dry methylene chloride (2.0 mL) at 0 °C was added freshly distilled triethylamine (158 μL, 1.75 mmol) followed by methanesulfonyl chloride (88.2 μL, 1.14 mmol). The mixture was stirred at room temperature for 8 h. The reaction was quenched with water and extracted with methylene chloride. The combined organic extracts were dried and then concentrated in vacuo. The crude product was purified by flash chromatography (10% ethyl acetate/hexane) to give compound **23a** as an oil in 71% yield: ^{1}H NMR ($CDCl_3$) δ 8.30 (1 H, s, 6-H), 7.50–7.34 (10 H, m, Ar H's), 4.97 (2 H, s, 5'-H's), 4.73 (2 H, s, PhCH_2O), 4.67 (1 H, s, 4'-H), 4.57 (2 H, s, PhCH_2O), 2.57 (3 H, s, 2-Me); ^{13}C NMR ($CDCl_3$) δ 153.7, 151.5, 145.5, 138.2, 137.6, 136.3, 130.7, 128.6, 128.4, 128.2, 128.0, 127.8 (Ar C's), 76.0 (PhCH_2O), 72.7 (PhCH_2O), 67.1 (C-5'), 35.4 (t, J = 23.0, C-4'), 19.7 (2-Me); high-resolution FAB-MS calcd for $C_{22}H_{22}{}^2H_1NO_2Cl$ (M + 1)$^+$ 369.1495, found 369.1448. Compound **23b** was prepared from **18b** by the same procedure in 75% yield. Its ^{1}H and ^{13}C NMR spectra are identical with those of **23a**.

Conversion of Pyridoxyl Chlorides 23a and 23b to (4'*R*)-[4'-^{2}H$_1$]-3,5'-*O*-Dibenzylpyridox-4'-yl Azide (21b) and (4'*S*)-[4'-^{2}H$_1$]-3,5'-*O*-Dibenzylpyridox-4'-yl Azide (21a). To a solution of pyridoxyl chloride **23a** (100 mg, 0.23 mmol) in dry THF (4 mL) were added sodium azide (30 mg, 0.46 mmol) and 15-crown-5 (46.5 μL, 0.23 mmol) at room temperature under argon. The resulting mixture was heated to 70 °C and stirred at that temperature overnight. After dilution with water and extraction with methylene chloride, the organic extracts were combined and concentrated in vacuo. The crude azide was purified by flash chromatography (10% ethyl acetate/hexane) to give **21b** as a colorless liquid in 92% yield: IR (neat) 3031, 2868, 2095, 1454, 1209, 1069 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.29 (1 H, s, 6-H), 7.43–7.25 (10 H, m, Ar H's), 4.91 (2 H, s, 5'-H's), 4.58, 4.57 (2 H's each, s, PhCH_2O), 4.43 (1 H, s, 4'-H), 2.58 (3 H, s, 2-Me); ^{13}C NMR ($CDCl_3$) δ 153.8, 152.3, 145.6, 137.5, 136.4, 136.3, 131.0, 128.8, 128.6, 128.5, 128.0, 127.9 (Ar C's), 76.2 (PhCH_2O), 72.7 (PhCH_2O), 67.4 (C-5'), 44.8 (t, J = 22.2, C-4'), 20.0 (2-Me). Compounds **21a** was prepared from **23b** in 90% yield by the same procedure as described above. Its ^{1}H and ^{13}C NMR spectra are identical with those of **21b**.

(4'*S*)-[4'-^{2}H$_1$]-3,5'-*O*-Dibenzylpyridoxamine (24a) and (4'*R*)-[4'-^{2}H$_1$]-3,5'-*O*-Dibenzylpyridoxamine (24b). Compound **21a** and **21b** were converted to pyridoxamines **24a** and **24b**, respectively, by a procedure identical with that described above for the synthesis of **11a** and **11b**. The ^{1}H and ^{13}C NMR spectra of these two compounds are identical and are similar to the spectra obtained for compounds **11a** and **11b** except that the integration of the signal at δ 3.83 accounts now for only one proton in **24a** and **24b** and the carbon signal at δ 37.7 diminishes to a small triplet (J = 22.5). High-resolution FAB-MS: calcd for $C_{22}H_{24}{}^2H_1N_2O_2$ (M + 1)$^+$ 350.1924, found 350.1924.

