Synthetic Methods and Reactions. 71.[1] Chlorotrimethylsilane/- and *tert*-Butyldimethylsilyl Chloride/Lithium Sulfide, Mild and Efficient Silylating Reagents

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Received April 30, 1979

A mixture of chlorotrimethylsilane/lithium sulfide (sodium sulfide) is found to be a remarkably powerful silylating agent. Silylation of alcohols can be carried out at room temperature under essentially neutral conditions to afford quantitative yields of silyl ethers. This reagent has also been utilized in the preparation of related *tert*-butyl dimethylsilyl ethers. Nitrocyclohexanes give silyl nitronates under the reaction conditions. Carbonyl compounds can be transformed into silyl enol ethers in the presence of triethylamine.

The trimethylsilyl group is extensively used for the protection of alcohols, carbonyls, and nitro compounds in organic syntheses.[2] A number of methods have been developed for the silylation of these functionalities involving various reagents such as chlorotrimethylsilane and base,[3-6] hexamethyldisilazane–chlorotrimethylsilane–pyridine,[3] hexamethyldisilazane and imidazole,[7] ethyl trimethylsilylacetate–tetra-*n*-butylammonium fluoride (ETSA–TBAF),[8] trimethylsilyl trifluoromethanesulfonate,[9,10] bis(trimethylsilyl)acetamide,[11] and hexamethyldisiloxane in the presence of acid.[12] In some of these methods the reaction takes place only in basic media and often involves forceful conditions,[3] particularly in the silylation of carbonyl compounds, thus rendering the method unsuitable for base- and/or heat-sensitive compounds.[7] Some of these reagents are also expensive, and thus their application is limited. In order to circumvent these problems, we have explored a new approach to perform trimethylsilylations.

Chlorotrimethylsilane in the presence of lithium sulfide acted as an extremely powerful silylating agent. It formed alkoxytrimethylsilanes in excellent yields from alcohols at room temperature. The method is applicable to the preparation of alkoxy-*tert*-butyldimethylsilanes (TBDMS) as well. Silylation of carbonyl compounds took place equally readily in the presence of an equivalent amount of triethylamine. The preparation of silyl nitronates from the corresponding nitro compounds was also studied. Secondary nitro compounds, such as nitrocyclohexanes, afforded high yields of the silyl nitronates, but primary nitro compounds, due to prevalent side reactions, gave only complex mixtures of products.

Silylation of alcohols took place very smoothly at ambient temperature when a mixture of alcohol, chlorotrimethylsilane, and lithium sulfide (in a 2:5:2 molar ratio) in dry acetonitrile was stirred overnight (eq 1). Yields

$$\underset{\mathbf{1a-i}}{2\mathrm{ROH}} + 2\mathrm{ClSiMe_3} + \mathrm{Li_2S} \xrightarrow{\mathrm{CH_3CN}} \underset{\mathbf{2a-i}}{2\mathrm{ROSiMe_3}} + 2\mathrm{LiCl} + \mathrm{H_2S} \quad (1)$$

were generally high, and the method provided an extremely mild, simple, and inexpensive way of trimethylsilylation under weakly acidic conditions. In addition, the method is general and, as summarized in Table I, equally applicable to primary, secondary, and tertiary alcohols, including sterically hindered alcohols whose silylations necessitate drastic conditions under conventional methods.[3]

Although the mechanism of the $ClSi(CH_3)_3/Li_2S$ silylations is not clear, the sulfide might complex with chlorotrimethylsilane, resulting in in situ formation of a hexamethyldisilathiane equivalent, which would be responsible for the remarkable silylating power of the reagent.[13] It has been reported[13] that hexamethyldisilathiane is a convenient silylating agent for primary alcohols. However, the reaction proceeded much slower in the case of secondary alcohols, and tertiary alcohols were rather inert even at reflux temperatures for several hours; e.g., *tert*-butyl alcohol gave the corresponding alkoxysilane only after heating under reflux for 400 h. In contrast, trimethylsilylation took place readily in all cases with $ClSi(CH_3)_3/Li_2S$ reagent, suggesting the mediation of sulfide ion in the reactions.[14] It should be mentioned here that a somewhat related silylating agent, (thiophenyl)triethylsilane, has been used in the preparation of some enol silyl ethers, but the reaction involved rather drastic conditions and was applicable only to easily enolizable ketones.[15]

