$CHCl_3$–C_5H_{12} to give 2.85 g (48.5%) of **7** as a colorless solid: mp 139–140 °C; IR (KBr) 3300 (OH stretching), 875 cm^{-1} (1,2,3,5-tetrasubstituted Ar); ^1H NMR ($CDCl_3$) δ 7.0–7.40 (m, 8, Ar H), 4.62 (s, 4, CH_2OH), 3.80 (s, 6, $ArCH_2Ar$), 1.20 (s, 36, $C(CH_3)_3$).

Anal. Calcd for $C_{45}H_{60}O_6$: C, 77.58; H, 8.62. Found: C, 77.10; H, 8.68.

Thermally Induced Dehydration of 2,6-Bis(hydroxymethyl)-4-*tert*-butylphenol (4). A solution of 5.0 g of **4** in 25 mL of xylene was refluxed for 4 h in an atmosphere of N_2. The xylene was removed by evaporation under reduced pressure, and the sticky residue was triturated with 30 mL of CH_3OH to leave 1.35 g (29.5%) of a colorless solid. Recrystallization from $CHCl_3$–CH_3OH yielded 7,15,23-tri-*tert*-butyl-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene (**3**) as glistening, very fine blades: mp 220–221 °C (lit[2] mp, 245 °C); ^1H NMR ($CDCl_3$) δ 8.50 (s, 1, OH), 7.05 (s, 2, ArH), 4.68 (s, 4, CH_2), 1.25 (s, 9, $C(CH_3)_3$); osmometric M_r ($CHCl_3$, 37 °C), 619 (calcd for 4·1/2 CH_3OH, 592); mass spectrum (EI, 90 eV), *m/e* 576 (calcd for *3*, 576).

Anal. Calcd for $C_{36}H_{48}O_6 \cdot 0.5CH_3OH$: C, 73.98; H, 8.39. Found: C, 74.12; H, 8.33.

The CH_3OH triturate deposited a white solid upon standing at room temperature, the ^1H NMR of which was similar to that of **3** except for the absence of the resonance at δ 8.50 arising from the OH groups. The osmometric M_r of this material was 1023, corresponding to ca. 5.5 monomeric units in what is presumed to be a linear oligomer.

Thermally Induced Dehydration of 3-[3-(Hydroxymethyl)-5-*tert*-butylsalicyl]-5-*tert*-butyl-2-hydroxybenzyl Alcohol (5). A 2-g sample of **5** was dissolved in 10 mL of xylene and refluxed for 4 h. From the cooled reaction mixture, 0.85 g of a white solid was separated by filtration and crystallized from $CHCl_3$–CH_3OH to yield 7,13,21,27-tetra-*tert*-butyl-29,30,31,32-tetrahydroxy-2,3,16,17-tetrahomo-3,17-dioxacalix[4]arene (**2**) as glistening, very small blades: mp 245 °C; IR (KBr) 3370 (OH stretching), 1075 (CO stretching), 875 cm^{-1} (1,2,3,5-tetrasubstituted Ar); ^1H NMR ($CDCl_3$) δ 8.96 (s, 4, OH), 7.31 (d, 4, J = 2.4 Hz, Ar H), 6.95 (d, 4, J = 2.4 Hz, Ar H), 4.63 (s, 8, CH_2OCH_2), 3.93 (s, 4, CH_2), 1.27 (s, 36, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 150.4 (Ar), 143.0 (Ar), 127.6 (Ar), 127.4 (Ar), 124.8 (Ar), 122.4 (Ar), 71.9 (CH_2OCH_2), 33.92 (CH_2), 31.48 ($C(CH_3)_3$); osmometric M_r ($CHCl_3$, 37 °C), 721 (calcd, 708).

Anal. Calcd for $C_{46}H_{60}O_6$: C, 77.97; H, 8.47. Found: C, 77.69; H, 8.56.

Removal of the xylene from the filtrate described above left 1.0 g of a glassy residue, which was indicated by TLC to be a mixture of the dihomooxa compound **1**, the tetrahomobisoxa compound **2**, and polymeric material in the approximate ratio of 2:5:6.

