tical ir spectra with those of the analyzed dipeptides in both series.

Racemization Rate Studies on Active Esters.—The racemization rate studies were carried out in tetrahydrofuran solution with active ester concentrations of 0.05 *M* and 1, 7, and 35 equiv of triethylamine at 23 ± 1°. The preparation and storage of all solutions for the rate studies using 7 equiv of triethylamine were carried out in a glove bag under a dry nitrogen atmosphere. The racemization experiments with 1 and 35 equiv of triethylamine were performed using anhydrous solutions in the open atmosphere. All kinetics were followed at 589 nm. The first observed rotations were taken within 5 min of mixing the reagents. The pseudo-first-order data for the 7 equiv of triethylamine were plotted and found to be linear up to 90% racemization for all the esters. The second-order rate constants listed in Table I were obtained by dividing the pseudo-first-order rate constants by the triethylamine concentration. An unweighted linear least-squares computer program was routinely used to evaluate all kinetic data.

The second-order racemization rate constants for 1 and 35 equiv of triethylamine were calculated from the initial rates and were identical within experimental error with those obtained from the racemization with 7 equiv of triethylamine.

For the experiments with 1 and 35 equiv of triethylamine, after 95% reaction time the tetrahydrofuran solutions were evaporated under vacuum and the residues were used for racemate identification. The racemized active esters were analyzed using infrared spectroscopy and thin layer chromatography. The residue from the 1-equiv experiments was compared in chloroform solution with the pure L isomer; in all cases the ir spectra of the DL isomers were essentially identical with that of the L isomer. A thin layer chromatogram ($CHCl_3$–MeOH, 9:1) showed the DL compound and a very small amount of phenol which may have resulted from the hydrolysis of the active esters during the course of the experiments. In the case of 35 equiv of triethylamine experiments the thin layer chromatograms indicated more extensive hydrolysis. The extent of hydrolysis seems to be parallel with the reactivity of the ester. This was supported by infrared spectra, which showed the free carboxyl group absorptions.

One racemized active ester from each series was isolated, recrystallized, and characterized by elemental analysis.

Racemized *N*-Carbobenzoxy-γ-methylglutamic Acid Pentachlorophenyl Ester.—The residue from the racemization experiment with 35 equiv of triethylamine was triturated with ether and filtered, mp 118–120°. After two recrystallizations from methanol the compound was dried over P_2O_5 under vacuum at 75° for 2 hr, mp 119–120°, $[\alpha]^{23}D$ 0.00 (*c* 2, ethyl acetate). *Anal.* Calcd for $C_{20}H_{16}NO_6Cl_5$: C, 44.19; H, 2.97. Found: C, 43.70; H, 2.97.

Racemized *N*-Carbobenzoxy-β-methylaspartic Acid Pentachlorophenyl Ester.—This ester was isolated similarly to the glutamic acid active ester which is described above. The crude compound, mp 125–126°, was recrystallized from methanol–water and a second time from methanol–ether, mp 122–124°, $[\alpha]^{23}D$ −0.9 (*c* 2, tetrahydrofuran). *Anal.* Calcd for $C_{19}H_{14}NO_6Cl_5$: C, 43.09; H, 2.66. Found: C, 42.71; H, 2.78.

Registry No.—*N*-Carbobenzoxy-γ-methyl-L-glutamic acid, 4652-65-7; *N*-carbobenzoxy-β-methyl-L-aspartic acid, 3160-47-2; triethylamine, 121-44-8; valine methyl ester, 4070-48-8; 1-cyclohexyl-3-(2-morpholinoethyl)-carbodiimide metho-*p*-toluenesulfonate, 4641-47-8; pentafluorophenol, 771-61-9; *N*-carbobenzoxy-γ-methylglutamic acid pentachlorophenyl ester racemate, 39994-03-1; *N*-carbobenzoxy-β-methylaspartic acid pentachlorophenyl ester racemate, 39994-04-2.

Acknowledgment.—This work was supported by Grant No. GM-08795 from the National Institutes of Health.