We also extended our studies to the preparation of the extensively used *tert*-butyldimethylsilyl (TBDMS) compounds[16-18] (eq 2). The generally used procedure for the

$$\underset{\mathbf{1a-e}}{\mathrm{ROH}} \xrightarrow[25\ ^\circ\mathrm{C}]{t\text{-}\mathrm{BuMe_2SiCl/Li_2S}} \underset{\mathbf{3a-e}}{\mathrm{ROSiMe_2}\text{-}t\text{-}\mathrm{Bu}} \quad (2)$$

(1) For part 70 in the series, see: Olah, G. A.; Arvanaghi, M.; Vankar, Y. D., submitted for publication in *Synthesis*.
(2) Reese, C. B. *Prot. Groups Org. Chem.* **1973**, 95–143. Also see: Colvin, E. W. *Q. Rev., Chem. Soc.* **1978**, *7*, 15–64.
(3) Langer, S. H.; Connell, S.; Wender, J. *J. Org. Chem.* **1958**, *23*, 50–8 and references cited therein.
(4) House, H. O.; Czuba, L. J.; Gall, M.; Olmstend, H. D. *J. Org. Chem.* **1969**, *34*, 2324–36.
(5) Torkelson, S.; Ainsworth, C. *Synthesis* **1977**, 431–2.
(6) Colvin, E. W.; Seebach, D. *J. Chem. Soc., Chem. Commun.* **1978**, 689–91.
(7) Torkelson, S.; Ainsworth, C. *Synthesis* **1976**, 722–4 and references cited therein.
(8) Nakamura, E.; Murotushi, T.; Shimizu, M.; Kuwajima, I. *J. Am. Chem. Soc.* **1976**, *98*, 2346–8.
(9) Simchen, G.; Kober, W. *Synthesis* **1976**, 259–61.
(10) A similar reagent has recently been generated in situ: Vorbruggen, H.; Krolikiewicz, K. *Synthesis* **1979**, 34–5.
(11) Kashutina, M. V.; Ioffe, S. L.; Tartakovskii, V. A. *Dokl. Akad. Nauk SSSR* **1974**, *218*, 109–12.
(12) Pinnick, H. W.; Bal, B. S.; Lajis, N. N., *Tetrahedron Lett.* **1978**, 4261–2.
(13) Although hexamethyldisilathiane can be prepared from sodium sulfide and chlorotrimethylsilane at high temperatures (~250 °C) in pressure reactors, there is almost no reaction between lithium sulfide and chlorotrimethylsilane at room temperature and atmospheric pressure. See: Abel, E. W. *J. Chem. Soc.* **1961**, 4933–5. For other methods of preparation see: Harpp, D. M.; Steliou, K. *Synthesis* **1976**, 721–2.
(14) We have previously observed iodide-ion catalysis in the cleavage of ethers and the conversions of alcohols to iodides and sulfoxides to sulfides using chlorotrimethylsilane/sodium iodide reagent. Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *Synthesis* **1979**, 61–2. Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.
(15) Ojima, I.; Nagai, Y. *J. Organomet. Chem.* **1973**, *57*, C42–4.

