

Table IV. Analyses of Compounds

R	R'	Formula	Calcd, %		Found, %	
			C	H	C	H
2-R-2-R'-1,3-Dithianes						
H	Me <sub>3</sub> Si	C <sub>7</sub> H <sub>16</sub> S <sub>2</sub> Si	43.70	8.38	43.66	8.37
H	Ph <sub>3</sub> Si	C <sub>22</sub> H <sub>22</sub> S <sub>2</sub> Si	69.78	5.86	70.69	5.66
CH <sub>3</sub>	Me <sub>3</sub> Si	C <sub>8</sub> H <sub>18</sub> S <sub>2</sub> Si	46.54	8.79	46.55	8.68
Me <sub>2</sub> Si	Me <sub>3</sub> Si	C <sub>10</sub> H <sub>24</sub> S <sub>2</sub> Si	45.39	9.14	46.67	9.14
CH <sub>3</sub>	Ph <sub>3</sub> Si	C <sub>23</sub> H <sub>24</sub> S <sub>2</sub> Si	70.35	6.16	70.56	5.83
CH <sub>3</sub>	α-NpPhMeSi	C <sub>22</sub> H <sub>24</sub> S <sub>2</sub> Si	69.42	6.35	68.94	6.24
Ph	α-NpPhMeSi	C <sub>27</sub> H <sub>26</sub> S <sub>2</sub> Si	73.25	5.92	73.67	6.10
Ph	Ph <sub>3</sub> Si	C <sub>26</sub> H <sub>26</sub> S <sub>2</sub> Si	73.96	5.76	73.71	5.70
Ph <sub>3</sub> Si	Ph <sub>3</sub> Si	C <sub>40</sub> H <sub>36</sub> S <sub>2</sub> Si	75.51	5.66	74.67	5.63
H	Ph <sub>3</sub> Ge	C <sub>22</sub> H <sub>22</sub> GeS <sub>2</sub>	62.47	5.21	62.69	5.23
Me	Ph <sub>3</sub> Ge	C <sub>23</sub> H <sub>24</sub> GeS <sub>2</sub>	63.22	5.49	63.24	5.41
H	Et <sub>3</sub> Ge	C <sub>10</sub> H <sub>22</sub> GeS <sub>2</sub>	43.06	7.89	42.70	7.73
Et <sub>2</sub> Ge	Et <sub>3</sub> Ge	C <sub>16</sub> H <sub>36</sub> Ge <sub>2</sub> S <sub>2</sub>	43.91	8.23	45.38	8.38
Me	Et <sub>3</sub> Ge	C <sub>11</sub> H <sub>24</sub> GeS <sub>2</sub>	45.10	8.20	45.06	8.06
Ph	Et <sub>3</sub> Ge	C <sub>16</sub> H <sub>26</sub> GeS <sub>2</sub>	54.16	7.34	54.25	7.56
Et <sub>2</sub> Ge	Me <sub>3</sub> Si	C <sub>13</sub> H <sub>30</sub> GeS <sub>2</sub> Si	44.46	8.55	44.76	8.32
H	Ph <sub>3</sub> Sn	C <sub>22</sub> H <sub>22</sub> S <sub>2</sub> Sn	56.31	4.73	56.99	4.92
Me	Ph <sub>3</sub> Sn	C <sub>23</sub> H <sub>24</sub> S <sub>2</sub> Sn	57.16	5.01	56.94	4.93
H	CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>2</sub>	C <sub>8</sub> H <sub>14</sub> S <sub>2</sub>	55.12	8.09	55.14	8.01
PhMeHSi	CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>2</sub>	C <sub>15</sub> H <sub>22</sub> S <sub>2</sub> Si	61.16	7.53	61.10	7.66
Ketones R—CO—R'						
CH <sub>3</sub>	Me <sub>3</sub> Si	C <sub>3</sub> H <sub>12</sub> SiO	51.66	10.41	51.66	10.71
CH <sub>3</sub>	α-NpPhMeSi	C <sub>19</sub> H <sub>18</sub> SiO	78.57	6.25	78.72	6.26
Ph	Et <sub>3</sub> Ge	C <sub>13</sub> H <sub>20</sub> GeO	58.95	7.56	58.28	7.46

thoroughly extracted with carbon tetrachloride. Evaporation of the solvent left 5.0 g (63%) of a viscous yellow oil, with carbonyl absorption at 6.14  $\mu$ . Distillation gave a clear yellow oil, bp 82–83° (0.15 mm).

