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The Synthesis of the Derivatives of Silacyclopentanol and Silacyclopentylamine

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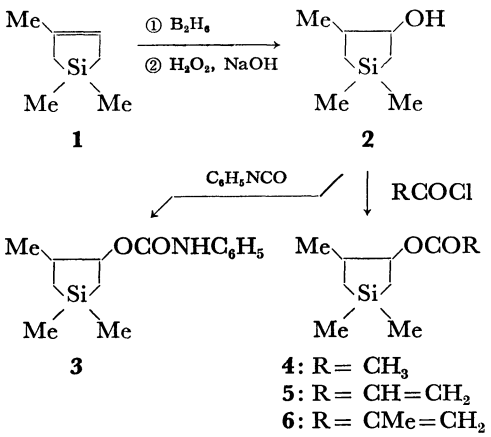
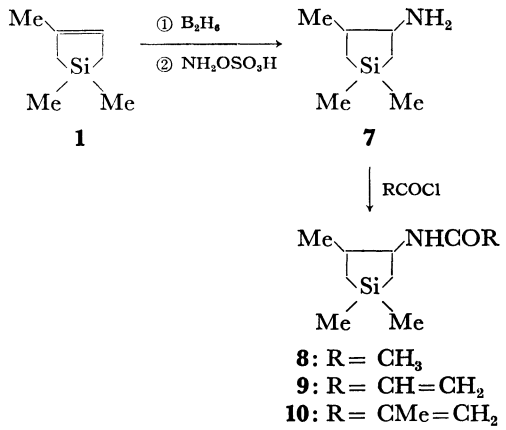
Recently, several papers have been reported on the synthesis and reactions of carbofunctional derivatives of silaheterocyclic compounds.[1] The present authors previously reported the synthesis[2] and polymerization[3] of silacyclo-pentene and -pentane derivatives. In this paper, we wish to report the synthesis of several new derivatives of silacyclopentanol and silacyclopentylamine 3,3,5-trimethyl-3-silacyclopentylphenylurethane (**3**), 1,1,3-trimethyl-4-acetoxy-1-silacyclopentane(**4**), 1,1,3-trimethyl-4-acryloxy-1-silacyclopentane(**5**), 1,1,3-trimethyl-4-methacryloxy-1-silacyclopentane(**6**), 1,1,3-trimethyl-4-amino-1-silacyclopentane(**7**), 1,1,3-trimethyl-4-acetylamino-1-silacyclopentane(**8**), 1,1,3-trimethyl-4-acryloylamino-1-silacyclopentane(**9**), and 1,1,3-trimethyl-4-methacryloylamino-1-silacyclopentane(**10**). The starting material, 1,1,3-trimethyl-1-silacyclopent-3-ene(**1**), was prepared in a 38% yield[2] by a modification of the method of Weyenberg *et al.*[4] The hydroboration and oxidation[5] of **1** with diborane and alkaline hydrogen peroxide gave 1,1,3-trimethyl-1-silacyclopentan-4-ol(**2**).[1b] **2** was reacted readily with phenyl isocyanate, acetyl chloride, acryloyl chloride, and methacryloyl chloride to afford **3**, **4**, **5**, and **6** respectively (Scheme 1).



Scheme 1.

3 was a highly viscous liquid soluble in common organic solvents, such as CCl_4, Et_2O, and EtOH. The esters of silacyclopentanol, **4**, **5**, and **6**, were liquid and stable under ordinary conditions. In the case of compounds **5** and **6**, the addition of a small amount of hydroquinone as a polymerization inhibitor was necessary for obtaining them in better yields. Other new silacyclopentane derivatives were synthesized according to Scheme 2. The amination of chloroalkylsilane with ammonia has been successfully employed in the preparation of aminoalkylsilane.[6] This method, however, cannot be used in the synthesis of silacyclopentylamine because of the instability of the chloroderivatives of silacyclopentane. *Via* hydroboration in diglyme, Brown and Zweifel[7] succeeded in preparing amines from hidered olefines, such as 1-methylcyclohexene, 1-methylcyclopentene, and α-pinene. By applying this method, hydroboration followed by treatment with NH_2OSO_3H in glyme (bp 82°C) in place of diglyme (bp 160°C), **7** was obtained in a 16.9% yield (Scheme 2). When tetrahydrofuran was used as the solvent, the yield of **7** was decreased to about 5%.



