rected), 230 ml. Following the procedure given for the purification of **6**, 340 mg (53%) of **8** was obtained as a lightly colored oil, after chromatography. A small amount was rechromatographed to give the analytical sample: ir (neat) 3450–2450 (broad OH), 1690 (C=O) cm^{-1}; nmr δ 0.88 (dist. t, 3 H, CH_2CH_3), 0.94 (d, 3 H, $CHCH_3$), 1.27 (br m, 6 H, 3 × CH_2), 1.72 (q, 2 H, $CH_2CH_2CO_2$), 2.12 (t, 2 H, $C{=}CCH_2CH_2$), 2.20 (br s, 1 H, CHC≡C), 2.38 (t, 2 H, CH_2CO_2), 2.82 (br m, 6 H, 3 × $C{=}CCH_2C{=}C$), 5.06–5.46 (m, 8 H, 4 × CH=CH), 11.15 (br s, 1 H, CO_2H).

Anal. Calcd for $C_{21}H_{34}O_2$: C, 79.19; H, 10.76. Found: C, 79.09; H, 10.96.

Acknowledgment. We are indebted to the following members of our Physical Chemistry Department under the direction of Dr. R. P. W. Scott: Dr. F. Scheidl for elemental analyses, Dr. T. Williams for nmr spectra, and Mr. S. Traiman for ir spectra.

Registry No.—**1**, 20334-69-4; **2**, 53292-96-9; **3**, 1191-85-1; **4**, 506-32-1; *cis*-**5**, 53369-62-3; *trans*-**5**, 53292-97-0; 14-*cis*-**6**, 53292-98-1; 14-*trans*-**6**, 53368-42-6; **7**, 53292-99-2; **8**, 53319-93-0; 2,5-hexadiyn-1-ol, 28255-99-4; phosphorus tribromide, 7789-60-8; 5-hexynoic acid, 53293-00-8; ethyl bromide, 74-96-4; 3-methyl-*cis*-2-octen-1-ol, 30804-78-5; 3-methyl-*trans*-2-octen-1-ol, 30804-71-8; 15-methyl-14-*cis*-eicosaen-5,8,11-triynoic acid, 53293-01-9; 15-methyl-14-*trans*-eicosaen-5,8,11-triynoic acid, 53293-02-0; 4-methyl-2-octyn-1-ol, 53369-63-4; 3-methyl-1-heptyne, 53293-03-1; 16-methyl-5,8,11,14-eicosatetraynoic acid, 53293-04-2.

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Synthesis of Di- and Tripeptides Containing 4-Aminocyclohexanecarboxylic Acid

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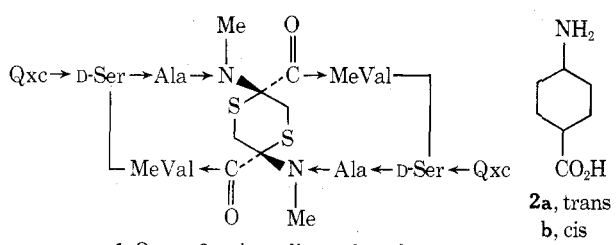
Studies of selected coupling methods for attachment of amino acid derivatives to *cis*- and *trans*-4-aminocyclohexanecarboxylic acid have shown diethylphosphoryl cyanide to be an effective coupling reagent. *N-tert*-Butyloxycarbonyl-*trans*-4-aminocyclohexanecarboxylic acid (**3a**) was converted, using diethylphosphoryl cyanide, to dipeptide **4a** by condensation with L-valine methyl ester. Dipeptide **4a** was transformed by deprotection and coupling with *N-tert*-butyloxycarbonyl-L-alanine to tripeptide **6a**. Similar transformations were effected using the *N-tert*-butyloxycarbonyl derivative **3b** of *cis*-4-aminocyclohexanecarboxylic acid. Other coupling procedures investigated were the carbodiimide, *p*-nitrophenyl active ester, and symmetrical anhydride methods; these methods were less satisfactory for effecting coupling to the above cyclohexaneamino acids.