**Hydroboration of Vinyltrimethylsilane.** To 800 ml of 1 M (0.8 mole) diborane in tetrahydrofuran<sup>19</sup> cooled in an ice bath was added 50 g (0.5 mole) of vinyltrimethylsilane with vigorous stirring. Stirring was continued over 18 hr at room temperature, and then, after cooling the reaction mixture to 0°, 50 ml of water was cautiously added, resulting in the precipitation of considerable white solid. Most of the tetrahydrofuran was removed under reduced pressure, and the precipitate (mainly boric acid) was thoroughly washed with methanol. The organoborane and methanol washings were neutralized with concentrated aqueous sodium hydroxide and then an additional 8.0 g (0.2 mole) of solid sodium hydroxide was added and dissolved by shaking. To the rapidly stirred mixture, 80 ml of 30% hydrogen peroxide (0.8 mole) was slowly added. After 1 hr stirring, water containing a little sodium chloride was added, and the mixture was thoroughly extracted with several portions of ether. The carbinol ether layers were back-extracted with dilute sodium chloride solution, and then were

dried. Rough distillation gave a total of 24.2 g (41%) of mixed 1- and 2-trimethylsilylethanol, bp 60–75°,  $n_D^{20}$  1.4200–1.4231.

**Oxidation of Trimethylsilylethanol.** To a solution of 4.1 g (0.0034 mole) of the above trimethylsilylethanol (estimated by vpc to contain 81% of the desired 1-trimethylsilylethanol) and 7.8 g (0.0034 mole) of pyridinium trifluoroacetate in 100 ml of dry dimethyl sulfoxide was added 14.5 g (0.0088 mole) of dicyclohexylcarbodiimide. The mixture, from which a large amount of white solid (dicyclohexylurea) precipitated, was stirred in the dark for 18 hr. After filtering off the solid, the solution was distilled at about 24 mm, and material boiling in the range 26–50° was collected in two Dry Ice traps. The distillate had very strong infrared absorption at 6.08  $\mu$ , and weaker absorption at 5.63 and 5.81  $\mu$ , probably due to small amounts of trifluoroacetic acid and an ester impurity. The distillate was taken up in ether and washed several times with water. The ketone was purified by vpc on an Aerograph Autoprep 70S instrument using a 6-ft SE 30 silicone gum rubber column, column temperature 80°, flow rate 300 ml/min, injection temperature 130°, elution time 34 min. It was identical in properties with the acetyltrimethylsilane prepared by the dithiane method, bp 113–114° (750 mm).

**Acknowledgment.** This research was supported by the National Research Council of Canada.

(19) Supplied by Metal Hydrides Co., Beverley, Mass.

## Synthesis of $\alpha$ -Silyl Ketones via 1,3-Dithianes

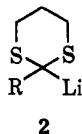
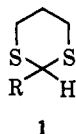
E. J. Corey, Dieter Seebach, and R. Freedman

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received September 2, 1966

**Abstract:** A new synthetic route to  $\alpha$ -silyl ketones involving two steps from readily available components is described.

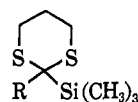
Recently we have described the generation of 2-lithio derivatives (2) from 1,3-dithianes (1) and the application of these nucleophilic reagents to the

synthesis of a wide variety of organic compounds, including aldehydes, ketones, 1,*n*-diketones,  $\alpha$ -hydroxy ketones,  $\alpha$ -keto acids, and  $\alpha$ -amino ketones.<sup>1</sup> The



efficiency with which substances of type 2 can be alkylated by reactive carbon halides suggested that similar nucleophilic displacements could be effected at electrophilic centers other than carbon, for example, at silicon, germanium, or phosphorus. The specific case of the halosilanes was selected for an initial study not only because of the availability and reactivity of these substances but also because the  $\alpha$ -silyl ketones to which a route would be provided are currently not available by simple and generally efficient methods.<sup>2</sup> Furthermore,  $\alpha$ -silyl ketones are of special interest in connection with the investigation of their chemical properties and also because of their unique spectral behavior in the ultraviolet and visible regions.<sup>2b,c,f,3-6</sup> The dithiane route seemed especially advantageous for the synthesis of  $\alpha$ -silyl ketones containing only non-conjugating substituents such as alkyl. These substances are well suited to the observation of the electronic transitions of the isolated  $\alpha$ -silyl ketone chromophore. During the course of our studies<sup>7</sup> along these lines, we learned that Professor A. G. Brook and co-workers had independently embarked on a similar investigation. We have consulted with them to avoid duplication of effort and have restricted the scope of our work accordingly.

