) was refluxed for 2 h in cyclohexane (120 mL). After the solution was cooled, $CdCl_2$ (8 g) was added to the well-stirred mixture (reaction time 0.5 h). After hydrolysis at pH 4 and ether extraction, the ethereal layer was treated identically as in the synthesis of **2b**, yielding 5.8 g of crude product. Elution on a Merck silica gel solumn resulted in a product mixture of **1b**–**1c** 80:20. Recrystallization from ethanol gave 3.3 g of **1b** as yellow crystals: mp 90 °C; 55% yield; NMR (in agreement with that of acenaphthylene[15]) δ 0.50 (s, 18 H, 2 $SiMe_3$), 7.28–7.90 (m, 6 H, aromatic).

One attempt from **2b** (12 g) provided 12.1 g of crude product, giving **1b** (7.5 g). A final wash of the silica gel column with Et_2O gave 3.3 g of another product. After a second elution with 250 mL of C_6H_{12}–$CHCl_3$ 1:1, a red oil was obtained corresponding to the practically pure **6** (2.7 g, 25% yield). A third elution (C_6H_{12}–$CHCl_3$ 70:30) afforded 1.2 g of very pure **6** (one spot by TLC), identified by mass spectrometry: *m/e* 267 (M), 252 (M – 15), 195 (M – 72), 73 (Me_3Si), and 44 (NMe_2): IR 2780 (NMe_2), 1603 cm^{-1} (C=C), besides bands characteristic of the Me_3Si group (1255, 840, and 755 cm^{-1}); NMR (in C_6H_{12}, 1.44 ppm) δ 0.41 (s, 9 H, 1 $SiMe_3$), 2.82 (s, 6 H, NMe_2), 6.58 (2 peaks, H_a, part A of an AB spectrum, $J_{a,b}$ = 6.7 Hz), 7.04 (s, H_c), 7.39 (center of a multiplet, 3 H, H_d, H_e, H_f), 7.88 (4 peaks, H_b, part B of an AB spectrum whose peaks are split by long-range coupling, J = 1.5 Hz); UV 7.49 × 10^{-5} mol L^{-1} in cyclohexane, 242 (4.39), 327.8 (3.97), 364 (3.90).

Synthesis of 1,5-Bis(trimethylsilyl)-1,5-dihydroacenaphthylene (3i). By refluxing (2 h) **2a** (4.5 g, 0.03 mol), *n*-BuLi (50 mL, 1.6 N in hexane, 0.08 mol), and TMEDA (80 mL) in cyclohexane (120 mL), we obtained the acenaphthylene dianion. Further condensation of Me_3SiCl (10 mL) and stirring for 0.5 h at 20 °C afforded unstable yellowish-white crystals in quantitative yield: NMR (comparable with that of 1,5-dideuterioacenaphthylene[14c]) δ 0 (m, 18 H, 2 $SiMe_3$[16]), 3.3 (m, 2 H, 2 CHSi), 5.80 (m, 2 H, H_2 and H_4), 6.35 (m, 1 H, H_3), 6.55–7.15 (m, 3 H, aromatic).

Elution of **3i** with cyclohexane on a silica gel column provided a mixture of **2i** (30%) and **2c** (70%). When **3i** was left for 72 h in CCl_4 solution (10% w/v) it decomposed completely, giving **2i** (70%), **2c** (15%), **2b** (5%), and **1i** (5%). All of these products were identified by comparison with authentic samples. **2i** was identified by NMR spectrometry: δ 0.02 (s, 9 H, $C_{sp^3}SiMe_3$), 0.46

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(14) A. G. Brook and A. Bassindale, *Mol. Rearrangements*, submitted.

(15) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **91**, 1534 (1969).

(16) The multiplet of $SiMe_3$ was, in fact, several singlets, indicating the presence of isomers *E* and *Z*.

(s, 9 H, $C_{Ar}SiMe_3$), 2.82 (m, 1 H, $C_{Ar}CHSi$), 3.31–3.54 (m, 2 H, $C_{Ar}CH_2C$, ABC spectrum), 6.90–7.85 (m, 5 H, aromatic, AB + ABC spectrum).

Synthesis of 1,5-Bis(trimethylsilyl)acenaphthylene (1i). **3i** (6 g, 0.02 mol) was converted to **1i** (6.3 g of crude product) by Harvey's method[7] (see the oxidation of **2b**). Elution of the crude product on a silica gel column with 500 mL of cyclohexane led to 5.4 g (92%) of yellow crystals. Recrystallization from ethanol afforded in the first crop 3.2 g (55%) of **1i**: mp 128 °C; NMR δ 0.38 (s, 9 H, $SiMe_3$ in position 1), 0.47 (s, 9 H, $SiMe_3$ in position 5), 7.00 (s, 1 H, ethylenic H), 7.16–7.87 (m, 5 H, aromatic, an ABC spectrum containing signals at 7.17, 7.28, 7.38, 7.40, 7.44, and 7.56 and an AB spectrum giving signals centered at 7.70 and 7.82); UV 5.06×10^{-5} mol L^{-1} in cyclohexane, 236.5 (4.46), and 331 (4.05).

