(w) 291, 207 (s). Anal. Calcd for $C_{21}H_{22}N_2O_5$ (mol wt 382.4): C, 65.96; H, 5.80; N, 7.32. Found: C, 65.88; H, 5.91; N, 7.37.

Benzyl 4,6-*O*-Benzylidene-α-D-mannopyranosido-[2,3:5′,6′]pyrazan-2′,3′-dione (27). Compound **24** (0.74 g, 2 mmol), diethyl oxalate (1.5 mL), and anhydrous ethanol (20 mL) were boiled on reflux for 20 h. Solvents were evaporated in vacuo, and the residue was treated with diisopropyl ether. The resulting crystals were filtered off and were recrystallized from hot dioxane by addition of 1 volume of tetrahydrofuran and 20 volumes of diisopropyl ether. Rapid stirring caused precipitation of an easily filterable form of **27**: 0.7 g (85%); mp 297 °C; $[\alpha]^{22}$ –60° (*c* 1.75, dioxane); mass spectrum (240–280 °C), *m/e* 410, 409 (w), 319 (m), 207, 107, 105, 91 (s). Anal. Calcd for $C_{22}H_{22}N_2O_6$ (mol wt 410.4): C, 64.38; H, 5.40; N, 6.83. Found: C, 63.84; H, 5.56; N, 6.79.

Registry No. **1**, 2873-29-2; **2**, 79698-04-7; **3**, 79698-03-6; **4**, 81625-86-7; **5**, 81625-87-8; **6**, 81625-88-9; **7**, 81625-89-0; **8**, 81625-90-3; **9**, 81625-91-4; **10**, 72869-11-5; **11**, 81625-92-5; **12**, 81625-93-6; **13**, 81625-94-7; **14**, 81625-95-8; **15**, 35905-39-6; **16**, 81625-96-9; **17**, 81625-97-0; **18**, 81625-98-1; **19**, 81625-99-2; **20**, 81626-00-8; **21**, 81626-01-9; **22**, 72869-08-0; **22a**, 81626-02-0; **23**, 72869-09-1; **23a**, 81655-20-1; **24**, 81626-03-1; **25**, 81626-04-2; **25a**, 81626-05-3; **26**, 81626-06-4; **27**, 81655-21-2; NaN_3, 26628-22-8; CO_2, 124-38-9; HMPT, 680-31-9.

Amino-Protecting Reagents: New Promising Reagents for *tert*-Butoxycarbonylation, Benzyloxycarbonylation, and [β-(Trimethylsilyl)ethoxy]carbonylation

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A new method for the preparation of *tert*-butyl- (**1d**), benzyl- (**1e**), and (β-trimethylsilyl)ethyl α-methoxyvinyl carbonates (**1f**) has been devised. The reaction of these reagents with amino compounds proceeds rapidly under mild conditions to give the corresponding *N*-*tert*-butoxycarbonylated (*N*-Boc), *N*-benzyloxycarbonylated (*N*-Z), and *N*-[β-(trimethylsilyl)ethoxy]carbonylated (*N*-Tmseoc) compounds in quantitative yields. Twenty-two examples using amines, amino alcohols, and amino acids were presented.

We have described[1] a preparation of α-methoxyvinyl carbonates (**1a–c**) and their utility for carboalkoxylation and carboaryloxylation of amines. The high reactivity of the reagents under extremely mild conditions (generally performed at 0–20 °C for 1 min–3 h) prompted us to prepare the similar introducing reagents *tert*-butyl- (**1d**), benzyl- (**1e**), and (β-trimethylsilyl)ethyl α-methoxyvinyl carbonate (**1f**) for the *tert*-butoxycarbonylation,[2,3] benzyloxycarbonylation,[2,3w,x,4] and [β-(trimethylsilyl)ethoxy]-carbonylation,[2,5] which are widely employed as useful aminoprotecting methods. However, the previous preparative method involving the reaction of bis[(carbomethoxy)-methyl]mercury with the corresponding chloroformate failed entirely to give the alkyl α-methoxyvinyl carbonates **1d–f** because of instability of the chloroformates.

We report here an efficient preparation of **1d–f** and their potential utility for amino protection.