The 2-lithio derivatives of a variety of 1,3-dithianes have been found to react smoothly and generally with chlorotrimethylsilane to afford the expected displacement products in good yield. Thus, from the 2-lithio derivatives of 1,3-dithiane itself and 2-methyl-, 2-*t*-butyl-, 2-phenyl-, and 2-trimethylsilyl-1,3-dithiane, the series 3a-e have been obtained readily.



- 3a, R = H  
 b, R = CH<sub>3</sub>  
 c, R = *t*-Bu  
 d, R = C<sub>6</sub>H<sub>5</sub>  
 e, R = (CH<sub>3</sub>)<sub>3</sub>Si

To demonstrate the synthesis of  $\alpha$ -silyl ketones, 3b, c, and d have been subjected to hydrolysis using mercuric chloride-mercuric oxide in aqueous methanol. The corresponding ketones, RC(=O)Si(CH<sub>3</sub>)<sub>3</sub> (4), R = CH<sub>3</sub>, *t*-Bu, and C<sub>6</sub>H<sub>5</sub>, were readily formed at reflux for periods of 1.5 to 3 hr and could be isolated. The yields obtained in these initial experiments were

(1) E. J. Corey and D. Seebach, *Angew. Chem.*, **77**, 1134, 1135 (1965); *Angew. Chem. Intern. Ed., Engl.*, **4**, 1075, 1077 (1965).

(2) Certain  $\alpha$ -silyl aryl ketones have been prepared by dibromination (N-bromosuccinimide) and hydrolysis of benzylsilanes. See (a) A. G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957); (b) A. G. Brook, R. Kivisikk, and G. E. Le Grow, *Can. J. Chem.*, **43**, 1175 (1965); (c) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *J. Am. Chem. Soc.*, **82**, 5102 (1960). Others have been obtained by the reactions of silyllithium compounds with carboxylic acid derivatives either directly [(d) D. Wittenberg and H. Gilman, *ibid.*, **80**, 4529 (1958)] or *via* secondary alcohols by oxidation [(e) A. G. Brook and G. J. D. Peddle, *J. Organometal. Chem.*, **5**, 106 (1966); (f) A. G. Brook and J. B. Pierce, *J. Org. Chem.*, **30**, 2566 (1965)].

(3) A. G. Brook and J. B. Pierce, *Can. J. Chem.*, **42**, 298 (1964).

(4) D. F. Harnish and R. West, *Inorg. Chem.*, **2**, 1082 (1963).

(5) R. West, *J. Organometal. Chem.*, **3**, 314 (1965).

(6) L. E. Orgel, quoted in E. B. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, Oxford, 1963, p 81.

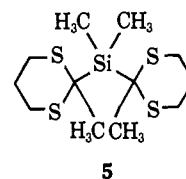
(7) Reported in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; see Abstracts, p 35K.

lowered because of the volatility of the products, which caused substantial losses during isolation. A considerable improvement is doubtless possible by the use of a nonvolatile organic solvent (*e.g.*, dimethyl sulfoxide)<sup>8</sup> and direct distillation of the volatile ketone from the hydrolysis mixture. The  $\alpha$ -silyl ketones 4, R = CH<sub>3</sub>, and 4, R = *t*-Bu, the first purely aliphatic members of this class, show quite similar ultraviolet absorption. In the case of 4, R = CH<sub>3</sub>, maxima were observed at 257, 356, 369, and 385 m $\mu$  with the peak at 369 having the largest extinction ( $\epsilon$  180) and with additional shoulders at 322, 333, and 345 m $\mu$ . The positions of the three maxima in the region 300-400 m $\mu$  for 4, R = CH<sub>3</sub>, are not greatly different from those reported<sup>2c</sup> for methyl triphenylsilyl ketone at 360, 372, and 382 m $\mu$ . This would seem to indicate that these electronic transitions of methyl triphenylsilyl ketone do not involve strong interaction between the carbonyl and phenyl units; the data are entirely consistent with the  $n \rightarrow \pi^*$  assignment for these bands.<sup>4-6</sup>

The nonconjugated  $\alpha$ -silyl ketones 4, R = CH<sub>3</sub>, and 4, R = *t*-Bu, exhibit absorption due to carbonyl in the infrared (CCl<sub>4</sub> solution) at 6.08 and 6.11  $\mu$ ; the carbonyl absorption of methyl triphenylsilyl ketone has been reported<sup>2c</sup> to occur at 6.08  $\mu$ .