The quinomycins[1] are a group of depsipeptide antibiotics that possess a depsipeptide lactone system interconnected by a 1,4-dithiane ring as shown for echinomycin (**1**). Our interest in the synthesis of quinomycin model systems that have a cyclohexane ring substituted for the dithiane moiety has resulted in an investigation of methods for attachment of amino acid derivatives to the simple model 4-aminocyclohexanecarboxylic acid (**2**).



2a, trans
b, cis

1, Qxc = 2-quinoxalinecarbonyl

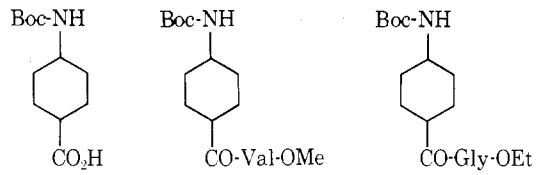
Interest in the preparation of peptide derivatives of 1-aminocyclopentane- and 1-aminocyclohexanecarboxylic acids was prompted by the reported[2] cytotoxic activity of the former substance. Amino acid derivatives were attached to the above cycloalkylamino acids by application of the acid chloride,[3a] carbodiimide,[3a-c] symmetrical anhydride,[3d] and oxazolone[3d] methods. Amino acids also have been attached to cyclohexylamine by use of active esters.[4]

In this study, *trans*-4-aminocyclohexanecarboxylic acid (**2a**)[5] was chosen as an appropriate model, since in the quinomycins the dithiane amino acid moiety has, in the 2,5 positions, amino and carboxyl groups in a trans relationship; studies were made also on the corresponding cis isomer **2b**. Conversion of **2** to the *N-tert*-butyloxycarbonyl derivative **3** was effected by standard procedures.[6] Initial attempts to couple glycine ethyl ester or L-alanine methyl ester to **3** using *N,N'*-dicyclohexylcarbodiimide[7] with or without added 1-hydroxybenzotriazole[8] were not successful. Similar failures employing the carbodiimide method in coupling reactions with cycloalkylamino acids have been observed.[3d,9]

Diethylphosphoryl cyanide recently has been shown[9] to be an effective coupling agent in peptide synthesis. Of significance, condensation of cyclohexylamine with benzoic acid was reported to give *N*-cyclohexylbenzamide in good yield using diethylphosphoryl cyanide, while none of the desired amide was obtained by the carbodiimide method.

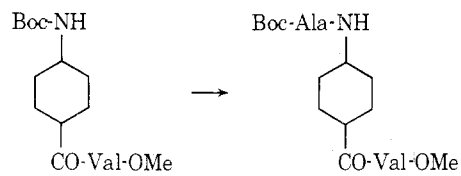
Treatment of *N-tert*-butyloxycarbonyl-*trans*-4-aminocyclohexanecarboxylic acid **3a** with L-valine methyl ester and diethylphosphoryl cyanide in dimethylformamide gave

dipeptide **4a** in 67% yield. In a similar manner, *N-tert*-butyloxycarbonyl-*cis*-4-aminocyclohexanecarbonyl-L-valine methyl ester (**4b**) was prepared in a yield of 64% from **3b**. Glycine ethyl ester was coupled to the cis isomer **3b** to give dipeptide **5** in a yield of 56% using the above method.



3a, trans **4a**, trans **5**
b, cis **b**, cis

Removal of the *N-tert*-butyloxycarbonyl group in dipeptides **4a** or **4b** with trifluoroacetic acid and subsequent coupling of *N-tert*-butyloxycarbonyl-L-alanine to the cyclohexyl amino group, using diethylphosphoryl cyanide, gave tripeptides **6a** and **6b** in yields of 44 and 47%, respectively.



