Me_2SO-d_6, 100 MHz) δ 3.88 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.77 and 4.92 (m, m, 1 H, H-6a), 6.52 and 6.57 (s, s, 1 H, H-3), 6.77 and 6.81 (s, s, 1 H, H-8), 8.06 and 8.15 (s, s, 1 H, H-11), 8.24 and 8.34 (s, s, 1 H, NCHO); mass spectrum, *m/e* (relative intensity) 341 (M^+, 96), 326 (4), 324 (5), 313 (9), 312 (9), 297 (9), 296 (16), 283 (100), 270 (45), 269 (48), 255 (16), 254 (19), 240 (21), 220 (32), 206 (76).

Starting with **1f** (340 mg, 0.8 mmol), 37 mg (29%) of **4c**, 4.5 mg of (3%) **2f**, and 158 mg of unreacted **1f** were separated. Compound **2f** was identical with our previous sample prepared by direct para–ortho′ phenolic coupling, see ref 16.

Preparation of (±)-Pallidine (4a). *N*-Formylnorisosalutaridine (**4c**) (14 mg, 0.04 mmol) was dissolved in methanol (2 mL) and 18% aqueous hydrogen chloride (0.5 mL). The reaction mixture was kept at 50 °C for 24 h under an argon atmosphere and then the methanol was removed under reduced pressure. The residue was basified with ammonium hydroxide and extracted with dichloromethane. The combined organic layer was dried and evaporated. The crude (±)-norisosalutaridine was purified by preparative TLC (dichloromethane–methanol (100:10, v/v) system with initial ammonia treatment), and N-methylated immediately with 98% formic acid (0.5 mL) and 38% aqueous formaldehyde solution (0.5 mL) (1 h reflux). The reaction mixture was basified with ammonium hydroxide and then extracted with dichloromethane. The organic layer was dried and evaporated. The remaining material was finally purified by preparative TLC (dichloromethane–methanol (150:12, v/v) system with initial ammonia treatment) to supply (±)-pallidine (**4a**) (2.2 mg, 16%), the spectral data of which correspond to those reported earlier[13] for the natural product, which does not separate from an authentic sample on TLC.[23]

Acknowledgment. We thank the CHINOIN Pharmaceutical and Chemical Works (Budapest) for financial support, E. Baitz-Gâcs for ^1H and ^{13}C NMR spectra, and J. Tamâs for the MS measurements.

Registry No. (±)-**1b**, 55869-76-6; (±)-**1c**, 72274-71-6; (±)-**1e**, 72258-92-5; (±)-**1f**, 72264-51-8; (±)-**2c**, 87167-77-9; (±)-**2f**, 87265-23-4; (±)-**3b**, 87332-78-3; (±)-**3c**, 88765-44-0; (±)-**4a**, 27841-88-9; (±)-**4b**, 37729-28-5; (±)-**4c**, 88996-27-4; (±)-norisosaletaridine, 89063-54-7; manganese tris(acetonylacetonate), 14284-89-0; vanadyl bis(acetonylacetonate), 3153-26-2.

(23) Special thanks are expressed to Prof. M. Shamma, The Pennsylvania State University, who was kind enough to provide us with a sample of natural pallidine.

Chlorine Migration in the Mass Spectra of *tert*-Butyldimethylsilyl Derivatives of Chloro Alcohols

Scott T. Hill† and Michael Mokotoff*

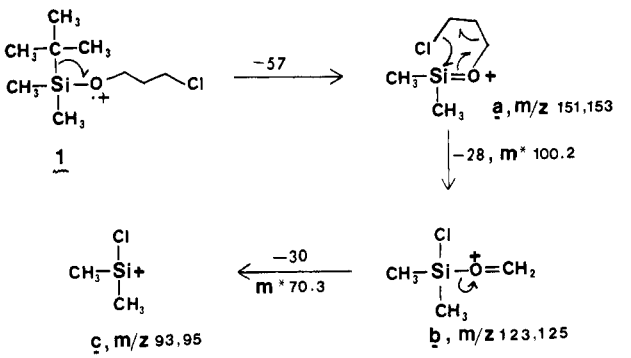
Department of Medicinal Chemistry, School of Pharmacy, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

Received July 21, 1983

In the course of synthetic studies toward a nitrogen analogue of phyllanthocin,[1] the aglycon of the antileukemic glycoside phyllanthoside, we needed to introduce a hydroxybutyl group. We chose to accomplish this via an organometallic reagent derived from the *tert*-butyldimethylsilyl ether of 4-chlorobutanol. Mass spectral analysis of this latter intermediate revealed an interesting skeletal rearrangement in which chlorine migrated to silicon.