Preparation of Alkyl α-Methoxyvinyl Carbonates 1d–f. Although direct O-carboalkoxylation of the enolate of methyl acetate with the corresponding chloroformate seems to be a simple route to the reagents **1**, complications were caused by the ambident nature of the enolate as observed in the preparation of isopropenyl carbonates.[1b] Since then, we have succeeded[1a] in the preparation of the α-methoxyvinyl carbonates (**1a–c**) involving the reaction of chlorocarbonate with bis[(carbomethoxy)methyl]mercury[6] as the enolate equivalent of methyl acetate in refluxing toluene (method A, Scheme I). However, this method suffers from many difficulties in the preparation of **1d–f** because of the instability of the chloroformate under the conditions used, the strict control of the reaction conditions needed, and the elaborate purification of the product from the reaction mixture.[7] Success was finally

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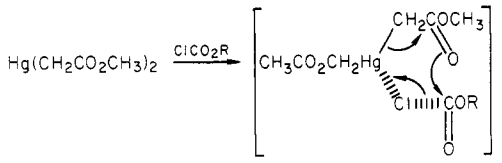
Table I. Preparation of Alkyl α-Methoxyvinyl Carbonates 1d-f

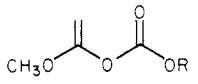
compd	R	yield,[a] %	bp (mmHg),[b] °C	IR ($CHCl_3$), cm^{-1}	^1H NMR ($CDCl_3$),[c] δ
1d[d]	t-C_4H_9	55	57-58 (4)	1760, 1670	1.48 (s, 9 H), 3.58 (d, J = 3.5, 1 H), 3.60 (s, 3 H), 3.76 (d, J = 3.5, 1 H)
1e[e]	$CH_2C_6H_5$	73	105-107 (0.7)	1770, 1675	3.58 (s, 3 H), 3.62 (d, J = 3.5, 1 H), 3.82 (d, J = 3.5, 1 H), 5.08 (s, 2 H), 7.25 (s, 5 H)
1f[f]	$CH_2CH_2Si(CH_3)_3$	65	108 (10)	1760, 1675	0.06 (s, 9 H), 1.10 (brt, 2 H), 3.68 (s, 3 H), 3.72 (d, J = 3.5, 1 H), 3.81 (d, J = 3.5, 1 H), 4.30 (brt, 2 H)

[a] Isolated yields were based on bis[(carbomethoxy)methyl]mercury. [b] Uncorrected boiling points are given. [c] J values are given in hertz. [d] Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 54.82; H, 8.24. [e] Exact mass calcd for $C_{11}H_{12}O_4$ 208.0733, found 208.0728. [f] Anal. Calcd for $C_9H_{18}O_3Si$: C, 49.51; H, 8.31. Found: C, 49.56; H, 8.61.

Scheme I

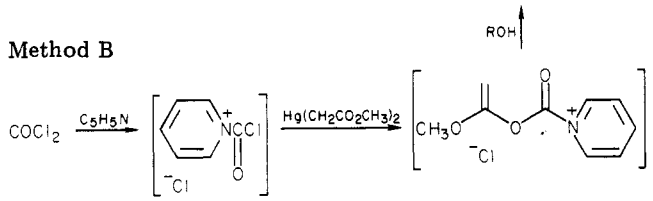
Method A





1a, R = C_2H_5
b, R = CH_3
c, R = C_6H_5
d, R = t-C_4H_9
e, R = $CH_2C_6H_5$
f, R = $CH_2CH_2Si(CH_3)_3$

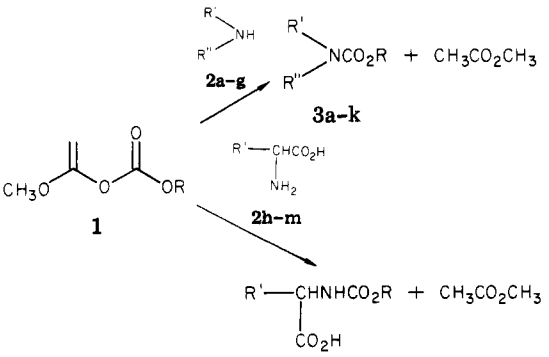
Method B



achieved by using the reaction of bis[(carbomethoxy)-methyl]mercury with phosgene[8] in the presence of pyridine followed by treatment in situ with the corresponding alcohol (method B, Scheme I). Processes involving the reaction of phosgene with other bases such as triethylamine, dimethylaniline, 4-benzylpyridine, quinoline, and γ,γ′-dipyridyl instead of pyridine were examined without satisfactory results. The characteristic point of the present method is the use of phosgene and alcohol in the presence of pyridine instead of the unstable chloroformate, and the reaction can be performed under mild conditions. The structures of **1d-f** were proved by microanalyses and IR and NMR spectral data. The data of structural importance are summarized in Table I. These reagents are very soluble in common organic solvents and can be handled under ordinary conditions.[9]