The 2-trimethylsilyl-1,3-dithiane derivatives are distillable liquids or solids which are stable toward heating at least below 150° and stable toward base and cold dilute aqueous acid. They exhibit infrared absorption at 10.9-11.0  $\mu$  and ultraviolet absorption near 250 m $\mu$ , as are characteristic of other 1,3-dithianes. The nmr spectra of the compounds 3a-e are fully consistent with the assigned structures: a sharp peak due to trimethylsilyl can be found in the range  $\tau$  9.75-9.95

The silylation reaction is evidently not limited to monochlorosilanes. Reaction of the 2-lithio derivative of 2-methyl-1,3-dithiane with dichlorodimethylsilane led to the interesting bis-1,3-dithiane (5) in 60% yield.



In conclusion, it may be stated that the use of lithium reagents from 1,3-dithianes provides a new and general approach to functionally substituted organosilicon compounds based on nucleophilic displacement reactions at silicon.

## Experimental Section<sup>9</sup>

**General Procedure for the Preparation of 2-Trimethylsilyl-1,3-dithianes (3).** An equimolar amount of neat chlorotrimethylsilane

(8) See A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Am. Chem. Soc.* **89**, 431 (1967).

(9) Microanalyses were carried out by Bernhardt Laboratories, Mülheim, Germany. The carbon-hydrogen analyses were performed using vanadium pentoxide to assist combustion. The silicon content was determined in several cases by oxidation to silica using nitric acid-sulfuric acid, but the assays were uniformly lower than expected, due to the volatility of the substances. Ultraviolet spectra were measured using a Cary Model 14 spectrophotometer, and infrared spectra were obtained using a Perkin-Elmer Infracord. A Varian Associates A-60 was utilized for the nmr spectra. Distillations were performed with exclusion of air by nitrogen.

is added dropwise to a solution of the lithium compound **2** stirred under nitrogen at  $-25^{\circ}$ . After a reaction time depending on the 2 substituent, 10 vol. % of water is added, and most of the tetrahydrofuran is removed on a rotating flask evaporator. Water and either pentane, ether, or methylene chloride are added, the layers are separated, and the aqueous phase is extracted several times with the solvent. The combined organic layers are washed successively with water, 10% potassium hydroxide, and water, dried over potassium carbonate, and evaporated to give the reaction product as a colorless liquid or solid.

**2-Trimethylsilyl-1,3-dithiane (3a).** From 44.40 mmoles of **2**,  $R = H$ ,<sup>1</sup> and 4.97 g (45.9 mmoles) of chlorotrimethylsilane was obtained, after a reaction time of 30 min at  $-25^{\circ}$  and 30 min at  $25^{\circ}$ , 8.643 g of crude product (using pentane as solvent for work-up). Distillation through a 15-cm column gave 223 mg (1.90 mmoles) of 1,3-dithiane and 5.786 g (70.6%, calculated from unrecovered dithiane) of pure **3a**, bp  $54.5^{\circ}$  (0.17 mm);  $n_D^{20}$  1.5331; infrared spectrum (neat): 3.35, 3.43, 3.50, 7.04, 7.98, 8.60, 9.20, 10.00, 10.96, 11.30, 11.8, 13.18, 13.67, and 14.3  $\mu$ ; nmr spectrum ( $CCl_4$ ): CH at 2 position of the dithiane at  $\tau = 6.36$  ppm, Si( $CH_3$ )<sub>3</sub> at  $\tau$  9.87 ppm, along with the typical dithiane peaks near  $\tau$  7 and 8 ppm, ratio 1:9:4:2; ultraviolet spectrum (cyclohexane):  $\lambda_{max}$  244.0 ( $\epsilon$  711) and 227 m $\mu$  (shoulder) ( $\epsilon \sim 800$ ).