Reactions of *tert*-Butyl Trimethylsilyl Carbonate and of Bistrialkylsilyl Carbonates with Amino Acids. Carbon-13 Chemical Shifts in Carbonates and Silyl Carbonate Derivatives

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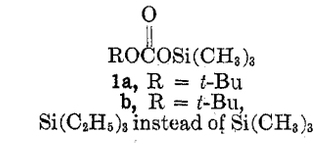
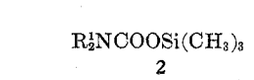
A number of bistrialkylsilyl carbonates, $R_3SiOC(=O)OSiR_3'$, have been prepared. The recently described *tert*-butyl trimethylsilyl carbonate (**1a**) has been shown to react with α-amino acid esters to form the corresponding silylurethanes, $RC(NHCOOR')HCOOR''$, where $R' = Si(CH_3)_3$. Under more drastic conditions, the completely silylated amino acid derivatives are formed. All of the silylated derivatives are hydrolyzed by moist ether to the parent amino acids or esters; with L-tyrosine, complete silylation followed by hydrolysis with moist ether regenerates the L-tyrosine, with no evidence of racemization. Bistriethylsilyl carbonate (**3c**) and *tert*-butyl triethylsilyl carbonate (**1b**) yield the same silylurethane from glycine ethyl ester. ^{13}C chemical shifts have been measured, and assignments of chemical shifts to specific types of carbon have been made for a series of carbonate esters, di- and tricarbonates, silyl carbonates, and *t*-BOC and other urethanes derived from glycine ethyl ester. As the number of carbonate groups in the molecule increases, the chemical shifts of the carbonyl carbons move to higher field. The presence of sulfur (in place of oxygen) next to the carbonyl carbon moves its chemical shift downfield ~16–18 ppm. Other regularities are noted.

Recently[1] we described the preparation of *tert*-butyl trimethylsilyl carbonate (**1a**) and related compounds;



1a, R = *t*-Bu
b, R = *t*-Bu, $Si(C_2H_5)_3$ instead of $Si(CH_3)_3$



2

it was shown that amines attacked **1a** to form the corresponding silylurethanes, $R_2'NCOOSi(CH_3)_3$, rather than the carbon urethanes (*t*-BOC derivatives), $R_2NCOOC(CH_3)_3$. Acid chlorides, however, attacked **1a** to form anhydrides, such as $ROC(=O)OC(=O)R^1$ (R = *t*-Bu, R^1 = CH_3 or OC_2H_5), presumably with the elimination of $ClSi(CH_3)_3$.

The present paper describes the reaction of **1a** with amino acids or their esters to form silylated derivatives analogous[2] to **2**. In a companion study in this labora-

(1) Y. Yamamoto and D. S. Tarbell, *J. Org. Chem.*, **36**, 2954 (1971).

(2) Similar silylated derivatives of amino acids, prepared in other ways, have been reported by H. R. Kricheldorf, *Synthesis*, 259 (1970); *Justus Liebigs Ann. Chem.*, **748**, 101 (1971); and earlier papers. Silylation of several amino acids by bis(trimethylsilyl)trifluoroacetamide for vpc analysis is reported by K. Bergstrom and J. Gurtler, *Acta Chem. Scand.*, **25**, 175 (1971), and references cited therein.

TABLE I

BISTRIALKYLSILYL CARBONATES, $RSiOC(=O)OSiR^1$

Compd[a]	Bp, °C (mm)	Yield, %	Ir, C=O (neat), cm^{-1}	Nmr (CCl_4), ppm
3b, R = $(CH_3)_3$; R^1 = $(C_2H_5)_3$	79–82 (3)	81	1705 1740	0.28 (s) 0.5–1.4 (m, A_3B_2)
3c, R = R^1 = $(C_2H_5)_3$	86–87 (1)	63	1705 1740	0.5–1.25 (m, A_3B_2)
3a, R = R^1 = $(CH_3)_3$	mp 26–30		1705, 1740 in CCl_4	0.28 (s)
3d, SiR = SiR^1 = $Si(CH_3)_2C(CH_3)_3$	90 (3), mp 60–63		1705 1735	0.25 (s), 0.93 (s) ratio 2:3