Amino Protection with Alkyl α-Methoxyvinyl Carbonates 1d-f. The reaction of the carbonates **1d-f** with amines **2a-g** is generally carried out by employing

Scheme II



equivalent amounts of the reagent and amine in an inert solvent such as methylene chloride or acetonitrile and usually brought to completion at low temperature for a short period to give a quantitative yield of the corresponding *N*-*tert*-butoxycarbonylated (*N*-Boc), *N*-benzyloxycarbonylated (*N*-Z), and *N*-[β-(trimethylsilyl)ethoxy]carbonylated (*N*-Tmseoc) amines **3a-k**, respectively (Scheme II). In the case of amino acids, carboalkoxylation was performed by stirring a dioxane-water solution of amino acids **2h-m** with equivalent amounts of the reagent for a short period to give a quantitative yield of the corresponding *N*-Boc, *N*-Z, and *N*-Tmseoc amino acids (**3l-v**). All known products were identified by comparison with authentic samples. New compounds were characterized by ^1H NMR, IR, exact mass, and analytical data. The amino acids used, with the exception of glycine, are of L configuration. The reaction conditions, yields, and physical data are summarized in Table II. The advantages of these reagents are found in the reaction conditions, the high yields, the absence of base except for the starting amine, easiness of procedures, and formation of volatile methyl acetate as a single side product.

As explained in the previous paper,[1a] the reaction occurs by initial addition of the amine to the carbonyl carbon of **1d-f**, subsequent decomposition proceeding with an inter- or intramolecular proton transfer accelerated by a favorable enol-keto transformation.[10]

(7) A small quantity of **1d-f** was detected in the reaction mixture on monitoring by TLC.

(8) Phosgene was generated in situ by treatment of trichloromethyl chloroformate with active carbon: Masuyama, A. *J. Synth. Org. Chem. Jpn.* **1976**, *34*, 431 and references cited therein. Trichloromethyl chloroformate was obtained from Hodogaya Chemical Co., Ltd., Tokyo.

(9) They do not polymerize at room temperature or upon distillation and can be allowed to stand at room temperature for a few weeks or to be stored in the refrigerator for more than several months after the reagent bottle is flushed with nitrogen or argon.

(10) Recently we have reported analogous types of useful silylating and acetylating reagents using enol-keto transformations: (a) Kita, Y.; Haruta, J.; Segawa, J.; Tamura, Y. *Tetrahedron Lett.* **1979**, 4311. (b) Kita, Y.; Segawa, J.; Haruta, J.; Tamura, Y. *Tetrahedron Lett.* **1980**, 3779. (c) Tamura, Y.; Yoshimoto, Y.; Sakai, K.; Haruta, J.; Kita, Y. *Synthesis* **1980**, 887. (d) Kita, Y.; Haruta, J.; Fujii, T.; Segawa, J.; Tamura, Y. *Synthesis* **1981**, 451. (e) Kita, Y.; Segawa, J.; Haruta, J.; Yasuda, H.; Tamura, Y. *J. Chem. Soc., Perkin Trans. 1*, **1982**, 1099.

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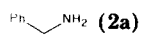
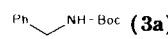
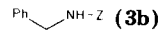
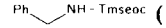
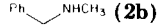
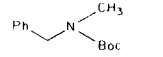
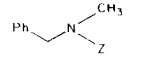
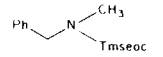
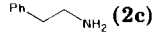
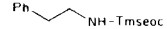
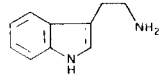
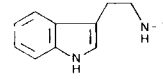
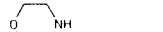
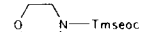
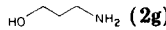
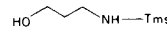
Table II. Preparation of *N*-Boc, *N*-Z, and *N*-Tmseoc Amines and Amino Acids