†Present address: Dickinson College, Department of Chemistry, Carlisle, PA 17013.

Scheme I



Scheme II

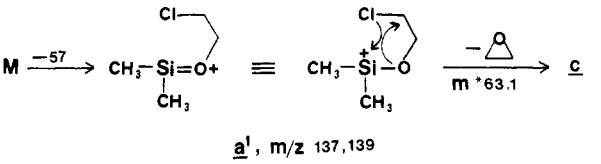


Table I. $\%\Sigma_{40}$ (Relative Intensity) Values for $(CH_3)_3CSi(CH_3)_2O(CH_2)_nCl$

n	M − 57	*m/z* 123 (ion b)	*m/z* 93 (ion c)
2	3.88 (12.1)	0.35 (1.1)	32.16 (100)
3	2.37 (10.5)	9.37 (41.6)	22.53 (100)
4	0.23 (1.5)	13.20 (84.5)	15.61 (100)
5	not detected	5.85 (18.6)	8.66 (27.5)

Mass spectral migrations of various groups to silicon are not without precedence,[2-5] but since the *tert*-butyldimethylsilyl group is so widely used as a blocking group in synthetic organic chemistry we felt that further studies were warranted. Therefore, we prepared a series of *tert*-butyldimethylsilyl-blocked chloro alcohols and found that this halogen to silicon migration is a common process in their electron-impact mass spectra.

The *tert*-butyldimethylsilyl ethers of 2-chloroethanol, 3-chloropropanol, 4-chlorobutanol, and 5-chloropentanol[6] were prepared by reacting the corresponding chloro alcohol with *tert*-butyldimethylsilyl chloride and imidazole in DMF.[7] Using the 3-chloropropanol derivative **1** as a model, we envisage the fragmentations shown in Scheme I as a plausible route to the major ions a–c. These fragmentations are analagous to the deuterium migration to silicon observed with trimethylsilyl ethers of variously deuterated 1-pentanols.[2] Furthermore, metastable ions at *m/z* 100.2 and 70.3 were observed for the transformations a → b and b → c, respectively. Confirmation of the composition of ions a–c was made by high-resolution mass spectroscopy.[8]

In all cases studied the ions resulting from chlorine migration to silicon were prominent (see Table I), except

(1) Kupchan, S. M.; LaVoie, E. J.; Branfman, A. R.; Fei, B. Y.; Bright, W. M.; Bryan, R. F. *J. Am. Chem. Soc.* **1977**, *99*, 3199.
(2) Diekman, J.; Thomson, J. B.; Djerassi, C. *J. Org. Chem.* **1967**, *32*, 3904.
(3) White, E. V.; McCloskey, J. A. *J. Org. Chem.* **1970**, *35*, 4241.
(4) Francis, A. J.; Morgan, E. D.; Poole, C. F. *Org. Mass Spectrom.* **1978**, *13*, 671.
(5) Sylvestre, M.; Masse, R.; Messier, F.; Fauteux, J.; Bisaillon, J.-G.; Beaudet, R. *Appl. Environ. Microbiol.* **1982**, *44*, 871.
(6) 5-Chlorpentanol was prepared by transesterification of 5-chloropentyl acetate with methanol; Fusari, S. A.; Greenlee, K. W.; Brown, J. B. *J. Am. Oil Chem. Soc.* **1951**, *28*, 416.
(7) Corey, E. J.; Venkateswarlu, A. *J. Am Chem. Soc.* **1972**, *94*, 6190.
(8) Ion a, $C_5H_{12}ClOSi$, *m/z* 151.0340 (calcd 151.0346); ion b, C_3H_8ClOSi, *m/z* 123.0035 (calcd 123.0032); ion c, C_2H_6ClSi, *m/z* 92.9942 (calcd 92.9927).

0022-3263/84/1949-1441$01.50/0

with the 2-chloroethoxy derivative where ion b was small. In fact, the mechanism to ion b shown in Scheme I would, in the 2-chloroethoxy case, necessitate the improbable loss of a methylene group. Therefore, ion b in the latter case must arise by a different mechanism, perhaps by exchange of the *tert*-butyl and chlorine groups followed by the loss of a neopentyl radical.[9] On the other hand, since ion c is the base peak in this same compound it must be formed by a mechanism different than that shown in Scheme I. It seems probable, at least in the 2-chloroethoxy derivative (and possibly in the other examples), that ion c arises from ion a', by a mechanism similar to that shown by Diekman, et al.[10] for 1,2-bis(trimethylsiloxy)ethane (see Scheme II). Indeed, this was substantiated by the observation of a metastable peak at m/z 63.1 for the transformation a' → c. It appears that the importance of ion c diminishes with an increase in the distance between chlorine and silicon (see Table I).