Scheme 2.

7 was a liquid miscible in common organic solvents and was stable under ordinary conditions. **7** was identified by an analysis of the IR and NMR spectra. (IR spectrum: silicon containing a five-membered ring,[8] 1080, 1030, and 1020 cm^{-1}; NMR spectrum: the two singlets at τ=9.91 and 9.88 for Si-$(CH_3)_2$ show that the silacyclopentane ring remains intact.) **7** was found to undergo reaction with acyl chlorides, such as acetyl chloride, acryloyl chloride, and meth-

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2) T. Araki, D. Terunuma, and T. Fuse, This Bulletin, **45**, 293 (1972).

3) T. Araki, D. Terunuma, T. Sato, N. Nagai, M. Furuichi, and S. Nakamura, *ibid.*, **44**, 2725 (1971).

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5) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **81**, 247 (1959).

6) L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951).

7) H. C. Brown and G. Zweifel, *ibid.*, **82**, 4708 (1960).

8) V. M. Vdovin, K. S. Pushchevaya, N. A. Belikova, and R. Syltanov, *Dokl. Akad. Nauk SSSR.*, **136**, 96 (1961).

acryloyl chloride, to yield **8**, **9**, and **10** respectively. Compounds **8**, **9**, and **10** were colorless crystals. Their structural assignment was done by the analysis of the IR and NMR spectra. The acryloyl and methacryloyl derivatives, **5**, **6**, **9**, and **10**, could be polymerized easily by a radical initiator, such as BPO or AIBN. More detailed studies of the polymerization of these compounds are in progress.

Experimental

The NMR spectra were measured by means of a Varian A-60 spectrometer, using tetramethylsilane as the internal standard. The infrared spectra were obtained on a Shimadzu IR-27C spectrophotometer.

Preparation of ***2***. To a tetrahydrofuran (30 ml) solution of 12.6 g (0.1 mol) of **1** cooled at 0°C, we added gaseous diborane generated from 1.9 g of sodium borohydride in diglyme and boron trifluoride etherate over a period of 2 hr. After this mixture had stood for 2 hr at room temperature, small chips of ice were added to hydrolyze the excess diborane. The solution was immersed in an ice bath, and 11 ml of 3M sodium hydroxide was added, followed by 11 ml of 30% hydrogen peroxide over a period of 1 hr. One hour later the organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over anhydrous sodium sulfate and distilled to yield 9.8 g (68%) of **2**. Bp 82—86°C/30 mmHg, n_D^{20} 1.4553.

Preparation of ***3***. Phenyl isocyanate (0.03 mol) was added to 3.6 g (0.025 mol) of **2** at room temperature. After 15 min at 75°C, a small amount of water was added to the mixture to hydrolyze the excess phenyl isocyanate. The mixture was then diluted with 20 ml of carbon tetrachloride. Filtration and distillation gave 4.0 g (75.3%) of **3**. NMR: τ 9.87 (s, 6H, CH_3–Si), 8.98 (d, 3H, C–CH_3), 8.40—9.50 (m, 4H, CH_2–Si), 7.80—8.30 (m, 1H, CH–Me), 5.41 (sextet, 1H, CH–O), 2.50—3.25 (m, 6H, –NH–Ph). IR: 3400(m), 2950 (m), 1720 (s), 1601 (m), 1550 (m), 1240 (s), 1075 (m), 1050 (m), 1030 (m), 850 (m). Bp 145—147°C/0.15 mmHg n_{20}^D 1.5303. Found: N, 5.47; Si, 10.53%. Calcd for $C_{14}H_{21}O_2NSi$: N, 5.32; Si, 10.62%.