[a] All compounds showed C and H analyses within 0.4% of calculated values, except for R = R^1 = $(CH_3)_3$, which, in spite of several trials, showed carbon 0.5% away.

tory, it has been found that the recently available[3] di-*tert*-butyl dicarbonates react smoothly with amino acid esters to form the corresponding urethanes, $R^1CH(NHCOOR)COOEt$ or $R^1CH(NHCOSR)COOEt$ (R = *t*-Bu).[4]

We have also prepared some bistrialkylsilyl carbonates **3**, as shown in Table I, and have examined one of them as a silylating agent.

Compounds in Table I were prepared as follows.

$$R_3SiOH \xrightarrow[2.\ CO_2\quad 3.\ R^1_3SiCl]{1.\ NaH} RSiOCOSiR^1$$

3a, R = R^1 = $(CH_3)_3$
b, R = Et_3; R^1 = $(CH_3)_3$
c, R = R^1 = $(Et)_3$
d, SiR = SiR^1 = $Si(CH_3)_2C(CH_3)_3$

$$R_3SiOCOONa + COCl_2 \longrightarrow R_3SiOCOSiR_3$$

$$\text{no } R_3SiOCOCOCOSiR_3$$

The action of the *tert*-butyl trialkylsilyl carbonates (**1a**, **1b**) and of the bistriethylsilyl carbonate **3c** on several amino acids and amino acid esters yielded the results shown in Table II. The free tyrosine was insoluble in the silyl carbonate; heating at 100° gave gradual reaction and solution, leading to the completely silylated derivative[2] of tyrosine. Glycine ethyl ester was very readily silylated, once on nitrogen, to form the urethane analog, $N(CH_2COOEt)HCOOSi(CH_3)_3$, under mild conditions with a trace of tertiary base; the ethyl ester group and the NH group are unaltered by this treatment.

The reaction of *tert*-butyl trimethylsilyl carbonate with 4-hydroxy-L-proline showed that an alcohol group could be silylated as easily as a phenolic OH.

The reactions with valine and serine show the low reactivity of the hydrogen on the carbamate nitrogen or perhaps the sensitivity of the N–Si bond formed. In the case of valine no silylation of the nitrogen was observed. It is unlikely that it was decomposed on heating, since the tyrosine compound survived distillation at a much higher temperature. It is unlikely that only the N–Si bond would be completely hydrolyzed and none of the other positions affected, particularly since every precaution was taken to avoid exposure to water. The nmr of the serine derivative suggested that about 25% of the compound was not substituted on the N–H. This may have been due to fast hydrolysis or incomplete reaction.

The reason for the unreactivity of the valine NH is not evident. It might be due to the increased steric hindrance of the isopropyl group.

The completely silylated compounds were hydrolyzed very rapidly, even by shaking with moist ether at room temperature. The silylated derivative prepared from L-tyrosine was hydrolyzed in this way to regenerate tyrosine of rotation identical with that of starting material, and therefore no racemization had occurred during silylation or hydrolysis.

Treating triethylsilanol with di-*tert*-butyl tricarbonate led to the mixture shown below, as indicated by ir and nmr spectra. Attempts to convert triethylsilano

$$(C_2H_5)_3SiOH + ROCOCOCOR \downarrow$$

$$ROCOSi(C_2H_5)_3 + ROCOCOR$$

R = *t*-Bu

to the corresponding tricarbonate, $R_3SiOCOOCOO-COOSiR_3$, by sodium hydride, CO_2, and $COCl_2$, in the usual way[3] gave a mixture, probably containing some of the tricarbonate, and more of the *tert*-butyl trialkylsilyl monocarbonate, as judged from the ir.