Hydrosilylation of Acenaphthylene (1a). A solution of **1a** (6.1 g, 0.04 mol) in benzene was added dropwise, under nitrogen atmosphere, to refluxing $MeSiHCl_2$ or Me_2SiHCl (6–8 g, excess) containing chloroplatinic acid (~50 mg), giving an exothermic reaction. The mixture was refluxed another 2 h to chase the remaining silane and then refluxed 12 h more after addition of an excess of MeMgI in Et_2O. After the mixture was cooled it was hydrolyzed in acidic medium and extracted with Et_2O; the ethereal layer was washed, neutralized, and dried with $MgSO_4$. After removal of Et_2O, **2c** was obtained (80% yield from $HSiMeCl_2$ and 85% from HSiMeCl): NMR δ 0 (s, 9 H, $SiMe_3$), 2.8–3.8 (m, ABC spectrum, 3 H, $-CH_2CH-$), 6.86–7.53 (m, 6 H, aromatic), the ABC spectrum being similar to that of 9-(trimethylsilyl)-9,10-dihydrophenanthrene;[17] UV 7.96×10^{-5} mol L^{-1} in cyclohexane, 2.35 (4.47), and 297 (3.97).

Synthesis of 1-(Dimethylsilyl)acenaphthene (2f). The product resulting from hydrosilylation of **1a** with $HSiMe_2Cl$ could be converted into **2f** by reduction of the mixture (after removing unreacted $HSiMe_2Cl$) with $LiAlH_4$ (1 g, excess) in Et_2O (50 mL) and refluxing the solution for 12 h. Hydrolysis (with caution) of the medium by a cold, saturated solution of NH_4Cl followed by standard workup provided **2f** (7.2 g, 86%): IR ν_{SiH} 2130 cm^{-1}; NMR δ −0.02 and 0 (d, J = 2.5 Hz, 6 H, $SiMe_2$), 2.76–3.80 (m, 3 H, ABC spectrum, $-CH_2CH-$), 4.04 (m, 1 H, SiH), 6.80–7.53 (m, 6 H, aromatic).

Synthesis of 1,3-Bis(1-acenaphthenyl)tetramethyldisiloxane (2g). The product resulting from hydrosilylation of **1a** with $HSiMe_2Cl$ (after removal of the unreacted hydrosilane), hydrolyzed in homogeneous acidic medium (acetone), afforded **2g**. It was isolated after neutralization, removal of H_2O, acetone, and benzene, treatment with H_2O (pH 7), ether extraction, washing of the ethereal layer, drying ($MgSO_4$), and finally evaporation. **2g** was recrystallized from ethanol: mp 90 °C; 95% yield. **2g** was also synthesized from **1a** and $HMe_2SiOSiMe_2H$ under the conditions described with $HSiMe_2Cl$ (60–70% yields). **2g** is a mixture of two diastereoisomers (two identical asymmetric carbons): IR $\nu_{(SiOSi)}$ 1060 cm^{-1}; NMR δ −0.3 (s, 6 H, 2 SiMe), −0.15 (s, 3 H, 1 SiMe), −0.1 (s, 3 H, 1 SiMe), 2.5–3.4 (m, ABC spectrum, 6 H, 2 $-CH_2CH-$), 6.7–7.5 (m, 12 H, aromatic).

Oxidation of Acenaphthene Monosilyl Derivatives. Oxidation of **2c**, **2f**, and **2g** with DDQ or chloranil, as described for **2b**, led to compounds given in the body of the paper. An attempt with DDQ–refluxing PhMe (instead of C_6H_6) permitted the conversion of **2g** into **1g** (60%) and **1a** (14%).

1f was identified by IR ($\nu_{(SiH)}$ 2130 cm^{-1}, $\nu_{(C=C)}$ 1630 cm^{-1} and $C_{sp^2}H$ absorption at 957 cm^{-1}) and NMR (δ 0.45 (d, J = 4.0 Hz, 6 H, $SiMe_2$), 4.65 (septet, 1 H, SiH), 7.18 (s, 1 H, ethylenic), 7.28–7.78 (m, 6 H, aromatic)).

1g: IR $\nu_{(C=C)}$ 1630 cm^{-1}, $\nu_{(SiOSi)}$ 1060 cm^{-1} and $C_{sp^2}H$ absorption at 940 cm^{-1}; NMR δ 0.48 (s, 12 H, 2 $SiMe_2$), 7.14 (s, 2 H, ethylenic), 7.27–7.75 (m, 12 H, aromatic); UV 1.61×10^{-5} mol L^{-1} in cyclohexane, 233 (4.72), and 326 (4.18).