Not surprisingly, when the mass spectra of the *tert*-butyldimethylsilyl ethers of both 3-bromopropanol and 4-bromobutanol were examined, an analogous bromine to silicon migration was observed. From this work and that of others,[3] we suggest that organic chemists examining the mass spectra of halogenated *tert*-butyldimethylsilyl ethers might observe ions such as b and c, in which halogen has migrated to silicon.

Experimental Section

^{1}H NMR (89.55 MHz) and ^{13}C NMR (22.5 MHz) spectra were recorded on a JEOL FX-90Q spectrometer using $CDCl_3$ as solvent and Me_4Si as an internal standard. Low-resolution mass spectra were obtained on a Finnigan 3200 GC spectrometer (column conditions, OV-17, injector at 200 °C, oven at 90 °C, programmed at 10°/min), the metastable data were obtained on an LKB Model 9000 spectrometer at both 15 and 70 eV, and high-resolution data were obtained from the Massachussetts Institute of Technology Mass Spectrometry Facility on a Varian MAT 731 spectrometer in the electron-impact mode. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The petroleum ether used had bp 38–56 °C.

(3-Chloropropoxy)dimethyl-*tert*-butylsilane (1) (General Procedure). A solution of 3-chloropropanol (5 mL) in dichloromethane (5 mL) was washed with deionized water (1 mL), 5% $NaHCO_3$ solution (1 mL, until the washes were basic), and a saturated NaCl solution (1 mL). The organic layer was dried ($MgSO_4$), concentrated and purified by Kugelrohr distillation (7 mm).[11]

tert-Butyldimethylsilyl chloride (1.99 g, 13.2 mmol) and imidazole (0.90 g, 13.2 mmol) were dissolved in anhydrous DMF (5 mL) under N_2. After 5 min, freshly distilled 3-chloropropanol (1.04 g, 11.0 mmol) was added. The reaction was allowed to stir overnight at room temperature under N_2. Workup involved addition of diethyl ether (30 mL) and washing the organic layer with deionized water (3 × 2.5 mL). The combined aqueous washes were reextracted with an equal volume of diethyl ether. The combined ethereal layers were dried ($MgSO_4$), and concentrated in vacuo, and the resulting oil was purified by column chromatography[7] on silica gel 60 (Merck 0.06–0.20 mm, column dimensions 1.5 × 45 cm) using 100 mL of petroleum ether initially, and the product was then eluted with petroleum ether/diethyl ether (70:30). The purest fraction afforded the following data: ^{1}H NMR δ 3.75 (t, J = 6 Hz, CH_2O),[12] 3.65 (t, J = 6 Hz, CH_2Cl),[12] 1.95 (apparent pentant, J = 6 Hz, $CH_2CH_2CH_2$), 0.90 (s, $C(CH_3)_3$), 0.07 (s, $Si(CH_3)_2$); ^{13}C NMR δ 59.4 (CH_2O), 41.6 (CH_2Cl), 35.6 ($CH_2CH_2CH_2$), 25.9 ($C(CH_3)_3$), 18.3 ($C(CH_3)_3$), −5.4 ($Si(CH_3)_2$).[13] Anal. Calcd for $C_9H_{21}ClOSi$: C, 51.79; H, 10.07. Found: C, 51.87; H, 10.02.

(2-Chloroethoxy)dimethyl-*tert*-butylsilane. Following the general procedure above afforded the corresponding 2-chloroethoxy derivative, which gave the following physical data: ^{1}H NMR δ 3.44 (t, J = 5 Hz, CH_2O),[12] 3.17 (t, J = 5 Hz, CH_2Cl),[12] 0.80 (s, $C(CH_3)_3$), 0.08 (s, $Si(CH_3)_2$); ^{13}C NMR δ 63.8 (CH_2O), 45.1 (CH_2Cl), 25.9 ($C(CH_3)_3$), 18.4 ($C(CH_3)_3$), −5.3 ($Si(CH_3)_2$).[13] Anal. Calcd for $C_8H_{19}ClOSi$: C, 49.35; H, 9.77. Found: C, 49.32; H, 9.91.