*Anal.* Calcd for  $C_7H_{16}S_2Si$ : C, 43.69; H, 8.38; S, 33.33. Found: C, 43.86; H, 8.21; S, 33.29.

**2-Methyl-2-trimethylsilyl-1,3-dithiane (3b).** After a reaction time of 2.5 hr at  $-25^{\circ}$ , 6.56 g (93%) of crude product was obtained from 34.1 mmoles of **2**,  $R = CH_3$ ,<sup>1</sup> and 4.01 g (37.1 mmoles) of chlorotrimethylsilane (using pentane as solvent for work-up). Distillation gave 5.530 g (78.4%); bp  $102^{\circ}$  (9.5 mm);  $n_D^{20}$  1.5343; infrared spectrum (neat): 3.33, 3.40, 3.50, 6.94, 7.07, 8.01, 9.12, 9.48, 9.92, 10.97, 11.36, 11.9, 13.23, 13.62, and 14.11  $\mu$ ; nmr spectrum ( $CCl_4$ ):  $CH_3$  at 8.18, Si( $CH_3$ )<sub>3</sub> at  $\tau = 9.86$  ppm, ratio 1:3; ultraviolet spectrum (cyclohexane):  $\lambda_{max}$  245.8 ( $\epsilon$  832) and 229.4 m $\mu$  ( $\epsilon$  628).

*Anal.* Calcd for  $C_8H_{18}S_2Si$ : C, 46.54; H, 8.79; S, 31.06. Found: C, 46.36; H, 8.88; S, 30.91.

**2-*t*-Butyl-2-trimethylsilyl-1,3-dithiane (3c).** From 49.40 mmoles of **2**,  $R = t\text{-Bu}$ , and 7.20 ml (6.18 g, 56.9 mmoles) of chlorotrimethylsilane was obtained 10.879 g of crude product, after a reaction time at  $-20^{\circ}$  of 3 days, using ether as solvent for work-up. Distillation of 960 mg at  $120^{\circ}$  (bath) (0.07 mm) gave 860 mg (corresponding to a yield from the starting *t*-butyl-1,3-dithiane of 79.7%) of a colorless, viscous liquid which crystallized; mp  $33.5\text{--}33.9^{\circ}$  (from methanol); infrared spectrum ( $CCl_4$ ): 3.34, 3.41, 3.50, 5 bands between 6.8 and 7.5, 8.04, 8.35, 10.92, 11.09, 11.85, and 14.7  $\mu$ ; nmr spectrum ( $CCl_4$ ): C( $CH_3$ )<sub>3</sub> at  $\tau = 8.82$ , Si( $CH_3$ )<sub>3</sub> at 9.74 ppm, ratio 1:1.

*Anal.* Calcd for  $C_{11}H_{24}S_2Si$ : C, 53.16; H, 9.73; S, 25.81. Found: C, 53.16; H, 9.66; S, 25.72.

**2-Phenyl-2-trimethylsilyl-1,3-dithiane (3d).** After combining 25.5 mmoles of **2**,  $R = C_6H_5$ , and 3.15 g (29.0 mmoles) of chlorotrimethylsilane at  $-30^{\circ}$  and allowing the temperature to rise to  $15^{\circ}$  within 4 hr, a yield of crude crystalline product of 6.17 g (90.1%) was obtained (using ether as solvent for work-up). The analytical sample (from methanol) had mp  $94.4\text{--}94.8^{\circ}$ ; infrared spectrum ( $CHCl_3$ ): 3.25, 3.36, 3.42, 3.53, 6.00, 6.33, 6.80, 7.00, 8.02, 9.19, 9.43, 10.71, 10.93, 11.24, 11.85, and 14.28  $\mu$ ; nmr spectrum ( $CDCl_3$ ): Si( $CH_3$ )<sub>3</sub> at  $\tau = 9.93$  ppm, with other signals as complex multiplets; ratio aromatic to dithiane to Si- $CH_3$  protons of 5:6:9.

*Anal.* Calcd for  $C_{14}H_{20}S_2Si$ : C, 58.15; H, 7.51; S, 23.88. Found: C, 58.18; H, 7.64; S, 23.72.