Thermally Induced Dehydration of 3-[3-[3-[3-(Hydroxymethyl)-5-*tert*-butylsalicyl]-5-*tert*-butylsalicyl]-5-*tert*-butylsalicyl]-5-*tert*-butyl-2-hydroxybenzyl Alcohol (7). A 0.75-g sample of **7** was dissolved in 4 mL of xylene and refluxed for 4 h. Upon cooling, 0.7 g of a white crystalline solid precipitated, which was removed by filtration and recrystallized from CH_2Cl_2–CH_3OH to afford 0.70 g (96%) of 7,13,19,25-tetra-*tert*-butyl-27,28,29,30-tetrahydroxy-2,3-dihomo-3-oxacalix[4]arene (**1**) as colorless needles, identical in all respects with the material previously described.[1]

Action of Base on 7,13,21,27-Tetra-*tert*-butyl-29,30,31,32-tetrahydroxy-2,3,16,17-tetrahomo-3,17-dioxacalix[4]arene (2). A mixture of 0.5 g of **2**, 0.008 mL of 10 N KOH, and 3 mL of xylene was heated at reflux for 4 h. From the cooled mixture, 0.22 g of a white solid was removed by filtration and shown by TLC to be mainly *p-tert*-butylcalix[8]arene. Recrystallization from $CHCl_3$ afforded a pure sample, mp 408–410 °C. Evaporation of the xylene filtrate left a solid residue, which was shown by TLC to contain *p-tert*-butylcalix[6]arene, *p-tert*-butylcalix[4]arene, the dihomooxa compound **1**, and polymeric material in the ratio of ca. 1:1:4:2. On the basis of these data, the yields of products are estimated to be cyclic octamer (48%), cyclic hexamer (5%), cyclic tetramer (5%), and dihomooxa compound (20.5%).

Action of Base on 7,13,19,25-Tetra-*tert*-butyl-27,28,29,30-tetrahydroxy-2,3-dihomo-3-oxacalix[4]arene (1). A mixture of 0.100 g of **1**, 0.03 mL of 10 N KOH, and 2 mL of xylene was heated at reflux for 4 h. The xylene was removed by evaporation under vacuum, and the residue was examined by TLC, which showed that no conversion to cyclic oligomers had occurred. Recrystallization of the residue from CH_2Cl_2–CH_3OH gave starting material, **1**. A similar reaction carried out with 0.6 mL of 10 N KOH (a 20-fold increase over the previous experiment) gave a crude product in which no cyclic oligomers could be detected by TLC analysis, although what are assumed to be linear oligomers appeared to be present.

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Registry No. **1**, 72251-68-4; **2**, 85097-23-0; **3**, 76543-12-9; **4**, 2203-14-7; **5**, 2467-07-4; **6**, 992-52-9; **7**, 85097-22-9; **8**, 78077-41-5; **9**, 35851-06-0; **10**, 65566-87-2; 2-[3-(5-*tert*-butylsalicyl)-5-*tert*-butylsalicyl]-4-*tert*-butylphenol, 810-52-6; *p-tert*-butylcalix[6]arene, 78092-53-2; *p-tert*-butylcalix[4]arene, 60705-62-6; *p-tert*-butylcalix[8]arene, 68971-82-4; *p-tert*-butylphenol, 98-54-4.

N^{ω}-Alkoxycarbonylation of α,ω-Diamino Acids with 2-(Trimethylsilyl)ethyl 4-Nitrophenyl Carbonate

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In connection with a larger project in peptide synthesis, we had a need for N^{ω}-protected derivatives of α,ω-diamino acids from which the protecting group could be cleaved under mild neutral conditions. A further requirement was that the protecting group had to be compatible with both benzyloxycarbonyl (Z) and *tert*-butyloxycarbonyl (Boc) groups. The [2-(trimethylsilyl)ethoxy]carbonyl (Teoc) group,[1-5] which is easily cleaved at room temperature with tetrabutylammonium fluoride and is stable to hydrogenolysis,[1] was considered attractive, provided that a method could be found to selectively remove not only the Cbz group but also the Boc group while keeping the Teoc group intact. Until now this goal has been elusive, inasmuch as Teoc was found to be labile under a variety of conventional Boc acidolysis conditions.[1] We sought to solve the problem of orthogonal Boc/Teoc deprotection by the application of selective methods of Boc cleavage similar to those that spare *tert*-butyl esters.[6]