[(4-Chlorobutyl)oxy]dimethyl-*tert*-butylsilane. Following the general procedure above afforded the corresponding (4-chlorobutyl)oxy derivative, which gave the following physical data: ^{1}H NMR δ 3.58 (apparent quartet, J = 6 Hz, 4 H, CH_2O, CH_2Cl), 1.75 (m, 4 H, CH_2CH_2), 0.88 (s, $C(CH_3)_3$), 0.04 (s, $Si(CH_3)_2$); ^{13}C NMR δ 62.4 (CH_2O), 45.1 (CH_2Cl), 30.3 (CH_2CH_2Cl), 29.6 (CH_2CH_2O), 26.6 ($C(CH_3)_3$), 18.4 ($C(CH_3)_3$), −5.2 ($Si(CH_3)_2$).[13] Anal. Calcd for $C_{10}H_{23}ClOSi$: C, 53.93; H, 10.34. Found: C, 54.17; H, 10.53.

[(5-Chloropentyl)oxy]dimethyl-*tert*-butylsilane. Following the general procedure above afforded the corresponding (5-chloropentyl)oxy derivative, which gave the following physical data: ^{1}H NMR δ 3.57 (apparent quartet, J = 6 Hz, 4 H, CH_2O, CH_2Cl), 1.78 (apparent pentant, J = 6 Hz, 4 H, $CH_2CH_2CH_2CH_2CH_2$), 1.53 (m, 2 H, $CH_2CH_2CH_2CH_2CH_2$), 0.88 (s, $C(CH_3)_3$), 0.05 (s, $Si(CH_3)_2$); ^{13}C NMR δ 62.8 (CH_2O), 44.9 (CH_2Cl), 32.5, 32.1 ($CH_2CH_2CH_2CH_2CH_2$), 26.0 ($C(CH_3)_3$), 23.3 ($CH_2CH_2CH_2CH_2CH_2$, 18.3 ($C(CH_3)_3$), −5.3 ($Si(CH_3)_2$).[13] Anal. Calcd for $C_{11}H_{25}ClOSi$: C, 55.81; H, 10.57. Found: C, 55.59; H, 10.68.

Acknowledgment. We thank Mr. Joseph Bender, University of Pittsburgh, School of Pharmacy, for obtaining the low-resolution mass spectral data, Dr. Alvin Marcus, University of Pittsburgh, Department of Chemistry, for obtaining the metastable data, and Drs. Catherine Costello and Henrianna Pang, Massachusetts Institute of Technology, for obtaining the high-resolution mass spectral data on the MIT Mass Spectrometry Facility (supported by NIH, Grant RR-00317).

Registry No. $(CH_3)_3CSi(CH_3)_2O(CH_2)_2Cl$, 89031-81-2; $(CH_3)_3CSi(CH_3)_2O(CH_2)_3Cl$, 89031-82-3; $(CH_3)_3CSi(CH_3)_2O(CH_2)_4Cl$, 89031-83-4; $(CH_3)_3CSi(CH_3)_2O(CH_2)_5Cl$, 85514-44-9; 3-bromopropyl *tert*-butyldimethylsilyl ether, 89031-84-5; 4-bromobutyl *tert*-butyldimethylsilyl ether, 89043-32-3; *tert*-butyldimethylsilyl chloride, 18162-48-6; 2-chloroethanol, 107-07-3; 3-chloropropanol, 627-30-5; 4-chlorobutanol, 928-51-8; 5-chloropentanol, 5259-98-3.

(9) We thank Dr. Lan Wong, University of Pittsburgh, School of Pharmacy, for this suggestion.

(10) Diekman, J.; Thomson, J. B.; Djerassi, C. *J. Org. Chem.* **1968**, *33*, 2271.

(11) Eaton, P. E.; Cooper, G. F.; Johnson, R. C.; Mueller, R. H. *J. Org. Chem.* **1972**, *37*, 1947.

(12) The proton shifts of the methylenes α to the chlorine and oxygen atoms were assigned by comparing the spectra of 5-chloropentyl acetate [δ 4.08 (CH_2O), 3.55 (CH_2Cl)] and 5-chloropentanol [δ 3.65 (CH_2O), 3.55 (CH_2Cl)].

(13) The position of the signals upfield of Me_3Si in the ^{13}C NMR spectra was confirmed by running the spectra with and without Me_3Si and by observing the $CDCl_3$ triplet. Furthermore, others have reported similar positions for Me–Si resonance (Soderquist, J. A.; Hassner, A. *J. Org. Chem.* **1983**, *48*, 1801. Roberts, R. A.; Schull, V.; Paquette, L. A. *Ibid* **1983**, *48*, 2076).

Aerosol Direct Fluorination: Syntheses of the Highly Branched Ketones *F*-Pinacolone and *F*-Provalone

James L. Adcock* and Mark L. Robin

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

Received October 19, 1983

The aerosol direct fluorination method provides a continuous process for the production of perfluorocarbons from hydrocarbons with efficient fluorine utilization and minimal fragmentation. The application of this process