^{13}C Nmr Chemical Shifts in Mono-, Di-, and Tricarbonates and in Silyl Carbonates.—The availability of samples of fairly complete series of these compounds, resulting from this and earlier work in this laboratory,[1,3] allowed the determination of the ^{13}C chemical shifts of the carbons, including the carbonyl carbons in varied environments. The results are shown in Table III; because not all of the compounds measured are described in the present paper, the structural formulas in the tables are numbered with Roman numerals to facilitate discussion of the trends observed.

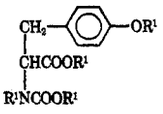
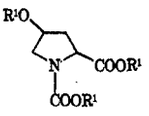
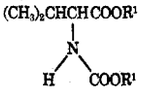
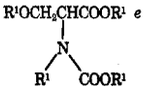
Discussion of ^{13}C Chemical Shifts.—The carbonate carbonyls absorb at the high-field end of the carbonyl region of the ^{13}C nmr spectrum. As the number of carbonate groups in the molecule increases, the chemical shifts of the carbonyl carbons move to higher field (compounds I, III, and VI, carbons c and d). The presence of sulfur in place of oxygen next to the carbonyl carbon drives its chemical shift downfield about 16–18 ppm (compounds IV, V, VII, and X, carbon c); however, the chemical shift of a carbonyl carbon one position removed from the sulfur (compounds IV, VII, and X, carbon d) moves slightly upfield. A nitrogen in place of the oxygen (compound XV,

(3) C. S. Dean, D. S. Tarbell, and A. W. Friederang, *J. Org. Chem.*, **35**, 3393 (1970).

(4) D. S. Tarbell, Y. Yamamoto, and B. M. Pope, *Proc. Nat. Acad. Sci. U. S.*, **69**, 730 (1972).

TABLE II

REACTIONS OF SILYL CARBONATES WITH AMINO ACIDS

Silylating agent (R = *t*-Bu)	Amino acid	Registry no.	Condition	Product,[c] R[1] = $Si(CH_3)_3$	Registry no.	Yield, %	Ir, C=O (neat), cm^{-1}
$ROCOOSi(CH_3)_3$	Gly	56-40-6	*a*	$R^1NCH_2COOR^1$ (COOR[1]) *d*	27762-05-6	89	1735, 1690
$ROCOOSi(CH_3)_3$	Tyr	60-18-4	*a*		40088-31-1	63	1730, 1690
$ROCOOSi(CH_3)_3$	Hypro	51-35-4	*a*		40088-32-2	78	1725, 1690
$ROCOOSi(CH_3)_3$	Val	72-18-4	*a*		40088-33-3	66	1680–1710 (broad)
$ROCOOSi(CH_3)_3$	Ser	56-45-1	*a*	 *e*	40088-34-4	72	1685–1720 (broad)
$ROCOOSi(CH_3)_3$	Gly OEt	459-73-4	*b*	$CH_2COOC_2H_5$ / $NHCOOR^1$	39982-07-5	82	3380 (NH), 1740–1760, 1680–1720
$ROCOOSi(C_2H_5)_3$	Gly OEt		*b*	$CH_2COOC_2H_5$ / $NHCOOSi(C_2H_5)_3$	39982-08-6	84	3370 (NH), 1745, 1690
$(C_2H_5)_3SiOCOOSi(C_2H_5)_3$	Gly OEt		*b*	$CH_2COOC_2H_5$ / $NHCOOSi(C_2H_5)_3$		84	3370 (NH), 1745, 1690

[a] Heated at 100° for *ca.* 16 hr. [b] Treated with a trace of Et_3N in ether at reflux or room temperature for 30 min. [c] Compounds were purified by distillation and showed satisfactory C and H analyses. The nmr spectra were in agreement with the expected values, and showed expected splitting patterns. [d] This compound was reported, along with some analogs, by H. R. Kricheldorf, *Synthesis*, 259 (1970), prepared by a different method. [e] The analogous DL-serine compound has been reported by H. R. Kricheldorf, ref *d* above.

carbon e) also drives the chemical shift to lower field. A carbonyl carbon with a nitrogen and a sulfur attached (compound XVI, carbon e) has a chemical shift in the same region as that with sulfur and oxygen attached. However, replacement of the *tert*-butyl groups with trialkylsilyl groups (compounds XII, carbon d, and XIII, carbon e) has only a very minor effect upon the chemical shift of the carbonyl carbon. Maciel[5] attributes the shifts to higher field upon attachment of more electronegative groups to the carbonyl carbon to a change in the π bond polarity of the carbonyl group owing to withdrawal of electrons from the carbonyl oxygen.