0022-3263/79/1944-4272$01.00/0

Table I. Preparation of Trimethylsilyl Ethers (See Eq 1)

substrate (1)	yield (2),[a] %	bp, °C (pressure, torr) obsd	bp, °C (pressure, torr) lit.	^{1}H NMR ($CDCl_3$), δ[e]
a, 1-nonanol	95	83-84 (3.5)	228.1-228.9 (744)[b]	
b, 1-undecanol	70[c]	107-108 (3.5)	190.6-191.6 (102)[b]	
c, cyclohexanol	90	58-60 (12)		3.8 (br, 1 H), 1.75 (m, 10 H), 0.41 (s, 9 H)
d, 2-methyl-2-norbornanol	95	57 (3.7)		2.36 (m, 2 H), 1.6 (m, 8 H), 1.58 (s, 3 H), 0.43 (s, 9 H)
e, 2-cyclohexen-1-ol	75	140 (760)		5.95 (d, 2 H), 4.67 (m, 1 H), 2.20 (m, 6 H), 0.31 (s, 9 H)
f, phenol	95	72 (14)	181.9-182.4 (742)[b]	
g, benzyl alcohol	95	103 (35)	92 (19)[d]	
h, phenyl isopropyl carbinol	95	74-77 (3.5)		7.16 (s, 5 H), 4.30 (d, 1 H), 1.88 (sep 1 H), 1.00 d (3 H), 0.83 (d, 3 H), 0.10 (s, 9 H)
i, cumyl alcohol	76[c]	73 (4.5)		7.38 (m, 5 H), 1.77 (s, 6 H), 0.33 (s, 9 H).

[a] Yield of pure distilled product. [b] See ref 3. [c] The unreacted starting material was recovered by column chromatography. [d] Gerrard, W.; Kilburn, K. D. *J. Chem. Soc.* **1956**, 1536. [e] Me_4Si used as the eternal standard.

Table II. Preparation of *tert*-Butyldimethylsilyl Ethers (See Eq 2)

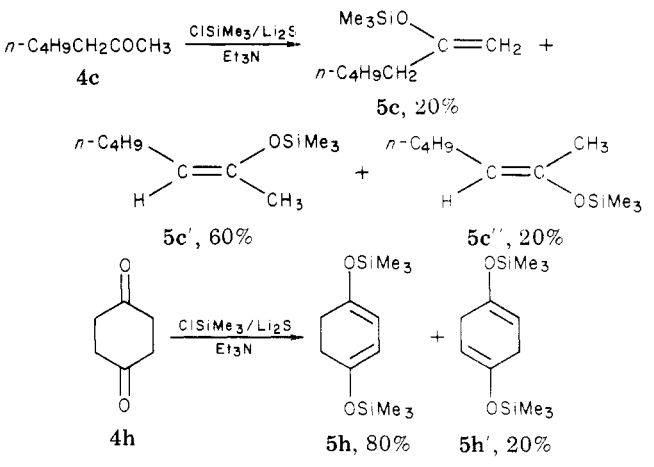
substrate (1)	yield (3),[a] %	bp, °C (torr)	^{1}H NMR ($CDCl_3$), δ[b]
a, 1-nonanol	95	71 (0.2)	3.75 (t, 2 H), 1.52 (m, 17 H), 1.2 (s, 9 H), 0.30 (s, 9 H)
b, cyclohexanol	90	57-58 (0.4)	3.90 (m, 1 H), 1.82 (m, 10 H), 1.26 (s, 9 H), 0.37 (s, 9 H)
c, 2-methyl-2-norbornanol	75	45-47 (0.2)	2.44 (m, 2 H), 1.74 (m, 8 H), 1.58 (s, 3 H), 1.22 (s, 9 H), 0.40 (s, 6 H)
d, cinnamyl alcohol	88	90-92 (0.3)	7.34 (br s, 5 H), 6.57 (s, 1 H), 6.42 (t, 1 H), 4.50 (d, 2 H), 1.29 (s, 9 H), 0.39 (s, 6 H)
e, benzyl alcohol	80	58-60 (0.2)	7.30 (s, 5 H), 4.82 (s, 2 H), 1.20 (s 9 H), 0.30 (s, 6 H)

[a] Isolated yield of pure distilled product. [b] Me_4Si used as the external standard.