4a, trans **6a**, trans
b, cis **b**, cis

Tripeptide **6a** thus represents a cyclohexane model of the tripeptide sequence containing the dithiane moiety present in the quinomycins.

Limited studies on application of the *p*-nitrophenyl active ester method[10] and the symmetrical anhydride method[3d] for attachment of amino acid derivatives to **3** have shown the above methods to be unpromising. Thus, the *p*-nitrophenyl ester of **3b** was observed not to couple to any appreciable extent with glycine ethyl ester in dimethylformamide. Addition of imidazole[4] to the reaction mixture caused reaction to occur; however, dipeptide **5** was obtained in a yield of only 20%. In the second method studied, reaction of **3b** with pivaloyl chloride gave the corresponding symmetrical anhydride[11] of **3b**, which upon reaction with L-valine methyl ester gave dipeptide **4b** in 10% overall yield. Efforts to maximize the yields obtained by the above two methods were not pursued further.

This study establishes that diethylphosphoryl cyanide is the reagent of choice for the attachment of amino acid derivatives to *cis*- or *trans*-4-aminocyclohexanecarboxylic acid. Further studies on the preparation of quinomycin model systems containing the above cyclohexane amino acids are underway.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-20A spectrophotometer. Nmr data were obtained with a Varian A-60 or XL-100 nmr spectrometer. Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6E mass spectrometrometer. Tlc data were measured on Brinkmann precoated silica gel plates in chloroform–methanol–acetic acid (85:10:5). Evaporations *in vacuo* were carried out with a Buchler rotary evaporator. Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich.

***N-tert*-Butyloxycarbonyl-*trans*-4-aminocyclohexanecarboxylic Acid (3a).** To a solution of 1.43 g (10 mmol) of *trans*-4-aminocyclohexanecarboxylic acid[5] and 0.80 g (20 mmol) of magnesium oxide in 30 ml of dioxane–water (1:1) was added 2.15 g (15 mmol) of *tert*-butyloxycarbonyl azide and the mixture was stirred at 45° overnight. Magnesium oxide was removed by filtration and washed with 50 ml of water. The filtrate was extracted with ether (3 × 25 ml), acidified with solid citric acid at 0°, and extracted with ethyl acetate (3 × 30 ml). The ethyl acetate solution was dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was recrystallized from ethyl acetate–petroleum ether (bp 60–90°) to give 1.56 g of white crystals (64%): mp 147–150°; nmr ($CDCl_3$) δ 3.5 (br s, cyclohexyl H_4), 2.6–1.5 (m, cyclohexyl except H_4), 1.45 (s, *tert*-butyl).

Anal. Calcd for $C_{12}H_{21}NO_4$: C, 59.2; H, 8.71; N, 5.76. Found: C, 59.18; H, 8.84; N, 5.57.

***N-tert*-Butyloxycarbonyl-*cis*-4-aminocyclohexanecarboxylic Acid (3b).** A solution of 2.86 g (20 mmol) of *cis*-4-aminocyclohexanecarboxylic acid[5] was treated as above for **3a** to give 3.95 g of white solid (81%), mp 163–168°. The solid was recrystallized from ethyl acetate: mp 167–169°; nmr (DMSO-d_6) δ 6.65 (d, 1 H, NH), 3.35 (s, 1 H, cyclohexyl H_4), 2.4 (s, 1 H, cyclohexyl H_1), 2.0–1.2 (m, 17 H, cyclohexyl except H_1 and H_4 and *tert*-butyl).

Anal. Calcd for $C_{12}H_{21}NO_4$: C, 59.2; H, 8.71; N, 5.76. Found: C, 59.40; H, 8.66; N, 5.66.