amine 2	product 3[a]	reaction conditions	yield,[b] %	bp,[c] °C (torr) [mp,[c,d] °C (recryst solv)]	$[\alpha]_D$ (*c*, solv; temp, °C),[e] deg
 (2a)	 (3a)	1d, CH_3CN, 55 °C, 10 h	92 (85)	[53-54 (ligroin)]	
	 (3b)	1e, CH_2Cl_2, 20 °C, 3.5 h	98 (95)	[83.5-84 (petroleum ether)]	
	 (3c)	1f, CH_2Cl_2, 20 °C, 1 h	90 (73)	158-160 (3.0)	
 (2b)	 3d	1d, CH_3CN, 50 °C, 2.5 h	99 (77)	73-74 (11)	
	 3e	1e, CH_3CN, 20 °C, 0.5 h	95 (76)	173-174 (2)	
	 3f	1f, CH_2Cl_2, 20 °C, 1 h	90 (80)	114-115 (0.9)	
 (2c)	 (3g)	1f, CH_2Cl_2, 20 °C, 1 h	94 (60)	174-175 (22)	
 2d	 3h	1f, CH_2Cl_2, 20 °C, 0.5 h	95 (87)	[69.5-70.5 (*n*-hexane)]	
 2e	 3i	1f, CH_2Cl_2, 20 °C, 0.5 h	97 (75)	92-93 (0.8)	
 2f	 3j	1f, CH_2Cl_2, 20 °C, 2 h	90 (85)	99-100 (1)	
 (2g)	 (3k)	1f, CH_2Cl_2, 20 °C, 1 h	95 (86)	143-145 (2)	
Gly (2h)	Boc-Gly (3l)	1d, dioxane-H_2O, 20 °C, 6 h	96	[88-89 (AcOEt-petroleum ether)]	
	Z-Gly (3m)	1e, dioxane-H_2O, 20 °C, 2 h	90	[123 ($CHCl_3$)]	
	Tmseoc-Gly (3n)	1f, dioxane-H_2O, 20 °C, 1.5 h	99	[47-48 (petroleum ether)]	
Ala (2i)	Boc-Ala (3o)	1d, dioxane-H_2O, 20 °C, 5 h	98	[80-81 (ether-petroleum ether)]	−24.8 (0.712, AcOH; 25)
	Z-Ala (3p)	1e, dioxane-H_2O, 20 °C, 1 h	91	[86-87 (AcOEt-petroleum ether)]	−14.5 (0.206, AcOH; 27)
Phe (2j)	Boc-Phe (3q)	1d, dioxane-H_2O, 20 °C, 7.5 h	98	[76-79 (AcOEt-petroleum ether)]	−3.91 (0.792, AcOH; 25)
	Z-Phe (3r)	1e, dioxane-H_2O, 20 °C, 5 h	91	[86-87 (AcOEt-petroleum ether)]	+5.54 (0.361, AcOH; 18)
Pro (2k)	Boc-Pro (3s)	1d, dioxane-H_2O, 20 °C, 5 h	98	[136-137 (MeC(O)Et-petroleum ether)]	−60.57 (0.974, AcOH; 25)
	Z-Pro (3t)	1e, dioxane-H_2O, 20 °C, 0.5 h	89	[76-77 (AcOEt-petroleum ether)]	−61.43 (0.171, AcOH; 20)
Val (2l)	Boc-Val (3u)	1d, dioxane-H_2O, 20 °C, 5 h	96	[78-79 (AcOEt-petroleum ether)]	−5.64 (0.46, AcOH; 25)
Ile (2m)	Boc-Ile (3v)	1d, dioxane-H_2O, 20 °C, 7,5 h	94	[66-68 (petroleum ether)]	+2.88 (0.792, AcOH; 25)