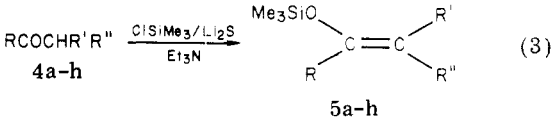
preparation of TBDMS ethers involved treatment of alcohols with *tert*-butyldimethylsilyl chloride in the presence of imidazole in dimethylformamide solution. The silylation of tertiary alcohols was, however, sluggish under these conditions.[17]

The silylation of alcohols with *tert*-butyldimethylsilyl chloride/lithium sulfide in acetonitrile occurred more readily than with chlorotrimethylsilane. The reaction was complete in 5–8 h in all the cases studied (**1a–e**). The results are summarized in Table II. The generality of the method is indicated as even a tertiary alcohol (**1c**) gave a high yield of the TBDMS ether. Another aspect of the method is that the reaction is carried out under nonbasic conditions and thus can serve as the only known safe procedure for the preparation of TBDMS ethers of base-sensitive compounds. The recently introduced silyl perchlorates should be handled with great care as they are highly sensitive and particularly explosive compounds.[17]

Scheme I



The silylation of aldehydes and ketones was also brought about very readily by using chlorotrimethylsilane/lithium sulfide in the presence of an equimolar amount of triethylamine (eq 3). Results are summarized in Table III.



(3)

Although in most cases the reaction proceeded at room temperature to give excellent yields, in some cases (**4c–e**) the yields were poor at room temperature. In these cases heating under reflux for several hours afforded satisfactory yields of the products. From all reactions, any unreacted starting material could readily be recovered. The deprotonation of carbonyl compounds occurred with thermodynamic control, giving product mixtures in which the more stable isomers predominated. Scheme I shows the product compositions of the (vinyloxy)silanes formed in the reactions of 2-heptanone (**4c**) and 1,4-cyclohexanedione (**4h**), as determined by the integration of appropriate peaks in the ^{1}H NMR spectra.

Whereas 1,4-cyclohexanedione (**4h**) gave high yields of bis enol silyl ethers **5h** and **5h'** even at room temperature, 1,3-cyclohexanedione (**4g**) gave, as with all known methods,[5,7] only the mono enol silyl ether. Attempts to prepare the bis enol silyl ethers by varying the reaction conditions were unsuccessful.

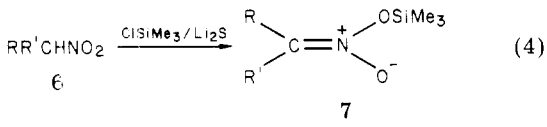
(16) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190–1.
(17) Barton, T. J.; Tully, C. R. *J. Org. Chem.* **1978**, *43*, 3649–53.
(18) Chaudhary, S. K.; Hernandez, O., *Tetrahedron Lett.* **1979**, 99–102.

Table III. Preparation of Enol Silyl Ethers (See Eq 3)

substrate (4)	reaction conditions: temp, °C	reaction conditions: time, h	yield (5),[a] %	bp, °C (pressure, torr): obsd	bp, °C (pressure, torr): lit.	^{1}H NMR ($CDCl_3$), δ[e]
a, cyclopentanone	25	16	95	70-71 (12)	74 (12)[b]	
b, cyclohexanone	25	16	95	74-75 (20)	74-75 (20)[b]	
c, 2-heptanone	81	16	68	78-79 (15)	94-95 (52)[b]	
d, acetophenone	81	16	60	88-90 (12)	89-91 (12)[b]	
e, α-tetralone	81	16	75	111 (4.5)		7.3 (m, 4 H), 5.35 (t, 1 H), 3.0 (m, 4 H), 0.61 (s, 9 H)
f, cyclohexanecarboxaldehyde	25	16	95	85 (15)		6.2 (m, 1 H), 2.35 (m, 4 H), 1.82 (m, 6 H), 0.51 (s, 9 H)
g, 1,3-cyclohexanedione	25	80	85[c]	80-81 (0.4)	83-85 (1)[c]	
h, 1,4-cyclohexanedione	25	16	95[d]	98 (3.6)	93-95 (2)[d]	