4: IR $\nu_{(SiOSi)}$ 980 cm^{-1}, $\nu_{(C=C)}$ 1620 cm^{-1}; NMR[18] δ −0.20, 0.22, 0.51, and 0.62 (all s, 3 H each, SiMe), 3.87 (AB spectrum, 2 H, $-CH_1H_2-$ of acenaphthene group, $J_{1,2} \simeq 18$ Hz).[19]

Oxidation of **2c** and **2g** by Harvey's method was carried out as described before (see the synthesis of **1b**). In the case of **2g**, it was necessary to use exactly 4 mol of *n*-BuLi for 1 mol of **2g** in order to avoid any cleavage of the Si–O bond.

Silylation of 1-Bromoacenaphthylene. 1-Bromoacenaphthylene[21] (2.3 g, 0.01 mol), anhydrous ether (30 mL), Me_3SiCl (1.5 g, 0.014 mol), and finely-divided lithium (0.02 mol) were refluxed for 50 h. Further treatment as previously described (hydrolysis, extraction, ...) afforded **1c** (1.9 g, ~85%) after evaporation, and it was purified by high-pressure LC as indicated before.

Intramolecular Cyclization of 1,3-Bis(1-acenaphthylenyl)tetramethyldisiloxane (1g). **1g** (0.5 g) dissolved in cyclohexane (150 mL, concentration = 7.68×10^{-3} mol L^{-1}) after deoxygenation was irradiated for 5 h while being stirred with an HPLN (400 W) Philips Lamp minus its external jacket and maintained cool by an air blower. The cyclohexane was removed and the crude **5** washed with ethanol and recrystallized from the same, mp 262–264 °C. Similar results were obtained with concentrations between 10^{-2} and 10^{-4} mol L^{-1}. A highly concentrated solution of **3i** was converted into **5** after several hours of exposure to daylight.

Ring Opening of Photoisomer (5). (a) **5** (100 mg) was warmed at 265 °C in a vacuum-sealed tube and converted quantitatively into **3i**. (b) **5** (100 mg) dissolved in cyclohexane (50 mL) was degassed with a N_2 stream and irradiated for 15 h with a Rayonnet (λ 2537 (and 1849) Å). Quantitative analysis of the final mixture by NMR spectrometry revealed the presence of **3i** (72%) and **5** (28%). **5**: NMR ($CDCl_3$ as solvent, Me_4Si as internal standard) δ 0.33 (s, 6 H, $SiMe_2$), 0.45 (s, 6 H, $SiMe_2$), 4.94 (s, 2 H, –CH–), 6.8–7.4 (m, 12 H, aromatic); IR (2 mg/200 mg of KBr) $\nu_{(SiC)}$ 1245 and $\nu_{(SiSi)}$ 940 cm^{-1}; UV 2.53×10^{-5} mol L^{-1} in cyclohexane, 222 (4.66), and 302 (3.97).

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Registry No. **1a**, 208-96-8; **1b**, 71582-66-6; **1c**, 71582-67-7; **1f**, 71582-68-8; **1g**, 71606-73-0; **1i**, 71582-69-9; **2a**, 83-32-9; **2b**, 71582-70-2; **2c**, 71582-71-3; **2d**, 71582-72-4; **2e**, 71582-73-5; **2f**, 71582-74-6; **2g** isomer 1, 71606-74-1; **2g** isomer 2, 71606-75-2; **2i**, 71582-75-7; **3i**, 71582-76-8; **4**, 71582-77-9; **5**, 71582-78-0; **6**, 71582-79-1; Me_3SiCl, 75-77-4; $HSiMe_2Cl$, 1066-35-9; $HMe_2SiOSiMe_2H$, 3277-26-7; 1-bromoacenaphthalene, 54736-49-1.

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(17) R. G. Harvey and P. P. Fu, *J. Org. Chem.*, 41, 3722 (1976).

(18) A deep yellow product suggested the presence of substituted acenaphthylene, but the characteristic sharp singlet at δ ~7.00 was not seen. H_3 gave rise to two peaks centered at δ 6.4, $J_{3,4}$ = 7 Hz, the shift being due to the protons position in the shielding cone of the acenaphthene ring.

(19) This result corresponds well with the value given by Sternhell et al.[20] for similar geminal coupling in 1-substituted acenaphthenes: $17.10 < J_{1,2} < 19.08$ Hz.

(20) C. K. Fay, J. G. Grutzner, L. F. Johnson, S. Sternhell, and P. M. Westerman, *J. Org. Chem.*, **38**, 3122 (1973).

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(22) The *n*-BuLi was titrated according to the work of Watson and Eastham: S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967).