The chemical shifts of the *tert*-butyl carbons do not yield any unexpected results. The central carbon attached to oxygen is more deshielded than that attached to sulfur, as would be expected from the electronegativities of the two atoms. The outer carbons are rather insensitive to the structure of the rest of the molecule.

Experimental Section[6]

***tert*-Butyl triethylsilyl carbonate (1b)** was prepared from potassium *tert*-butylcarbonate and triethylchlorosilane by the method described earlier for the trimethylsilyl compound[1] **1a**, in 58% yield: bp 62–64° (1 mm); ir (CCl_4) 1755, 1720 cm^{-1} (C=O); nmr (CCl_4) 1.43 (s, 9 H), 0.6–1.35 ppm (m, 5 H, C_2H_5).

Anal. Calcd for $C_{11}H_{24}O_3Si$: C, 56.85; H, 10.41. Found: C, 56.60; H, 10.21.

Triethylsilyl Trimethylsilyl Carbonate (3b).—A 50% dispersion of sodium hydride (0.55 g) was washed with three 10-ml portions of THF and suspended in 30 ml of THF. To the suspension was added dropwise a solution of triethylsilanol[7] (1.38 g) in THF (20 ml) with stirring at room temperature; stirring was continued for an additional 45 min. Dry CO_2 gas was then passed for 30 min into the mixture, cooled with an ice–salt bath. A solution of chlorotrimethylsilane (1.09 g) in THF (15 ml) was added dropwise. Stirring and cooling were continued for 30 min more. An insoluble material was filtered off. The solvent was removed at room temperature, and distillation of the residual liquid gave a colorless liquid (2 g, 81%), bp 79–82° (3 mm).

Anal. Calcd for $C_{10}H_{24}O_3Si_2$: C, 48.34; H, 9.74. Found: C, 48.64; H, 9.72.

The other compounds in Table I were prepared by similar procedures. The bistrimethylsilyl carbonate decomposed on attempted distillation.

Complete Silylation of Tyrosine (Table II, Method A).—A mixture of 2.9 g (0.015 mol) of *tert*-butyl trimethylsilyl carbonate (**1a**) and 0.45 g (0.0025 mol) of L-tyrosine (99+%, Aldrich, used without purification) was heated at 90–100° (bath temperature) for 16 hr with stirring. Distillation of the reaction mixture gave a colorless, viscous liquid, bp 146–150° (0.3 mm), 0.8 g (63% based on tyrosine). Its properties were ir (liquid film) 1730, 1690 cm^{-1} (C=O); nmr (CCl_4) singlets of $Si(CH_3)_3$ groups at 0.11, 0.35, 0.38, and 0.41, a multiplet of $-CHCH_2-$ at 2.7–3.9, and four aromatic protons at 6.7–7.16 ppm.

Anal. Calcd for $C_{22}H_{43}O_5NSi_4$: C, 51.42; H, 8.43; N, 2.72. Found: C, 51.77; H, 8.63; N, 2.97.

Hydrolysis of silylated tyrosine was carried out by dissolving 0.75 g of the silylated compound in 30 ml of moist ether and stirring for 30 min at room temperature. The solvent was evaporated and the residue was dried at reduced pressure by an aspirator. The residual solid (0.3 g) was dissolved in 5 ml of 1 *N* HCl, and the insoluble material (possibly a polymer of silicone compound) was removed by filtration. The clear layer was

(5) G. E. Maciel, *J. Chem. Phys.*, **42**, 2746 (1965).