[a] Isolated yield of pure distilled product. [b] See ref 4. [c] Only mono enol silyl ether was isolated. See ref 7. [d] Only bis enol silyl ether was obtained. See ref 5. [e] Me_4Si used as the external standard.

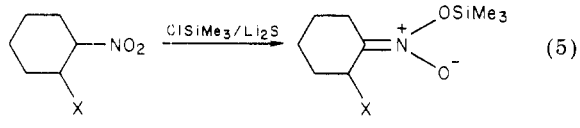
We have also studied the silylation of nitro compounds (6) with the chlorotrimethylsilane/lithium sulfide reagent to obtain silyl nitronates (7) (eq 4). Attempts to prepare



(4)

6 7

silyl nitronates from nitromethane, nitropentane, and cyclohexylnitromethane, all of which are primary nitro compounds, however, resulted in a complicated mixture of products, due to prevalent side reactions.[11,19] On the other hand, secondary nitrocyclohexanes (**6a,b**) gave high yields of the nitronate esters (**7a,b**) when reacted with chlorotrimethylsilane/lithium sulfide reagent at room temperature (eq 5).



(5)

6a, X = H
b, X = F

7a, X = H
b, X = F

These silylation reactions could also be carried out in the presence of sodium sulfide; however, the reaction proceeded less rapidly, presumably due to the lower solubility of sodium sulfide in acetonitrile. Our attempts to prepare azides or cyanides starting from alcohols by using $ClSiMe_3/NaN_3$ or $ClSiMe_3/NaCN$, respectively, in refluxing dimethylformanide also resulted only in the formation of silyl ethers.

In view of the wide applicability of silyl protective groups in organic syntheses, the present lithium sulfide mediated, mild, and nonbasic method should find useful application.

Experimental Section

Materials. All starting materials were commercially available, in generally 98% or higher purity, and were used without purification. Lithium sulfide was obtained from Alfa Ventron. 1-Nitro-2-fluorocyclohexane was prepared by the nitrofluorination of cyclohexene.[20] Acetonitrile was purified and stored over molecular sieves.

Infrared and ^{1}H NMR spectra were obtained on Perkin-Elmer Model 297 and Varian Associates Model EM360L spectrometers, respectively. Tetramethylsilane was used as an external standard. Thin-layer chromatography was carried out on silica gel plates with hexane as an eluent.

General Procedure for Silylation of Alcohols with Chlorotrimethylsilane/Lithium Sulfide. To a well-stirred suspension of lithium sulfide (0.92 g, 20 mmol) in dry acetonitrile (25 mL) was added freshly distilled chlorotrimethylsilane (6.3 mL, 50 mmol) under a nitrogen atmosphere. To this mixture was then added a solution of the corresponding alcohol (20 mmol) in acetonitrile (15 mL), and the stirring was continued until the completion of the reaction, during which time the color of the solution generally changed from colorless to green. The progress of the reaction was monitored by TLC at regular intervals. Soon after the completion of the reaction, the mixture was taken up in ether (50 mL), washed successively with water (2 × 50 mL) and brine (25 mL), and dried over anhydrous sodium sulfate. Evaporation of the ethereal extract afforded pure silyl ethers which were further purified by distillation. IR and ^{1}H NMR spectra of the products were in agreement with the reported spectral data.