[a] The microanalyses of all novel products were in satisfactory agreement with the calculated values. [b] Yields were based on the amine or amino acid, and the purity of the products (≥95%) was determined by GLC, NMR, and TLC. Distilled or recrystallized yields carried out on an 1-3-mmol scale of amine with 1.0-1.1 equiv of reagent are given in parentheses. All products obtained from amino acids were purified by following descriptions in the literature. The melting points before recrystallization: **31**, 81-84.5 °C; **3m**, 120-121 °C; **3n**, 47-48 °C; **3o**, 77-79.5 °C; **3p**, 83-84.5 °C; **3q**, 74-78 °C; **3r**, 84-85 °C; **3s**, 123.5-124 °C; **3t**, 73-74 °C; **3u**, 74-78 °C; **3v**, 62-63.5 °C. [c] Uncorrected boiling and melting points are given. [d] The reported melting points (in °C) are as follows: **3a**, lit.[11] 53-54; **3b**, lit.[11] 95-95.5, lit.[12] 90-91; **31**, lit.[3a] 88.5-89, lit.[13] 94-95; **3m**, lit.[4a] 120, lit.[14,15] 119-120; **3o**, lit.[3a] 83-84, lit.[16] 81; **3p**, lit.[17] 87; **3q**, lit.[3a] 79-80, lit.[18] 85-87; **3r**, lit.[19] 88-89, lit.[20] 87; **3s**, lit.[3a] 136-137, lit.[16] 133-134; **3t**, lit.[19] 77, lit.[21] 78-80, lit.[22] 76-77; **3u**, lit.[3a] 77-79, lit.[16] 80; **3v**, lit.[13] 66-68. [e] Optical rotations of the known compounds were within the limit of error in comparison with the reported values. The reported $[\alpha]_D$ values (in degrees) are as follows: **3o**, lit.[3a] −22.4 (*c* 2.1, AcOH), 25 °C, lit.[16] −24.9 (*c* 2.05, AcOH), 22 °C; **3p**, lit.[17] −13.9 (*c* 2, AcOH), 27 °C; **3q**, lit.[3a] −0.8 (*c* 4.96, AcOH), 25 °C, lit.[18] −4.1 (*c* 5, AcOH); **3r**, lit.[19] +5.1 (*c* 2, EtOH), 22 °C, lit.[20] +5.3 (*c* 6.6, AcOH), 18 °C; **3s**, lit.[3a] −60.2 (*c* 2.01, AcOH), 25 °C, lit.[16] −60.8 (*c* 2.04, AcOH) AcOH), 25 °C; **3t**, lit.[19] −60.5 (*c* 2, AcOH), 20 °C, −40.6 (*c* 2, EtOH), 20 °C, lit.[21] −61.0 (*c* 2, AcOH), 23 °C, lit.[22] −61.7 (*c* 5.3, AcOH), 20 °C; **3u**, lit.[3a] −5.8 (*c* 1.21, AcOH), 25 °C, lit.[16] −6.9 (*c* 2.01, AcOH), 28 °C; **3v**, lit.[3a] +3 ± 0.5 (*c* 2.005, AcOH), 25 °C, lit.[13] +2.5 (*c* 1, AcOH), 25 °C.

Experimental Section[23]

Preparation of Bis[(Carbomethoxy)methyl]mercury. Through a stirred suspension of mercury(II) oxide (21.7 g, 0.1 mol) and mercury(II) acetate (31.8 g, 0.01 mol) in dry methanol (217 mL) at room temperature was gently bubbled ketene, generated by the thermal decomposition of acetone. The reddish suspension turned into a white suspension. Stirring for an additional 12 h under the same conditions gave a gray clear solution. The reaction mixture was concentrated in vacuo to give a white solid. The solid was washed with ether, dried under reduced pressure, and recrystallized from ethyl acetate to give the mercury compound: 18.7 g (54%); mp 98–99 °C (lit.[6] mp 100 °C); IR ($CHCl_3$) 1680, 1240 cm^{-1}; NMR ($CDCl_3$) δ 2.14 (s, 4 H), 3.64 (s, 6 H).

General Preparation of Alkyl α-Methoxyvinyl Carbonates (1a, d–e) by Method B (Hood!). To a well-stirred dry methylene chloride solution of phosgene[8] (3.4 M, 33 mL, 115 mmol) was added dropwise a solution of pyridine (10.9 g, 138 mmol) in methylene chloride (110 mL) at −20 °C over 5 min under argon. White-blue crystals precipitated with the addition of pyridine, and stirring was continued for 15 min under the same conditions. Then, a solution of bis[(carbomethoxy)methyl]mercury (50 g, 140 mmol) in dry methylene chloride (115 mL) was added dropwise to the cooled stirred mixture, which turned yellow and then was stirred for 1 h under the same conditions. To the resultant orange mixture was added dropwise a solution of the corresponding alcohol (345 mmol) in dry methylene chloride (58 mL) over 5 min under argon. The mixture was stirred at −20 °C for 15 min and at 0 °C for 30 min. *n*-Pentane (300 mL) was added to the stirred mixture, which was stirred for another 30 min and then at 25 °C for 30 min, while a red syrup was formed. After much of the excess phosgene was blown out of the system with argon (connected to a hood aspirator), the solution was separated from the syrup, and the residual syrup was extracted with ether (2 × 50 mL). The combined organic layer was washed with water (3 × 100 mL) and saturated aqueous sodium chloride (100 mL), dried over $MgSO_4$, and concentrated. Distillation gave a 55–73% yield of the desired carbonates (**1d–f**). The results are listed in Table I.