***N-tert*-Butyloxycarbonyl-*trans*-4-aminocyclohexanecarbonyl-L-valine Methyl Ester (4a).** To an ice-cold solution of 0.98 g (4.0 mmol) of *N-tert*-butyloxycarbonyl-*trans*-4-aminocyclohexanecarboxylic acid and 0.86 g (4.4 mol) of L-valine methyl ester hydrochloride in 10 ml of dimethylformamide was added 0.72 g (4.4 mol) of diethylphosphoryl cyanide[9] and 0.84 g (8.4 mmol) of triethylamine. The reaction mixture was stirred for 1 hr at 0° and for 3 hr at room temperature. The solution was diluted with water and extracted with ethyl acetate. The ethyl acetate extract was washed with 10% sodium bicarbonate, 10% citric acid, and water and dried over anhydrous sodium sulfate. The solvent was evaporated *in vacuo* to give 0.95 g (67%) of while solid: mp 183–186°; R_f 0.51; $[\alpha]^{21}D$ −15.4° (*c* 1.8, ethanol); nmr ($CDCl_3$) δ 6.05 (m, NH), 4.55 (m, NH and α-H, 2 H), 3.72 (s, OCH_3, 3 H), 3.40 (m, cyclohexyl H_4, 1 H), 2.5–1.1 (m, cyclohexyl protons, valyl methine), 1.45 (s, *tert*-butyl), 0.9 (q, valyl isopropyl), last three peaks integrated to 24 protons. An analytical sample was prepared by recrystallization from ethyl acetate–petroleum ether (bp 60–90°): mp 185.5–187.5°.

Anal. Calcd for $C_{18}H_{32}N_2O_4$ (356.4): C, 60.7; H, 9.03; N, 7.85. Found: C, 60.6; H, 8.81, N, 7.52.

***N-tert*-Butyloxycarbonyl-*cis*-4-aminocyclohexanecarbonyl-L-valine Methyl Ester (4b). (a) Diethylphosphoryl Cyanide Method.** To an ice-cold solution of 0.98 g (4.0 mmol) of *N-tert*-butyloxycarbonyl-*cis*-4-aminocyclohexanecarboxylic acid and 0.86 g (4.4 mmol) of L-valine methyl ester hydrochloride in 10 ml of dimethylformamide were added 0.72 g (4.4 mmol) of diethylphosphoryl cyanide[9] and 0.84 g (8.4 mmol) of triethylamine. The reaction mixture was stirred for 1 hr at 0° and for 3 hr at room temperature. The solution was diluted with 10 ml of water and extracted with ethyl acetate (3 × 10 ml). The ethyl acetate solution was washed with 10% sodium bicarbonate, water, 10% citric acid, and water and dried over anhydrous sodium sulfate. The solvent was evaporated *in vacuo* to give 1.13 g of white solid. The white solid was recrystallized from ethyl acetate–petroleum ether to afford 0.91 g (64%) of white crystals: mp 129–131°; R_f 0.78; $[\alpha]^{21}D$ −10.6° (*c* 2, DMF); nmr ($CDCl_3$) δ 6.4 (d, 1 H, N-H), 4.9 (d, 1 H, NH), 4.8 (m, 1 H, α-hydrogen), 3.7 (m, 4 H, *O*-methyl, cyclohexyl H_4), 2.5–1.5 (m, 10 H, cyclohexyl except H_4, valyl methine), 1.45 (s, 9 H, *tert*-butyl), 0.9 (q, 6 H, valyl nonequivalent isopropyl).

Anal. Calcd for $C_{17}H_{32}N_2O_4$: C, 60.6, H, 9.05; N, 7.86. Found: C, 60.6; H, 9.25; N, 7.76.