Preparation of ***4***. To a mixture of 4.8 g (0.033 mol) of **2** and 4 g (0.04 mol) of triethylamine in 30 ml of dry ether was added 3.1 g (0.04 mol) of acetyl chloride in 10 ml of dry ether at 0°C with stirring. Then the mixture was refluxed for 1.5 hr. The ether layer was separated from precipitates of triethylamine hydrochloride. The ether layer was washed with five 20 ml portions of water, and then dried over anhydrous sodium sulfate. Distillation gave 3.14 g (68.4%) of **4**. NMR: τ 9.80, 9.83 (two singlets, 6H, CH_3–Si), 9.01 (d, 3H, C–CH_3), 8.50—9.75 (m, 4H, CH_2–Si), 8.05 (s, 3H, CO–CH_3), 5.40 (sextet, 1H, CH–O). IR: 2935 (m), 1740 (s), 1250 (s), 1080 (m), 1050 (s), 1025 (m), 850 (s). Bp 100—104°C/70 mmHg, n_D^{20} 1.4438. Found: Si, 14.34%. Calcd for $C_9H_{18}O_2Si$: Si, 15.08%.

Preparation of ***5***. The synthesis procedure was similar to that described above. To a solution of 4.8 g of **2** and 4 g of triethylamine in 30 ml of dry ether, we added 3.62 g (0.04 mol) of acryloyl chloride in 10 ml of dry ether in the presence of a small amount of hydroquinone as a polymerization inhibitor. NMR: τ 9.82, 9.85 (two singlets, 6H, CH_3–Si), 9.01 (d, 3H, C–CH_3), 8.40—9.70 (m, 4H, CH_2–Si), 7.70—8.30 (m, 1H, CH–Me), 5.35 (sextet, 1H, CH–O), 3.50—4.40 (m, 3H, CH=CH_2). IR: 2950 (m), 1735 (s), 1610 (s), 1210 (m), 1070 (m), 1050 (w), 1020 (w), 850 (m). Yield, 2.24 g (34.1%); Bp 58—61°C/3.5 mmHg, n_D^{20} 1.4580. Found: Si, 13.24%. Calcd for $C_{10}H_{18}O_2Si$: Si, 14.30%.

Preparation of ***6***. The procedure was similar to that used for **4**. To a solution of 4.8 g of **2** and 4 g of triethylamine in 30 ml of dry ether, we added 4.17 g (0.04 mol) of methacryloyl chloride in 10 ml of dry ether in the presence of a small amount of hydroquinone. NMR: τ 9.82, 9.86 (two singlets, 6H, CH_3–Si), 9.05 (d, 3H, C–CH_3), 7.40—8.30 (m, 1H, CH–Me), 5.40 (sextet, 1H, CH–O), 4.56 (m, 1H, C=CH), 4.00 (m, 1H, C=CH). IR: 2980 (m), 1725 (s), 1640 (m), 1300 (m), 1250 (m), 1180 (s), 1070 (m), 1050 (m), 1020 (m), 840 (s). Yield, 1.96 g (37.1%); Bp 77—79°C/2.5 mmHg, n_D^{20} 1.4590. Found: Si, 12.83%. Calcd for $C_{11}H_{20}O_2Si$: Si, 13.36%.

Preparation of ***7***. To a flask containing 12.6 g (0.1 mol) of **1** in 30 ml of glyme at 0°C, we added gaseous diborane generated from 1.9 g of sodium borohydride in diglyme and boron trifluoride etherate over a period of 2 hr. After this mixture had stood 2 hr at room temperature, a solution of 13.6 g (0.12 mol) of hydroxylamine-*O*-sulfonic acid in 25 ml of glyme was added; the solution was then refluxed for 4 hr. The reaction mixture was cooled, treated with 20 ml of concentrated hydrochloric acid, and poured into 200 ml of water. The acidic phase was extracted with ether to remove glyme and the residual boronic acid. The aqueous solution was then made strongly alkaline with sodium hydroxide, and the amine was extracted with ether. The ether extract was dried over potassium hydroxide and distilled. NMR: τ 9.00—9.70 (m, 4H, Si–CH_2), 9.04 (d, 3H, C–CH_3), 8.80 (m, 2H, –NH_2), 7.38 (octet, 1H, CH–N). IR: 3350 (w), 3250 (w), 2940 (s), 1580 (m), 1450 (m), 1400 (m), 1360 (m), 1250 (s), 990 (w), 830 (s). Yield, 2.40 g (16.9%); Bp 74—75°C/42 mmHg, n_D^{20} 1.4535. Found: N, 9.50; Si,18.22%. Calcd for $C_7H_{17}NSi$: N, 9.77; Si, 19.53%.