Similarly, ethyl α-methoxyvinyl carbonate (**1a**), which was obtained in a 43–54% yield by method A, was prepared: 88% yield; bp 85–91 °C (24 mmHg) [lit.[1a] bp 88–90 °C (26 mmHg)].

Typical Procedure for Conversion of Amine into (Carboalkoxy)amine. To a stirred solution of benzylamine (**2a**, 1 mmol) in methylene chloride (5 mL) was added **1e** (1.1 mmol) at room temperature. After 3.5 h, the solvent was removed in vacuo, and the residual syrup was tritulated with petroleum ether to give crystals. Recrystallization from petroleum ether gave pure (benzyloxycarbonyl)benzylamine (**3b**), identical in all respects with an authentic sample.

The unknown (carboalkoxy)amines **3c–k** prepared from the appropriate alkyl α-methoxyvinyl carbonates and amines are as follows.

[[β-(Trimethylsilyl)ethoxy]carbonyl]benzylamine (3c): NMR ($CDCl_3$) δ 0.04 (s, 9 H) 1.01 (br t, 2 H), 4.16 (br t, 2 H), 4.28 (d, 2 H), 4.4–5.2 (br s , 1 H), 7.23 (s, 5 H); IR ($CHCl_3$) 1700 cm^{-1}. Anal. Calcd for $C_{13}H_{21}NO_2Si$: C, 62.11; H, 8.42; N, 5.57. Found: C, 62.35; H, 8.62; N, 5.68.

***N*-(*tert*-Butoxycarbonyl)-*N*-methylbenzylamine (3d)**: NMR ($CDCl_3$) δ 1.48 (s, 9 H), 2.81 (s, 3 H), 4.43 (s, 2 H), 7.72 (s, 5 H); IR ($CHCl_3$) 1680 cm^{-1}; exact mass calcd for $C_{13}H_{19}NO_2$ 221.1415, found 221.1420.

***N*-(Benzyloxycarbonyl)-*N*-methylbenzylamine (3e)**: NMR ($CDCl_3$) δ 2.88 (s, 3 H), 4.49 (s, 2 H), 5.18 (s, 2 H), 7.25 (s, 10 H); IR ($CHCl_3$) 1670 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.23; H, 6.83; N, 5.51.

***N*-[[β-(Trimethylsilyl)ethoxy]carbonyl]-*N*-methylbenzylamine (3f)**: NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.06 (br t, 2 H), 2.81 (s, 3 H), 4.21 (br t, 2 H) 4.43 (s, 2 H), 7.20 (s, 5 H); IR ($CHCl_3$) 1670 cm^{-1}. Anal. Calcd for $C_{14}H_{23}NO_2Si$: C, 63.35; H, 8.73; N, 5.28. Found: C, 63.13; H, 8.83; N, 5.51.

***N*-[[β-(Trimethylsilyl)ethoxy]carbonyl]phenethylamine (3g)**: NMR ($CDCl_3$) δ 0.04 (s, 9 H), 0.98 (br t, 2 H), 2.80 (t, 2 H), 3.43 (q, 2 H), 4.15 (br t, 2 H), 7.23 (s, 5 H); IR ($CHCl_3$) 1700 cm^{-1}. Anal. Calcd for $C_{14}H_{23}NO_2Si$: C, 63.35; H, 8.73; N, 5.28. Found: C, 63.67; H, 8.78; N, 5.36.

***N*-[[β-(Trimethylsilyl)ethoxy]carbonyl]tryptamine (3h)**: NMR ($CDCl_3$) δ 0.05 (s, 9 H), 0.94 (br t, 2 H), 2.90 (br t, 2 H), 3.44 (br q, 2 H), 4.14 (br t, 2 H), 4.30 (br s, 1 H), 6.6–7.7 (m, 5 H), 8.43 (br s, 1 H); IR ($CHCl_3$) 1690 cm^{-1}. Anal. Calcd for $C_{16}H_{24}N_2O_2Si$: C, 63.12; H, 7.94; N, 9.20. Found: C, 63.38; H, 8.09; N, 9.32.