In this note we report the synthesis of the N^{ω}-Teoc derivatives of lysine, ornithine, and 2,4-diaminobutyric acid from their copper complexes. The reagent, 2-(trimethylsilyl)ethyl 4-nitrophenyl carbonate was prepared from 2-(trimethylsilyl)ethanol and *p*-nitrophenyl chloroformate. The literature synthesis of 2-(trimethylsilyl)ethanol by $LiAlH_4$ reduction of ethyl 2-(trimethylsilyl)acetate[7] was found to be difficult and gave unsatisfactory yields, due in part to the formation of an insoluble complex during the reaction. In addition, problems were encountered when

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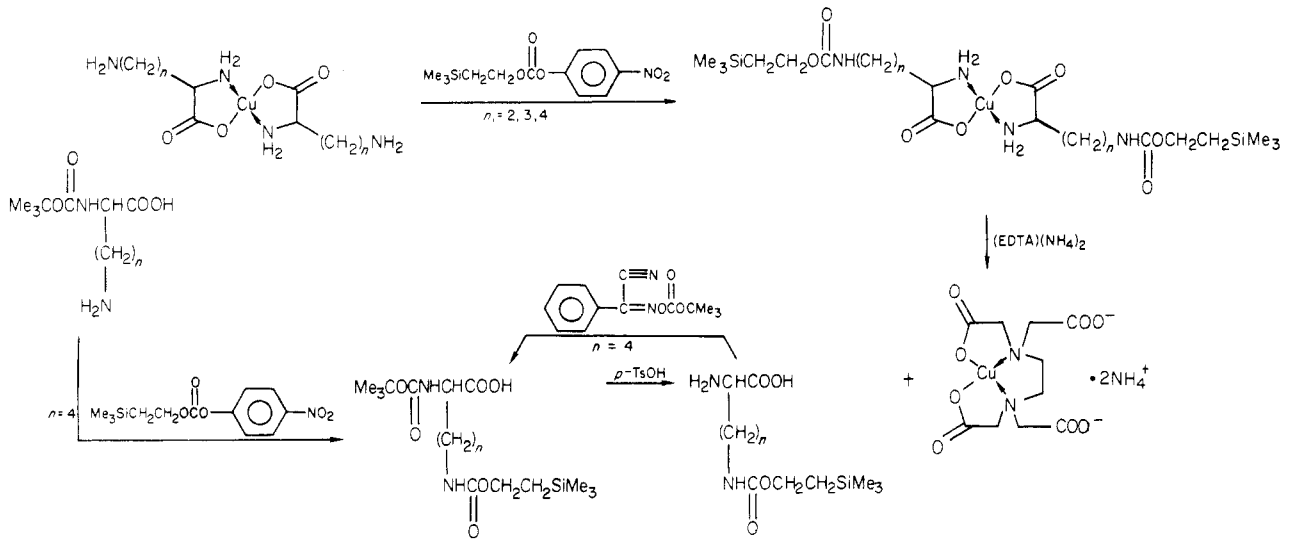
Scheme I



N^{α}-Boc-N^{ϵ}-Teoc-L-lysine $n = 2$; N^{γ}-Teoc-L-2,4-diaminobutyric acid
$n = 3$; N^{δ}-Teoc-L-ornithine
$n = 4$; N^{ϵ}-Teoc-L-lysine

reduction was attempted on a large scale because of the need to use very large volumes of ether. Use of the THF·BH_3 complex instead of $LiAlH_4$ provided a simple and inexpensive means of obtaining 2-(trimethylsilyl)-ethanol in 80% yield. During the preparation of this manuscript, a third method appeared in the literature,[8] utilizing paraformaldehyde and the Grignard reagent from (chloromethyl)trimethylsilane.

The previously reported conversion of 2-(trimethylsilyl)ethanol to the chloroformate with phosgene, followed by addition of *p*-nitrophenol to give the mixed carbonate in 58% yield,[5] was judged to be lengthy and hazardous on a large scale. Reaction of 2-(trimethylsilyl)ethanol with commercially available 4-nitrophenyl chloroformate gave an 87% yield of the desired reagent in one-third the time.