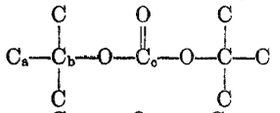
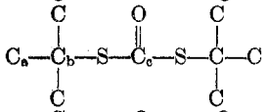
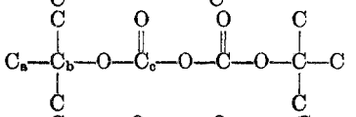
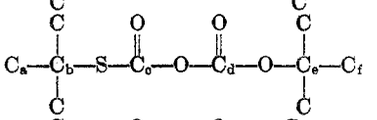
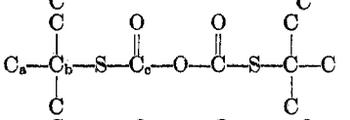
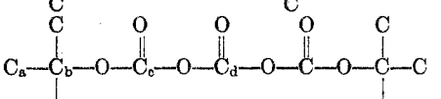
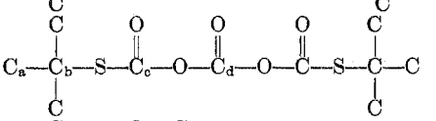
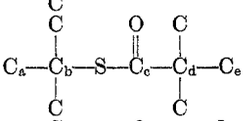
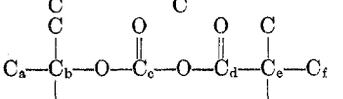
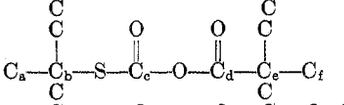
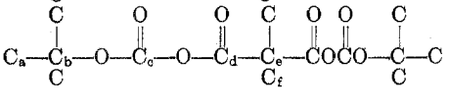
(6) Instrumentation was as reported in earlier studies;[3] microanalyses were by Galbraith Laboratories.

(7) L. H. Sommer and L. J. Tyler, *J. Amer. Chem. Soc.*, **76**, 1030 (1954).

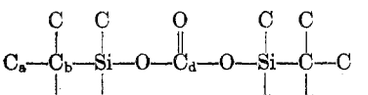
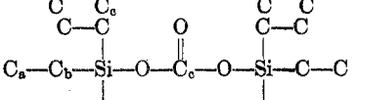
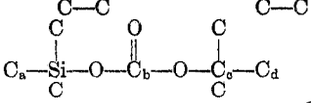
TABLE III

CHEMICAL SHIFTS OF ^{13}C FROM CS_2

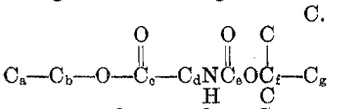
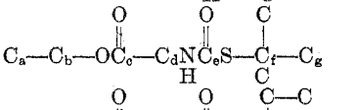
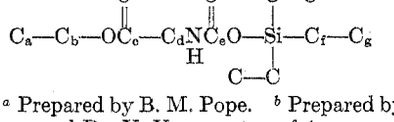
A. Carbonates, Esters, and Carbonic Anhydrides

Compd	No.	C_a	C_b	C_c	C_d	C_e	C_f	
	I	164.9	113.2	40.4				
	II	162.4	142.5	3.9				
	III[a]	164.8	108.0	45.8				
	IV[c]	163.0	144.5	28.3	46.6	107.7	165.2	
	V	163.5	144.0	28.8				
	VI[a]	165.5	105.7	48.1	49.0			
	VII	163.2	142.3	30.2	50.7			
	VIII[b]	162.2	145.5 or 146.0	−12.5	145.5 or 146.0	164.6		
	IX[b]	165.0 or 165.8	108.2	44.7	16.5	157.4	165.0 or 165.8	
	X[b]	162.9	144.2	28.4	20.5	152.5	165.8	
	XI[c]	165.2	107.2	46.8	26.1	141.9	171.2	