General Procedure for the Silylation of Alcohols with *tert*-Butyldimethylsilyl Chloride/Lithium Sulfide. A procedure similar to the one with chlorotrimethylsilane was employed in this case. A 5.0-mmol sample of the substrate alcohol, 7.5 mmol of lithium sulfide, and 10 mmol of *tert*-butyldimethylsilyl chloride were reacted in 15 mL of dry acetonitrile. The reactions were generally complete in 5–6 h, except in the case of **1c** which required 8 h. After aqueous workup the crude products always contained *tert*-butyldimethylsilanol among other impurities, which were removed by distilling the TBDMS ether under vacuum. The purified products revealed expected IR and ^{1}H NMR characteristics (see Table II).

General Procedure for the Preparation of Enol Silyl Ethers from Carbonyl Compounds. To a well-stirred suspension of lithium sulfide (1.5 g, 30 mmol) in dry acetonitrile (25 mL) in a 100-mL round-bottom flask fitted with a water condenser and nitrogen inlet was added chlorotrimethylsilane (6.3 mL, 50 mmol). To this mixture were added the carbonyl compound (20 mmol) and triethylamine (3 mL, 20 mmol) in succession, and the solution was either allowed to stir at room temperature or heated under reflux (see Table III for exact conditions). The progress of the reaction was monitored by removing aliquots periodically and analyzing them after workup by TLC or IR. Soon after the completion of the reaction (except in the cases of **4c** and **4d**, in which the reaction was stopped after 16 h), the mixture was taken up in ether (50 mL) and washed thoroughly with ice-cold aqueous 5% HCl solution (4 × 50 mL) to remove all basic and water-soluble impurities. The ethereal extract was washed with ice-cold aqueous 5% $NaHCO_3$ solution (50 mL), water (50 mL), and brine (25 mL). It was dried over anhydrous sodium sulfate and subjected to distillation under reduced pressure to obtain crude enol silyl ethers. The products were further purified by distillation to obtain spectrally (^{1}H NMR and IR) pure enol silyl ethers.

General Procedure for the Preparation of Silyl Nitronates from Nitro Compounds. The silylation of nitro compounds was carried out by a procedure similar to the one outlined for the silylation of alcohols. Nitrocyclohexanes **6a** or **6b** (10 mmol) were

(19) Torssell, K.; Zeuthen, O. *Acta Chem. Scand., Ser. B* **1978**, *32*, 118–24.
(20) Olah, G. A.; Nojima, M. *Synthesis* **1973**, 785–6.

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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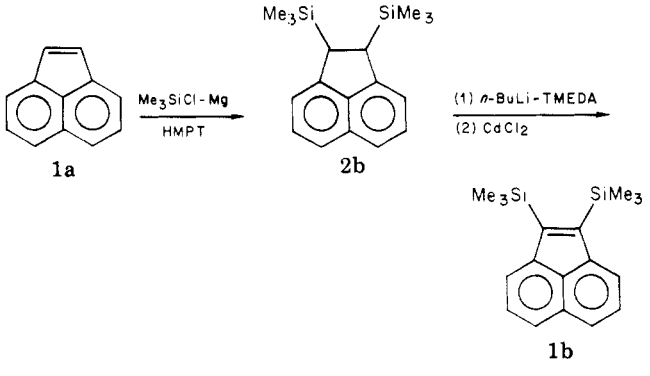
Received August 4, 1978

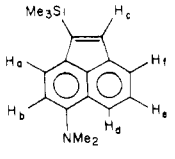
The title compounds were prepared from acenaphthylene **1a** or acenaphthene **2a** by appropriate silylation reactions followed by oxidation. Of the various reagents used for oxidation, *n*-BuLi–TMEDA–$CdCl_2$ (Harvey's reagent) was found to be the most convenient, as it did not induce partial desilylation. 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]



(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. Félix, J. Dunoguès, F. Pisciotti, and R. Calas, *Angew. Chem., Inter. Ed. Engl.*, **16**, 488 (1977).
(4) Me_3SiCl–Li–THF, a more reactive reagent than Me_3SiCl–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).

0022-3263/79/1944-4275$01.00/0