Selective ω-terminal substitution of the copper complexes of α,ω-diamino acids was accomplished in 90–95% yield, as shown in Scheme I. Sequestration of the metal with ethylenediaminetetraacetic acid (EDTA) gave the protected amino acids in 98-100% yield. The position of attachment of the Teoc group was verified by reaction of 2-(trimethylsilyl)ethyl 4-nitrophenyl carbonate with N^{α}-Boc-L-lysine, as well as by alternative synthesis from N^{ϵ}-Teoc-L-lysine and 2-[[(*tert*-butyloxycarbonyl)oxy]imino]-2-phenylacetonitrile.[9] Since both routes gave N^{α}-Boc-N^{ϵ}-Teoc-L-lysine, the position of the Teoc group on the ϵ-nitrogen was unambigously established.

Previous workers have stated that the sensitivity of the Teoc group toward acid militates against its use in peptide synthesis schemes requiring a Boc group to be removed before Teoc removal.[1] This problem was easily overcome by using acidolysis conditions previously shown to cleave Boc groups while leaving *tert*-butyl esters intact.[6] Thus heating of N^{α}-Boc-N^{ϵ}-Teoc-L-lysine with 1 molar equiv of *p*-toluenesulfonic acid at 60–65 °C for 20 min gave N^{ϵ}-Teoc-L-lysine in 96% yield. Since it is already known that Teoc groups are stable to hydrogenolysis,[1] it now becomes feasible to contemplate the use of the Teoc group in orthogonal protection schemes of the type Z/Boc/Teoc.

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Experimental Section

Proton NMR spectra were obtained on a Varian T-60A instrument with a ^1H decoupler and are reported in δ units relative to Me_4Si as the internal standard. IR spectra were recorded on a Perkin-Elmer Model 137B double-beam spectrophotometer. Melting points were measured in a Mel-Temp apparatus (Laboratory Devices, Inc., Cambridge, MA) in glass capillaries and are corrected against standards (A. H. Thomas microtest set no. 6608-M10). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Thin-layer chromatography (TLC) was performed on 5 × 20 cm glass plates coated with 250-μm silica gel (Analtech GHLF). Compounds were eluted with *n*-BuOH/AcOH/H_2O (3:1:1) and detected with ninhydrin spray (Pierce Chemical Co., Rockford, IL) and iodine vapor. All amino acids and Boc derivatives were obtained from Chemical Dynamics Corp., Plainfield, NJ. Ethyl 2-(trimethylsilyl)acetate was prepared by the Fessenden method.[10] Copper complexes of the amino acids were prepared by the method of Taurins.[11] BH_3·THF and trimethylchlorosilane were obtained from Alfa Products, Danvers, MA.

2-(Trimethylsilyl)ethanol. A solution of 80 g of ethyl 2-(trimethylsilyl)acetate (0.50 mol) in 75 mL of tetrahydrofuran was cooled to −10 °C. Over a 2-h period, 0.58 L of 1.02 M BH_3·THF complex (0.59 mol) was added through the septum with the aid of a slight nitrogen pressure.[12] The colorless solution was allowed to warm to room temperature and was left for 2 days. The contents of the reaction flask were transferred to a flask containing 1.5 L of methanol. After being stirred for 20 h under nitrogen, the solution was concentrated at 25–28 °C until only 280 mL remained. This was vacuum distilled through a 45-cm Vigreux column. Following a 75-mL forerun, a 46.1-g fraction (78.1% yield) was obtained; bp 30–32 °C (0.9 mmHg) [lit.[10] bp 95 °C (100 mmHg)].

2-(Trimethylsilyl)ethyl 4-Nitrophenyl Carbonate. A 6.88-g portion of 4-nitrophenyl chloroformate (0.034 mol) was dissolved in 50 mL of dichloromethane in a 100 mL three-neck flask equipped with a thermometer, condenser (drying tube), and addition funnel. A solution of 4.0 g of 2-(trimethylsilyl)ethanol (0.34 mol) and 3 mL of dry pyridine in 5 mL of dichloromethane was added to the stirred chloroformate solution over a 20-min period, during which the temperature rose to 40 °C. After returning to