B. Silyl Carbonates

	XII	166.8	174.6	197.2	41.4			
	XIII	186.2	188.0	41.4				
	XIV	191.5	41.8	112.0	163.2			

C. *t*-BOC and Other *N*-Acyl Derivatives of Glycine Ethyl Ester

	XV[d]	178.7	132.0	22.7	150.0	37.1	115.6	162.5
	XVI[d]	178.8	131.7	23.7	150.5	25.5	145.3	162.0
	XVII[d]	178.7	131.9	22.9	149.7	37.6	187.8	186.1

[a] Prepared by B. M. Pope. [b] Prepared by R. L. Stanley. [c] Prepared by Dr. Y. Yamamoto, unpublished work. [d] Prepared by B. M. Pope and Dr. Y. Yamamoto, ref 4.

neutralized with 10% $NaHCO_3$. The precipitate formed was taken up by filtration, washed with a small amount of cold water, and dried over P_2O_5 at 56° *in vacuo;* 0.15 g of colorless solid, which decomposed at 309–312°, was obtained. Its optical rotation was $[\alpha]^{25}D$ −9.8° (*c* 4, 1 *N* HCl). L-Tyrosine used as starting material decomposed at 310–312° and its optical rotation was $[\alpha]^{25}D$ −10.0° (*c* 4, 1 *N* HCl).

The completely silylated glycine was likewise hydrolyzed to glycine, identified as hippuric acid.

Action of *tert*-Butyl Trimethylsilyl Carbonate with Glycine Ethyl Ester. Method B.—A solution of 2.8 g (0.0147 mol) of *tert*-butyl trimethylsilyl carbonate (**1a**), 1.5 g (0.0147 mol) of glycine ethyl ester, and 3 drops of Et_3N in 30 ml of dry ether was refluxed for 30 min. The reaction mixture was evaporated at reduced pressure by an aspirator and distilled. A colorless liquid, bp 86–87° (0.6 mm), 2.6 g (82%), was obtained with the following properties: ir (liquid film) 3380 (NH, broad), 1740–1760 (C=O), 1680–1720 cm^{-1} (C=O, broad); nmr (CCl_4) 0.28 [s, $Si(CH_3)_3$], 1.29 (t, $-CH_2CH_3$, J = 7.5 Hz), 4.17 (q, $-CH_2CH_3$, J = 7.5 Hz), 3.8 (d, NCH_2C, J = 6 Hz), 5.7 ppm (broad, NH). The ratios of protons were correct.

Anal. Calcd for $C_8H_{17}O_4NSi$: C, 43.81; H, 7.81; N, 6.39. Found: C, 44.03; H, 7.74; N, 6.33.

Hydrolysis of *N*-Trimethylsiloxycarbonyl Glycine Ethyl Ester to Glycine Ethyl Ester.—To a solution of 1.5 g of *N*-trimethylsiloxycarbonyl glycine ethyl ester in 20 ml of ether was added 0.5 ml of water with stirring at room temperature. Subsequently $MgSO_4$ was added, filtered off, and washed well with ether. The filtrate was combined with washings and evaporated. Distillation of the residual-liquid gave 0.5 g (83%) of glycine ethyl ester, bp 46–48° (10 mm), of which the ir spectrum (liquid film) and the nmr spectrum were identical in all respects with those of an authentic sample.

It was confirmed that the filtrate contained hexamethyldisiloxane, $(CH_3)_3SiOSi(CH_3)_3$, by vpc.

Action of *tert*-Butyl Trimethylsilyl Carbonate with L-4-Hydroxyproline (Method A).—A mixture of 2.9 g (0.015 mol) of *tert*-butyl trimethylsilyl carbonate and 0.3277 g (0.0025 mol) of L-4-hydroxyproline was treated as in the tyrosine case. Distillation gave a colorless liquid, bp 111° (0.1 mm), 0.7595 g (78%), with the following properties: ir (liquid film) 1690 and 1725 cm^{-1} (C=O, broad); nmr ($CDCl_3$) 0.12 (s, 9 H), 0.27 and 0.29 (two s, 9 H) and 0.30 (s, 9 H) [$Si(CH_3)_3$], 2.16 (m, 2 H ring protons, 3 position), 3.62 (m, 2 H ring protons, 5 position), 4.5 ppm (m, 2 H, ring protons, 2 and 4 positions).