***N*-[[β-(Trimethylsilyl)ethoxy]carbonyl]morphorine (3i)**: NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.01 (br t, 2 H), 3.43 (m, 8 H), 4.12 (br t, 2 H); IR ($CHCl_3$) 1670 cm^{-1}. Anal. Calcd for $C_{10}H_{21}NO_3Si$: C, 51.91; H, 9.15; N, 6.05. Found: C, 51.85; H, 9.35; N, 6.19.

***N*-[[β-(Trimethylsilyl)ethoxy]carbonyl]imidazole (3j)**: NMR ($CDCl_3$) δ 0.06 (s, 9 H), 1.15 (br t, 2 H), 4.46 (br t, 2 H), 7.0 (br s, 1 H), 7.35 (br s, 1 H), 8.06 (br s, 1 H); IR ($CHCl_3$) 1740 cm^{-1}. Anal. Calcd for $C_7H_{16}N_2O_2Si$: C, 50.91; H, 7.60; N, 13.19. Found: C, 50.93; H, 7.61; N, 13.33.

γ-[[[β-(Trimethylsilyl)ethoxy]carbonyl]amino]propanol (3k): NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.0 (br t, 2 H), 1.72 (q, 2 H), 3.30 (q, 2 H), 3.67 (br q, 2 H), 4.13 (br t, 2 H), 4.95 (br s, 1 H); IR ($CDCl_3$) 1680 cm^{-1}. Anal. Calcd for $C_9H_{21}NO_3Si$: C, 49.28; H, 9.65; N, 6.39. Found: C, 49.21; H, 9.77; N, 6.67.

Typical Procedure for Conversion of an Amino Acid into a (Carboalkoxy)amino Acid. To a solution of L-phenylalanine (**2j**, 1 mmol) in dioxane–water (1:1, 4 mL) was added triethylamine (1.5 mmol). After the mixture was stirred at room temperature for 30 min, a solution of **1d** (1 mmol) in dioxane (0.5 mL) was added, and the mixture was stirred at room temperature for 5 h, acidified by 5% methanolic citric acid (pH 3–5), and extracted with ethyl acetate (3 × 15 mL). The extract was washed with saturated aqueous sodium chloride, dried over $MgSO_4$, and concentrated in vacuo to give a solid, which was recrystallized from ether–petroleum ether to give pure (*tert*-butoxycarbonyl)-L-phenylalanine (**3q**), identical in all respects with an authentic sample.[3a]

The unknown [[β-(trimethylsilyl)ethoxy]carbonyl]glycine (**3n**) was prepared from **1f** and glycine: NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.01 (br t, 2 H), 3.95 (d, 2 H), 4.16 (br t, 2 H), 5.24 (br s, 1 H), 7.87 (br s, 1 H); IR ($CDCl_3$) 1710 cm^{-1}. Anal. Calcd for $C_8H_{17}NO_4Si$: C, 49.28; H, 9.65; N, 6.39. Found: C, 49.21; H, 9.77; N, 6.67.

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Registry No. **1a**, 74877-64-8; **1d**, 81616-10-6; **1e**, 81616-11-7; **1f**, 81616-12-8; **2a**, 100-46-9; **2b**, 103-67-3; **2c**, 64-04-0; **2d**, 61-54-1; **2e**, 110-91-8; **2f**, 288-32-4; **2g**, 156-87-6; **2h**, 56-40-6; **2i**, 56-41-7; **2j**, 63-91-2; **2k**, 147-85-3; **2l**, 72-18-4; **2m**, 73-32-5; **3a**, 42116-44-9; **3b**, 39896-97-4; **3c**, 81616-13-9; **3d**, 81616-14-0; **3e**, 81616-15-1; **3f**, 81616-16-2; **3g**, 81616-17-3; **3h**, 81616-18-4; **3i**, 81616-19-5; **3j**, 81616-20-8; **3k**, 81616-21-9; **3l**, 4530-20-5; **3m**, 1138-80-3; **3n**, 81616-22-0; **3o**, 15761-38-3; **3p**, 1142-20-7; **3q**, 13734-34-4; **3r**, 1161-13-3; **3s**, 15761-39-4; **3t**, 1148-11-4; **3u**, 13734-41-3; **3v**, 13139-16-7; bis[(carbomethoxy)methyl]mercury, 3600-21-3; phosgene, 75-44-5; ethyl alcohol, 64-17-5; *tert*-butyl alcohol, 75-65-0; benzyl alcohol, 100-51-6; 2-(trimethylsilyl)ethanol, 2916-68-9.

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