(b) Symmetrical Anhydride Method. A stirred and cooled solution of 0.98 g (4.0 mmol) of *tert*-butyloxycarbonyl-*cis*-4-aminocyclohexanecarboxylic acid and 0.40 g (4.0 mmol) of triethylamine in dry benzene was treated with 0.48 g (4.0 mmol) of pivaloyl chloride. The solution was stirred at 0° for 2 hr and then stirred overnight at room temperature. The solution was filtered and the filtrate was evaporated under reduced pressure. Petroleum ether (bp 30–60°) was added and the solution was allowed to stand in a refrigerator for 3 days. A solid (0.51 g) was collected by filtration; an nmr spectrum showed this material to be the symmetrical anhydride. This solid, which did show a second minor spot in tlc, was not further purified for use in the next step of the reaction.

To an ice-cold mixture of 0.18 g (1.1 mmol) of L-valine methyl ester hydrochloride and 0.12 g of triethylamine in benzene was added the above anhydride. The reaction mixture was stirred at 0° for 1 hr and at room temperature overnight. The solvent was removed *in vacuo* and the residue was triturated with 10% sodium bicarbonate, 10% citric acid, and water to give 0.15 g (yield 10%) of **4b**, mp 131–132°.

***N-tert*-Butyloxycarbonyl-*cis*-4-aminocyclohexanecarbonylglycine Ethyl Ester (5).** To a precooled solution of 0.49 g (2.0 mmol) of *N-tert*-butyloxycarbonyl-*cis*-4-aminocyclohexanecarb-

oxylic acid in 10 ml of dimethylformamide were added 0.36 (2.2 mmol) of diethylphosphoryl cyanide, 0.31 g (2.2 mmol) of glycine ethyl ester hydrochloride, and 0.42 g (4.2 mmol) of triethylamine. The reaction mixture was stirred for 1 hr at 0° and 3 hr at room temperature. The solution was diluted with 10 ml of water and extracted with ethyl acetate (2 × 10 ml). The ethyl acetate solution was washed with 10% sodium bicarbonate, water, 10% citric acid, and water and dried over anhydrous sodium sulfate. The solvent was evaporated *in vacuo* to give 0.57 g of an oil. The oil was crystallized from ether–petroleum ether (bp 60–90°) to give 0.36 g (56%) of white crystals: mp 224–226°; R_f 0.77; nmr ($CDCl_3$) δ 6.9 (m, 1 H, NH), 5.05 (d, 1 H, NH), 4.2 (q, 2 H, ethyl ester methylene), 3.95 (d, 2 H, α-hydrogens), 3.7 (br s, 1 H, cyclohexyl H_4), 2.5–0.9 (m, 21 H, cyclohexyl except H_4, *tert*-butyl, and ethyl ester methyl).

Anal. Calcd for $C_{16}H_{28}N_2O_5$: C, 58.5; H, 8.59; N, 8.53. Found: C, 58.6; H, 8.49; N, 8.37.

Attempts to prepare **5** using the *N,N'*-dicyclohexylcarbodiimide-1-hydroxybenzotriazole method[8] were unsuccessful.

***N-tert*-Butyloxycarbonyl-L-alanyl-*trans*-4-aminocyclohexanecarbonyl-L-valine Methyl Ester (6a).** *N-tert*-Butyloxycarbonyl-*trans*-4-aminocyclohexanecarbonyl-L-valine methyl ester (0.89 g, 2.5 mmol) was dissolved in 5 ml of trifluoroacetic acid. After 1 hr, the solvent was removed *in vacuo*. To the residue was added 5 ml of dimethylformamide, 0.27 g (2.7 mmol) of triethylamine, and 0.48 g (2.48 mmol) of *N-tert*-butyloxycarbonyl-L-alanine. The solution was cooled to 0° and 0.42 g (2.58 mmol) of diethylphosphoryl cyanide and 0.27 g (2.7 mmol) of triethylamine were added. The reaction mixture was stirred for 1 hr at 0° and overnight at room temperature. The solution was diluted with water and extracted with ethyl acetate. The organic phase was washed with 10% $NaHCO_3$, water, and 10% citric acid. The ethyl acetate was removed *in vacuo* to give 0.64 g of a white solid which was recrystallized from ethyl acetate–ether to give 0.47 g (44%) of **6a**: mp 216–218°; R_f 0.57; $[\alpha]^{21}D$ −33.5° (*c* 1.5, ethanol); nmr ($CDCl_3$) δ 6.35 (m, 2 H, NH), 5.3 (d, 1 H, NH), 4.52 (m, 1 H, α-hydrogen), 4.10 (m, 1 H, α-hydrogen), 3.70 (s superimposed on m, 4 H, *O*-methyl and cyclohexyl H_4), 2.3–1.0 (m, valyl methine and cyclohexyl excluding H_4), 1.42 (s, *tert*-butyl), 1.32 (d, alanyl methyl), 0.91 (q, valyl isopropyl), integration for last four peaks totals 28 hydrogens.