Preparation of ***8***. Into a mixture of 1.43 g (0.01 mol) of **7** and 1.2 g (0.012 mol) of triethylamine in 20 ml of dry ether, we stirred 0.94 g (0.012 mol) of acetyl chloride in 10 ml of dry ether at 0°C. After the addition was completed, the mixture was stirred at room temperature for 3 hr. The ether layer was separated from precipitates of triethylamine hydrochloride, and then washed with five 15 ml portions of water. The ether solution was dried over anhydrous sodium sulfate. On the evaporation of the solvent, we obtained 1.43 g (77.5%) of a colorless solid product. This product was recrystallized from petroleum ether. NMR: τ 9.86 (s, 6H, CH_3–Si), 9.02 (d, 3H, C–CH_3), 8.50—9.60 (m, 4H, CH_2–Si), 8.07 (s, 3H, O=C–CH_3), 7.40—8.30 (m, 1H, CH–Me), 2.31 (d, 1H, NH). IR: 3300 (m), 3150 (w), 2950 (m), 1650 (s), 1560 (m), 1300 (m), 1250 (m), 1085 (w), 1070 (m), 1040 (w), 850 (s). Yield, 1.04 g (56.3%); Mp 99.5—100°C. Found: N, 7.40; Si, 14.76%. Calcd for $C_9H_{19}OSi$: N, 7.56; Si, 15.10%.

Preparation of ***9***. The synthesis procedure was similar to that described above. Into a mixture of 1.43 g (0.01 mol) of **7** and 1.2 g (0.012 mol) of triethylamine in 20 ml of dry ether, we stirred 1.09 g (0.012 mol) of acryloyl chloride in 10 ml of dry ether at 0°C in the presence of a small amount of hydroquinone. NMR: τ 9.88, 9.91 (two singlets, 6H, CH_3–Si), 9.00 (d, 3H, C–CH_3), 8.40—9.50 (m, 4H, CH_2–Si), 7.80—8.50 (m, 1H, CH–Me), 6.32 (m, 1H, CH–N), 4.50 (q, 1H, CH=C), 3.70 (t, 2H, C=CH_2), 2.32 (d, 1H, CH–N). IR: 3330 (m), 3130 (w), 3080 (m), 1660 (s), 1610 (m), 1550 (m), 1250 (m), 1160 (m), 1070 (m), 1000 (w), 980 (m), 840 (m). Yield, 1.20 g (61.3%); Mp 114—115°C. Found: N, 6.95; Si, 13.01%. Calcd for $C_{10}H_{19}OSi$: N, 7.90; Si, 14.18%.

Prepatation of ***10***. The procedure was similar to that described above. To a solution of 1.43 g (0.01 mol) of **7**

and 1.2 g (0.012 mol) of triethylamine in 20 ml of dry ether, we added 1.25 g (0.012 mol) of methacryloyl chloride in 10 ml of dry ether in the presence of hydroquinone. NMR: τ 9.89, 9.92 (two singlets, 6H, CH_3–Si), 9.00 (d, 3H, C–CH_3), 8.40—9.50 (m, 4H, CH_2–Si), 8.13 (s, 3H, O=C–CH_3), 7.80—8.60 (m, 1H, CH–Me), 6.33 (m, 1H, CH–N), 4.78 (m, 1H, C=CH), 4.40 (m, 1H, C–CH), 3.40 (d, 1H, NH). IR: 3300 (m), 2940 (m), 1660 (m), 1620 (s), 1540 (s), 1250 (m), 1160 (m), 1070 (m), 1005 (m), 980 (w), 840 (s). Yield, 1.37 g (64.8%); Mp 102—103°C. Found: N, 6.49; Si, 12.82%. Calcd for $C_{11}H_{21}NOSi$: N, 6.63; Si, 13.24%.

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