**2,2-Bis(trimethylsilyl)-1,3-dithiane (3e).** The lithium compound **2**,  $R = (CH_3)_3Si$ , was prepared as usual at  $-25^{\circ}$  for 45 min. Hydrolysis with deuterium oxide gave 2-deuterio-2-trimethylsilyl-1,3-dithiane in 93% yield with a deuterium content of  $>98\%$  (by nmr analysis), confirming the formation of the lithio derivative. From 15.68 mmoles of **2**,  $R = (CH_3)_3Si$ , and 1.975 g (18.15 mmoles) of chlorotrimethylsilane, after a reaction time of 11 hr at  $0^{\circ}$ , 3.996 g (96.3%) of colorless product was obtained (using ether as solvent for work-up). Distillation of 529 mg at  $120^{\circ}$  (bath) (3 mm) gave the analytical sample, 500 mg (91%), which crystallized occasionally;  $n_D^{20}$  1.5407; mp  $29.6\text{--}30.0^{\circ}$  (from methanol at  $-20^{\circ}$ ); infrared spectrum ( $CCl_4$ ): 3.36, 3.42, 3.52, 7.05, 8.00, 9.98, 10.93, 11.22, 11.75, 13.90, and 14.6  $\mu$ ; nmr spectrum ( $CCl_4$ ): along with the usual dithiane multiplets only one peak at  $\tau = 9.79$  ppm, ratio 1:3; ultraviolet spectrum (cyclohexane):  $\lambda_{max}$  242.8 m $\mu$  ( $\epsilon$  1181).

*Anal.* Calcd for  $C_{10}H_{24}S_2Si$ : C, 45.39; H, 9.14; S, 24.24. Found: C, 45.48; H, 9.16; S, 24.03.

**Dimethylbis-2-(2-methyl-1,3-dithianyl)silane (5).** After combining 0.100 mole of freshly distilled dichlorodimethylsilane with 0.186 mole of **2**,  $R = CH_3$ , at  $-60^{\circ}$  and keeping the mixture at  $-20^{\circ}$  for 4 days, 32.757 g of a viscous oil was obtained (using  $CH_2Cl_2$  as solvent for work-up). Methanol (50 ml) was added, and the mixture was stirred at  $0^{\circ}$  for 30 min, furnishing 17.702 g (58.65%) of colorless crystals; analytical sample, mp  $65.5\text{--}66.3^{\circ}$  (from methanol); infrared spectrum ( $CHCl_3$ ): 3.34, 3.40, 3.52, 6.94, 7.07, 8.00, 9.48, 10.98, 11.37, 11.9, and 12.2  $\mu$ ; nmr spectrum ( $CDCl_3$ ): Si( $CH_3$ )<sub>3</sub> at  $\tau = 9.52$ ,  $CH_3$  at 7.85 ppm, ratio 1:1; ultraviolet spectrum (cyclohexane):  $\lambda_{max}$  248.4 ( $\epsilon$  1694) and 232.0 m $\mu$  ( $\epsilon$  1428).

*Anal.* Calcd for  $C_{12}H_{24}S_4Si$ : C, 44.39; H, 7.45; S, 39.51; Si, 8.65. Found: C, 44.30; H, 7.29; S, 39.38; Si, 8.04.

**General Procedure for the Hydrolysis of 2-Trimethylsilyl-1,3-dithianes (3) to Give Acyltrimethylsilanes 4.** Aqueous methanol is placed into a flask wrapped in aluminum foil, and 1 equiv of crude 2-trimethylsilyl-1,3-dithiane **3**, 2.2 equiv of mercuric chloride, and 1.5 equiv of mercuric oxide are added. The mixture is stirred vigorously and heated at reflux for 1.5–2.5 hr. The solution is filtered with shielding from light, and the filter residue is washed with boiling methanol. The filtrate is poured into three times its volume of water. The combined organic layers from five extractions with ether or pentane are washed once with concentrated ammonium acetate and twice with water and dried over sodium sulfate in the dark. Most of the solvent is removed by fractional distillation through a silvered column packed with glass helices with the distillation flask wrapped in aluminum foil, and the residue is distilled through a 15-cm column.