Anal. Calcd for $C_{21}H_{37}N_3O_6$: C, 59.0, H, 8.72; N, 9.83. Found: C, 58.8; H, 9.06; N, 9.62.

***N-tert*-Butyloxycarbonyl-L-alanine-*cis*-4-aminocyclohexanecarbonyl-L-valine Methyl Ester (6b).** *N-tert*-Butyloxycarbonyl-*cis*-4-aminocyclohexanecarbonyl-L-valine methyl ester (0.71 g, 2.0 mmol) was dissolved in 3 ml of trifluoroacetic acid and allowed to stand overnight. The solvent was removed *in vacuo*, the residue was dissolved in 10 ml of dimethylformamide, and 0.21 g (2.1 mmol) of triethylamine and 0.38 g (2.0 mmol) of *N-tert*-butyloxycarbonyl-L-alanine were added. The solution was cooled to 0° and 0.33 g (2.0 mmol) of diethylphosphoryl cyanide and 0.21 g (2.1 mmol) of triethylamine were added. The reaction mixture was stirred at 0° for 1 hr and at room temperature overnight. The mixture was diluted with water and extracted with ethyl acetate (3 × 10 ml). The ethyl acetate extracts were washed with 10% sodium bicarbonate, water, and 10% citric acid. The organic phase was dried over anhydrous sodium sulfate and concentrated *in vacuo* to give 0.40 g of an oil (47%). This oil was crystallized from ethyl acetate–cyclohexane to give white crystals: mp 146–148°; R_f 0.78; $[\alpha]^{21}D$ − 12.6° (*c* 2.0, DMF); nmr ($CDCl_3$) δ 6.4 (d, 1 H, NH), 6.1 (d, 1 H, NH), 4.9 (d, 1H, NH), 4.7–3.8 (m, 3 H, α-hydrogens, cyclohexyl H_4), 3.70 (s, 3 H, methyl ester), 2.5–1.9 (m, 2 H, valyl methine, cyclohexyl H_1), 1.7 (br s, 8 H, cyclohexyl excluding H_1 and H_4), 1.45 (s, 9 H, *tert*-butyl), 1.35 (d, 3 H, alanyl methyl), 0.90 (q, 6 H, valyl isopropyl).

Anal. Calcd for $C_{21}H_{37}N_3O_6$: C, 59.0; H, 8.72; N, 9.83. Found: C, 59.3; H, 8.57; N, 9.60.

***p*-Nitrophenyl *N-tert*-Butyloxycarbonyl-*trans*-4-aminocyclohexanecarboxylate.** To a precooled solution of 0.96 g (3.95 mmol) of *N-tert*-butyloxycarbonyl-*trans*-4-aminocyclohexanecarboxylic acid and 2.20 g (15.8 mmol) of *p*-nitrophenyl in 5 ml of dimethylformamide was added 0.90 g (4.35 mmol) of *N,N'*-dicyclohexylcarbodiimide. The reaction mixture was stirred overnight at room temperature following which the dicyclohexyl urea was removed by filtration and the filtrate was evaporated *in vacuo* at 40°. The residue was crystallized from ethanol to give 0.67 g of white crystals (62%): mp 156–158°; R_f 0.76; nmr ($CDCl_3$) δ 1.8 (q, 4 H, nitrophenyl), 4.5 (d, 1 H, NH), 3.4 (s, 1 H, cyclohexyl H_4), 2.7–1.4 (m, 18 H, cyclohexyl except H_4, *tert*-butyl).