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room temperature, the solution stood for 2 h. Extraction with 150 mL of 0.5 N HCl, washing of the organic layer to neutrality, drying (anhydrous Na_2SO_4), and evaporation under reduced pressure at 75 °C for 1.5 h gave an oil. Trituration of this residue with 185 mL of hexane (bp 66–68 °C) yielded a white precipitate, which was identified on the basis of it NMR spectrum as 4-nitrophenyl carbonate. Evaporation of the hexane solution remaining after filtration of the solid (room temperature, 2 h) left an oil, which was stirred with 150 mL of ice-cold water containing a drop of 2 N formic acid. The white precipitate that formed was filtered and dried overnight at room temperature under reduced pressure (0.007 mmHg): yield 8.3 g (87%); mp 35–36 °C [lit.[5] mp 34.3–35.9 °C].

General N^{ω}-Alkoxycarbonylation Procedure. To a solution of 1 mmol of the copper(II) complex of L-lysine, L-ornithine, or L-2,4-diaminobutyric acid dihydrochloride dihydrate in 5 mL of 2 M Na_2CO_3 at 50 °C was added a solution of 0.60 g of 2-(trimethylsilyl)ethyl 4-nitrophenyl carbonate (2.1 mmol) in 1 mL of warm ethanol. The temperature was raised to 76 °C, and another 20 mL of ethanol was added over 10 min. The mixture was refluxed for 45 min, cooled to room temperature, and diluted to 300 mL by slow addition of distilled water. Cooling to 10 °C produced a solid, which was collected and triturated with distilled water (3 × 50 mL) until all traces of yellow color due to *p*-nitrophenol were gone. After the final filtration, the product was recrystallized from ethanol/water, and the pale-blue crystals (plates) were dried in vacuo overnight at 95–100 °C; yield 90–95%.

Bis[N^{ϵ}-[[2-(trimethylsilyl)ethoxy]carbonyl]-L-lysinato]copper(II): mp 248–249 °C (darkening at 218 °C); TLC R_f 0.66; IR (KBr) cm^{-1} 3300, 2900, 1670, 1610, 1515, 1370, 1250, 1140, 1060, 940, 860, 835. Anal. Calcd for $C_{24}H_{50}N_4Si_2CuO_8$: C, 44.87; H, 7.87; N, 8.72; Si, 8.74; Cu, 9.89. Found: C, 44.70; H, 7.74; N, 8.73; Si, 8.87; Cu, 9.71.

Bis[N^{δ}-[[2-(trimethylsilyl)ethoxy]carbonyl]-L-ornithinato]copper(II): mp 239–240 °C (darkening at 212 °C); TLC R_f 0.67; IR (KBr) cm^{-1} 3300, 2900, 1670, 1610, 1515, 1380, 1240, 1130, 1040, 940, 860, 835. Anal. Calcd for $C_{22}H_{46}N_4Si_2CuO_8$: C, 43.01; H, 7.55; N, 9.12; Si, 9.14; Cu, 10.34. Found: C, 42.88; H, 7.51; N, 9.05; Si, 9.08; Cu, 10.28.

Bis[N^{γ}-[[2-(trimethylsilyl)ethoxy]carbonyl]-L-2,4-diaminobutyrato]copper(II): mp 229–230 °C (darkening at 214 °C); TLC R_f 0.68; IR (KBr) cm^{-1} 3200, 2860, 1670, 1600, 1500, 1370, 1320, 1240, 1170, 1130, 1040, 1010, 940, 860, 835. Anal. Calcd for $C_{20}H_{42}N_4Si_2CuO_8$: C, 40.97; H, 7.22; N, 9.56; Si, 9.58; Cu, 10.84. Found: C, 40.74; H, 7.15; N, 9.36; Si, 9.37; Cu, 10.62.

Sequestration of Copper(II). General Procedure. A suspension of 1.0 mmol of the binary copper(II) complex of N^{ϵ}-Teoc-L-lysine, N^{δ}-Teoc-L-ornithine, or N^{γ}-Teoc-L-2,4-diaminobutyric acid in 20 mL of 0.12 M ethylenediaminetetraacetic acid in 10% aqueous ammonia was heated until all the solids dissolved, giving a blue solution. The solution was left to cool to room temperature over 2.5 h and then placed in the freezer for 3 h. The precipitate was filtered, washed with ice-cold water (2 × 5 mL), and dried in vacuo at 95–100 °C; yield 82–83%. The washings and combined mother liquor were concentrated by boiling to a volume of 10 mL, cooled slowly to room temperature, and placed in the refrigerator for 2 days, during which a second crop precipitated. The solid was filtered, washed, and dried as above, bringing the total yield to 98–100%.