**Phenyl Trimethylsilyl Ketone (4,  $R = C_6H_5$ ).** Hydrolysis of 3.00 g (11.17 mmoles) of **3d** in 110 ml of methanol–water (10:1) gave 1.45 g (73%) of crude product as a yellow-green oil (reaction time 1.25 hr, using ether as solvent for work-up). Distillation of 372 mg at  $55^{\circ}$  (bath) (1.3 mm) [lit.<sup>2c</sup>  $42\text{--}44^{\circ}$  (0.02 mm)] furnished 308 mg (58%) of pure ketone; infrared spectrum (neat): 3.28, 3.39, 3.46, 6.19 (lit.<sup>2c</sup> 6.18), 6.28, 6.33, 6.91, 8.00, 8.24, 8.51, 11.82, 12.76, 13.18, and 14.4  $\mu$ ; nmr spectrum (neat): Si( $CH_3$ )<sub>3</sub> at  $\tau = 9.65$  ppm, ratio of aromatic protons (2 sets of multiplets) to  $CH_3$  protons of 5:9; ultraviolet spectrum (cyclohexane):  $\lambda_{max}$  445, 423 ( $\epsilon$  127), 403, 385 (shoulder), 372 (shoulder), and 250 m $\mu$  ( $\epsilon$  14,500) [lit.<sup>2c</sup> in ethanol 402 ( $\epsilon$  117), 413 ( $\epsilon$  118), 252 ( $\epsilon$  11,700)].

**Methyl Trimethylsilyl Ketone (4,  $R = CH_3$ ).** Hydrolysis of 25.00 g (0.121 mole) of **3b** in 250 ml of methanol–water (9:1) (reaction time 2.0 hr) gave 5.834 g of crude ketone after removal of the solvent pentane. Distillation yielded 3.50 g (25%) of the mobile, volatile ketone; bp  $\sim 115^{\circ}$ ; infrared spectrum ( $CCl_4$ ): 3.08, 3.39, 3.46, 6.08 (carbonyl absorption), 7.12, 7.49, 8.00, 8.81, and 11.82  $\mu$ ; nmr spectrum ( $CCl_4$ ): two singlets at  $\tau = 7.82$  ( $CH_3$ ) and 9.82 ppm (Si( $CH_3$ )<sub>3</sub>), ratio 1:3; ultraviolet spectrum (cyclohexane):  $\lambda_{max}$  385, 369 ( $\epsilon$  180), 356, 257, shoulders at 345, 333, and 322 m $\mu$  ( $\epsilon \sim 20$ ); mass spectrum (four largest peaks in order of decreasing intensity): 73 (Si( $CH_3$ )<sub>3</sub>), 45, 43 ( $CH_3\text{--}CO$ ), 116 (molecular ion).

*Anal.* Calcd for  $C_8H_{11}OSi$ : C, 51.66; H, 10.41. Found: C, 51.71; H, 10.63.

***t*-Butyl Trimethylsilyl Ketone (4,  $R = t\text{-Bu}$ ).** Hydrolysis of 10.9 g (43.8 mmoles) of crude **3c** in 185 ml of methanol–water (17.5:1) (reaction time of 2.5 hr) furnished 5.005 g of residue after removal of the solvent pentane through a 60-cm column; vpc analysis showed that the volatile components of this mixture were composed of  $\sim 60\%$  of **4**,  $R = t\text{-Bu}$ , 38% of pentane, and 2% of an unidentified substance. Distillation through a 10-cm column gave 2.50 g (36%) of pure ketone as a slightly greenish yellow, mobile liquid of pleasant, camphoraceous odor, bp  $76\text{--}77^{\circ}$  (66 mm);  $n_D^{20}$  1.4266; infrared spectrum (neat): 3.08, 3.37, 3.40, 3.43, 3.48, 6.11  $\mu$  (carbonyl absorption); the same value was obtained with a  $CCl_4$  solution, 6.78, 7.35, 7.99, 11.85, and 13.22  $\mu$ ; nmr spectrum ( $CCl_4$ ): two extremely sharp singlets at  $\tau = 8.95$  (C( $CH_3$ )<sub>3</sub>) and 9.78 ppm (Si( $CH_3$ )<sub>3</sub>); ultraviolet spectrum (cyclohexane):  $\lambda_{max}$  367 m $\mu$  ( $\epsilon$  200), with no distinct fine structure but some shoulders.

*Anal.* Calcd for  $C_8H_{13}OSi$ : C, 60.69; H, 11.46. Found: C, 60.57; H, 11.13.

**Acknowledgments.** We are indebted to Mr. D. N. Crouse for assistance in some of the experimental work. This investigation was supported by grants from the National Science Foundation and the National Institutes of Health.