Anal. Calcd for $C_{18}H_{24}N_2O_6$: C, 59.3; H, 6.63; N, 7.76. Found: C, 59.2; H, 6.68; N, 7.48.

***p*-Nitrophenyl *N-tert*-Butyloxycarbonyl-*cis*-4-aminocyclohexanecarboxylate.** To an ice-cold solution of 0.97 g (4.07 mmol) of *N-tert*-butyloxycarbonyl-*cis*-4-aminocyclohexanecarboxylic acid and 2.28 g (16.4 mmol) of *p*-nitrophenol in 40 ml of ethyl acetate was added 0.92 g (4.5 mmol) of *N,N'*-dicyclohexylcarbodiimide and the reaction mixture was stirred overnight at 0°. *N,N'*-Dicyclohexylurea was removed by filtration and the filtrate was evaporated *in vacuo* to give an oil that slowly crystallized. Recrystallization from anhydrous ethanol gave 1.71 g (80%) of product: mp 132–134°; R_f 0.74; nmr ($CDCl_3$) δ 1.8 (q, 4 H, nitrophenyl), 3.6 (br s, 1 H, cyclohexyl H_4), 2.7 (br s, 1 H, cyclohexyl H_1), 2.4–1.6 (m, 8 H, cyclohexyl), 1.45 (s, 9 H, *tert*-butyl).

Preparation of *N-tert*-Butyloxycarbonyl-*cis*-4-aminocyclohexanecarbonylglycine Ethyl Ester (5) by the Active Ester Method. To a solution of 0.73 g (2 mmol) of *p*-nitrophenyl *N-tert*-butyloxycarbonyl-*cis*-4-aminocyclohexanecarboxylate and 0.28 g (2 mmol) of glycine ethyl ester hydrochloride in 5 ml of DMF was added 0.21 g (2 mmol) of triethylamine. After stirring overnight, tlc analysis of the reaction mixture indicated little reaction to have occurred. Imidazole (2.0 g) was added and the reaction mixture was stirred for 7 hr at which time tlc analysis showed the reaction to be complete. The reaction mixture was diluted with ethyl acetate and the organic phase was washed with 10% $NaHCO_3$, 10% citric acid, and water. The organic phase was dried over anhydrous magnesium sulfate and concentrated *in vacuo* to give 0.23 g of an oil. The residue was recrystallized from ether–petroleum ether (bp 60–90°) to yield 0.13 g (20%) of **5**, mp 125–128°. Tlc comparison of this material with a sample of **5** prepared above showed identical R_f values.

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Registry No.—**2a,** 3685-25-4; **2b,** 3685-23-2; **3a,** 53292-89-0; **3b,** 53292-90-3; **4a,** 53292-91-4; **4b,** 53368-40-4; **5,** 53292-92-5; **6a,** 53292-93-6; **6b,** 53368-41-5; *tert*-butyloxycarbonyl azide, 1070-19-5; L-valine methyl ester hydrochloride, 6306-52-1; pivaloyl chloride, 3282-30-2; glycine ethyl ester hydrochloride, 623-33-6; *N-tert*-butyloxycarbonyl-L-alinine, 15761-38-3; *p*-nitrophenyl *N-tert*-butyloxycarbonyl-*trans*-4-aminocyclohexanecarboxylate, 53292-94-7; *p*-nitrophenol, 100-02-7; *p*-nitrophenyl *N-tert*-butyloxycarbonyl-*cis*-4-aminocyclohexenecarboxylate, 53292-95-8.

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