N^{ϵ}-[[2-(Trimethylsilyl)ethoxy]carbonyl]-L-lysine (N^{ϵ}-Teoc-L-lysine): mp 231–232 °C; TLC R_f 0.65; IR (KBr) cm^{-1} 3350, 2900, 2320, 1670, 1620, 1460, 1400, 1330, 1240, 1130, 1060, 860, 840; NMR (CD_3OD + 1 drop CF_3CO_2H) δ 0.04 (s, 9 H), 0.90 (m, 2 H), 1.27–2.25 (m, 6 H), 3.10 (t, 2 H), 3.95 (t, 1 H), 4.08 (t, 2 H), 5.11 (s, 5 H). Anal. Calcd for $C_{12}H_{25}N_2SiO_4$: C, 49.80; H, 8.71; N, 9.68; Si, 9.70. Found: C, 49.66; H, 8.90; N, 9.56; Si, 10.04.

N^{δ}-[[2-(Trimethylsilyl)ethoxy]carbonyl]-L-ornithine (N^{δ}-Teoc-L-ornithine): mp 228–229.5 °C; TLC R_f 0.65; IR (KBr) cm^{-1} 3300, 2900, 2320, 1680, 1580, 1520, 1400, 1320, 1250, 1170, 1130, 1060, 940, 860, 840; NMR (CD_3OD + 1 drop CF_3CO_2H) δ 0.04 (s, 9 H), 0.90 (m, 2 H), 1.25–2.25 (m, 4 H), 3.10 (t, 2 H), 3.95 (t, 1 H), 4.08 (t, 2 H), 5.11 (s, 5 H). Anal. Calcd for $C_{11}H_{23}N_2SiO_4$: C, 47.97; H, 8.42; N, 10.17; Si, 10.20. Found: C, 47.74; H, 8.64; N, 10.04; Si, 10.00.

N^{γ}-[[2-(Trimethylsilyl)ethoxy]carbonyl]-L-2,4-diaminobutyric acid (N^{γ}-Teoc-L-2,4-diaminobutyric acid): mp 223–224 °C; TLC R_f 0.66; IR (KBr) cm^{-1} 3260, 2880, 1670, 1570, 1500, 1400, 1240, 1170, 1120, 1040, 970, 860, 840, 760; NMR (CD_3OD + 1 drop CF_3CO_2H) δ 0.04 (s, 9 H), 0.90 (m, 2 H), 1.25–2.25 (m, 2 H), 3.10 (t, 2 H), 3.95 (t, 1 H), 4.08 (t, 2 H), 5.11 (s, 5 H). Anal. Calcd for $C_{10}H_{21}N_2SiO_4$: C, 45.95; H, 8.10; N, 10.72; Si, 10.74. Found: C, 45.76; H, 8.19; N, 10.80; Si, 10.96.

N^{α}-(*tert*-Butyloxycarbonyl)-N^{ϵ}-[[2-(trimethylsilyl)ethoxy]carbonyl]-L-lysine (N^{α}-Boc-N^{ϵ}-Teoc-L-lysine). Method A. To a solution of 2.46 g of N^{α}-Boc-L-lysine (10.0 mmol) in 25 mL of 2 M Na_2CO_3 was added 2.89 g of 2-(trimethylsilyl)ethyl 4-nitrophenyl carbonate, and the heterogeneous mixture was stirred at room temperature for 2 days. To the resulting homogeneous yellow solution was then added 7.25 g of sodium dithionite (1.4 equiv), causing bleaching of the yellow color (reduction of *p*-nitrophenol to *p*-aminophenol). The solution was then acidified with 2 N HCl and extracted with chloroform (3 × 100 mL). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure to an oil, from which the last traces of volatile material were removed by heating to 65–70 °C for 4 h and further storage under high vacuum at 25 °C for 4 days: yield 3.80 g (93%); IR (KBr) cm^{-1} 3400, 2900, 1680, 1550, 1410, 1350, 1240, 1160, 1050, 940, 860, 840, 780; NMR (CCl_4) δ 0.04 (s, 9 H), 0.95 (m, 2 H), 1.43 (s, 3 H), 1.25–2.30 (m, 6 H), 3.15 (m, 2 H), 4.12 (m, 3 H), 5.00–5.80 (s, 3 H). Anal. Calcd for $C_{17}H_{34}N_2SiO_6$: C, 52.28; H, 8.77; N, 7.17; Si, 7.19. Found: C, 52.13; H, 8.70; N, 7.05; Si, 7.47.