Anal. Calcd for $C_{15}H_{33}NO_5Si_3$: C, 46.00; H, 8.49. Found: C, 45.84; H, 8.33.

Action of *tert*-Butyl Trimethyl Carbonate with L-Valine (Method A).—A mixture of 2.9 g (0.015 mol) of *tert*-butyl trimethylsilyl carbonate and 0.2907 g (0.00248 mol) of L-valine was treated as in the tyrosine case. Distillation gave a colorless liquid, bp 90° (1.2 mm), 0.4982 g (66%), with the following properties: ir (liquid film) 3330 (NH, broad), 1680–1710 cm^{-1} (C=O, broad); nmr ($CDCl_3$) 0.26 (s, 9 H), 0.28 (s, 9 H) [$Si(CH_3)_3$], 0.94 (d, 3 H, J = 7 Hz), 1.01 [d, 3 H, J = 7 Hz, $CH(CH_3)_2$], 2.10 [m, 1 H, $CH(CH_3)_2$], 4.28 (pair of d, 1 H, J = 4 and 9 Hz, α proton), 5.34 ppm (d, 1 H, J = 9 Hz, NH).

Anal. Calcd for $C_{12}H_{27}NO_4Si_2$: C, 47.18; H, 8.91. Found: C, 47.13; H, 8.89.

Action of *tert*-Butyl Trimethylsilyl Carbonate with L-Serine (Method A).—A mixture of 2.9 g (0.015 mol) of *tert*-butyl trimethylsilyl carbonate and 0.2621 g (0.0025 mol) of L-serine was treated as in the tyrosine case. Distillation gave a colorless liquid, bp 117° (0.5 mm), 0.7835 g (72%), with the following properties: ir (liquid film) 3440 (NH, weak), 1685–1720 cm^{-1} (C=O, broad); nmr ($CDCl_3$) 0.08 (s, 9 H), 0.23, 0.24, 0.26, and 0.30 (all s, 27 H) [$Si(CH_3)_3$], 4.06 (m, 3 H, α and β protons), 5.68 (d, J = 9 Hz, 1/4 H, NH).

Anal. Calcd for $C_{16}H_{39}NO_5Si_4$: C, 43.90; H, 8.98. Found: C, 43.60; H, 8.67.

Determination of ^{13}C Chemical Shifts.—The nmr spectra were taken on a Varian XL-100-15 spectrometer locked on deuteriobenzene. Except where the diluteness of the solution required accumulation, all of the spectra were single scan spectra taken with heteronoise decoupling of the protons. All of the spectra were taken in perdeuteriobenzene solution. The concentrations depended upon the availability of the compounds and their solubility in benzene. The chemical shifts were measured from deuteriobenzene and converted to parts per million from carbon disulfide by the equation[8]

$$S_{benzene} - S_{CS_2} = 65.0 \text{ ppm}$$

Assignments were made by comparison of spectra in the above series, along with data from the literature.

Registry No.—**1a,** 30882-87-2; **1b,** 39981-88-9; **3a,** 39981-89-0; **3b,** 39981-90-3; **3c,** 37170-06-2; **3d,** 39981-92-5; **I,** 34619-03-9; II, 16118-32-4; III, 24424-99-5; IV, 39981-96-9; V, 22085-40-1; VI, 24424-95-1; VII, 22085-39-8; VIII, 28058-96-0; IX, 39982-01-9; X, 28058-95-9; XI, 39982-03-1; XII, 14719-37-0; XVI, 37787-80-7; XVII, 39982-08-6; potassium *tert*-butyl carbonate, 39982-09-7; triethylchlorosilane, 994-30-9; triethylsilanol, 597-52-4; chlorotrimethylsilane, 75-77-4.

(8) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966, p 1003.