Method B. To a solution of 0.33 g of N^{ϵ}-Teoc-L-lysine (1.13 mmol) in 15 mL of 2 N Na_2CO_3 was added 0.307 g of 2-[[(*tert*-butyloxycarbonyl)oxy]imino]-2-phenylacetonitrile (1.25 mmol). The resultant solution was stirred overnight at 25 °C, and then extracted with chloroform (4 × 25 mL). The aqueous layer was acidified with 2 N HCl and extracted again with $CHCl_3$ (5 × 15 mL). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure at 25 °C to give an oil. Removal of the last traces of volatile material from this residue as described in the preceding experiment left 0.397 g (90% yield) of the desired product. TLC, IR, and NMR properties of the samples prepared by methods A and B were identical.

Selective Removal of N^{α}-Boc in the Presence of N^{ϵ}-Teoc. To a solution of 2.66 g of N^{α}-Boc-N^{ϵ}-Teoc-L-lysine (6.82 mmol) in 25 mL of ether was added a solution of 1.13 g of *p*-toluenesulfonic acid (6.89 mmol) in 5 mL of ethanol. Transfer of the *p*-toluenesulfonic acid was completed with the aid of 5 mL of ether. The solution was placed on a rotary evaporator and the ether removed at room temperature. Then, with continuing evacuation, the bath temperature was raised to 60–65 °C for 20 min, during which gas evolution was evident. The solid residue was taken up in 50 mL of distilled water and dissolved by addition of 1.4 mL of 5 N ammonium hydroxide at 30–35 °C. Upon being cooled back to 20–25 °C, the solution deposited a copious white solid, which was filtered and washed with 20 mL of water. The combined filtrate and washings were evaporated to dryness under reduced pressure (40 °C, 1.5 h). The white solid remaining was triturated with 20 mL of distilled water, filtered, and washed with another 15 mL of water. The combined solids were dried in vacuo at 80–90 °C overnight; yield 1.19 g (96%). Spectroscopic and mixture melting point measurements showed the product to be N^{ϵ}-Teoc-L-lysine, identical with the compound described above.

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Registry No. Ethyl 2-(trimethylsilyl)acetate, 4071-88-9; 2-(trimethylsilyl)ethanol, 2916-68-9; 4-nitrophenyl chloroformate, 7693-46-1; 2-(trimethylsilyl)ethyl 4-nitrophenyl carbonate, 80149-80-0; L-2,4-diaminobutyric acid copper complex, 54987-85-8; L-ornithine copper complex, 53109-82-3; L-lysine copper complex, 21512-99-2; bis[N^{γ}-[[2-(trimethylsilyl)ethoxy]carbonyl]-L-2,4-diaminobutyrato]copper(II), 85167-77-7; bis[N^{γ}-[[2-(trimethylsilyl)ethoxy]carbonyl]-L-ornithinato]copper(II), 85167-78-8; bis[N^{ϵ}-[[2-(trimethylsilyl)ethoxy]carbonyl]-L-lysinato]copper(II), 85167-79-9; N^{γ}-Teoc-L-2,4-diaminobutyric acid, 85167-73-3; N^{δ}-Teoc-L-ornithine, 85167-74-4; N^{ϵ}-Teoc-L-lysine, 85167-75-5; N^{α}-Boc-L-lysine, 13734-28-6; N^{α}-Boc-N^{ϵ}-Teoc-L-lysine, 85167-76-6; 2-[[(*tert*-butoxycarbonyl)oxy]imino]-2-phenylacetonitrile, 58632-95-4.