4'-*N*-Camphanyl-(4'*S*)-[4'-^{2}H$_1$]-3,5'-*O*-dibenzylpyridoxamine (25a) and 4'-*N*-Camphanyl-(4'*R*)-[4'-^{2}H$_1$]-3,5'-*O*-dibenzylpyridoxamine (25b). To a solution of (−)-camphanic acid (45.4 mg, 0.23 mmol) in 0.5 mL of freshly distilled methylene chloride was added a solution of amine **24a** (40 mg, 0.115 mmol) and 1,3-dicyclohexylcarbodiimide (47.4 mg, 0.23 mmol) in 1 mL of methylene chloride. The resulting reaction mixture was stirred for 20 min at room temperature under an argon atmosphere. The desired product then was isolated by filtration of the reaction mixture through Celite and washing of the Celite pad twice with methylene chloride. The dried organic filtrates were concentrated in vacuo followed by flash chromatography (33% ethyl acetate/hexane) to give **25a** as a colorless liquid. The yield was 93%: ^{1}H NMR ($CDCl_3$) δ 8.22 (1 H, s, 6-H), 7.50–7.29 (11 H, m, Ar H's and NH), 4.90, 4.85 (1 H each, benzylic AB q, J = 10.9, 5'-H's), 4.67, 4.62 (1 H, benzylic AB q, J = 11.9, PhCH_2O), 4.56 (2 H, s, PhCH_2O), 4.48 (ca. 1 H, d, J_{NH} = 5.8, 4'-H_R), 2.56 (3 H, s, 2-Me), 2.50–2.40 and 1.93–1.56 (4 H, m, camphanic CH_2's), 1.06, 1.05, 0.76 (3 H's each, s, camphanic Me's);[23] ^{13}C NMR ($CDCl_3$) δ 178.0, 166.6 (C=O's), 153.9, 152.1, 145.8, 138.6, 137.3, 136.3, 130.8, 128.8, 128.6, 128.3, 128.1, 128.0 (Ar C's), 75.9 (PhCH_2O), 72.8 (PhCH_2O), 67.5 (C-5'), 58.1 (t, J = 21.8, C-4'), 19.7 (2-Me), 92.3, 55.2, 53.9, 34.0, 30.7, 16.6, 9.7 (camphanic C's). Compounds **24b** was converted to **25b** by a procedure similar to that described above for the synthesis of **25a**. Spectra of **25b** are identical with those obtained for **25a** except for the appearance of a new resonance at δ 4.54 (ca. 1 H, d, J = 5.8, 4'-H_S) and the disappearance of the 4'-H_R signal at δ 4.48–4.50 (Figure 1). High-resolution FAB-MS: calcd for $C_{32}H_{36}{}^2H_1N_2O_5$ (M + 1)$^+$ 530.2781, found 530.2766.

Acknowledgment. This work is supported by National Institutes of Health Grant GM 35906. H.-w.L. also thanks the National Institutes of Health for a Research Career Development Award (GM 00559).

Additions and Corrections

Vol. 55, 1990

Dale L. Boger,* Takayoshi Ishizaki, Paul A. Kitos, and Oranart Suntornwat. Synthesis of *N*-(*tert*-Butyloxycarbonyl)-CBI, CBI, CBI-CDPI$_1$, and CBI-CDPI$_2$: Enhanced Functional Analogues of CC-1065 Incorporating the 1,2,9,9a-Tetrahydrocyclopropa[*c*]benz[*e*]indol-4-one (CBI) Left-Hand Subunit.

Page 5825. Legend for Scheme II: (a) 2.0 equiv of (t-BuO_2C)$_2$O, dioxane, 95 °C, 3 h, 96%; (b) 1.2 equiv of *N*-bromosuccinimide, catalytic H_2SO_4, THF, −60 °C, 5 h, 98%; (c) 1.3 equiv of NaH, 3.0 equiv of 3-bromopropyne, 24 °C, 3 h, 99%; (d) 2.0 equiv of Bu_3SnH, 0.2 equiv of AIBN, benzene, 80 °C, 1 h; (e) 6 equiv of Me_2S–BH_3 THF, 0–25 °C, 3 h; 2 N NaOH, 30% H_2O_2, 0–25 °C, 1 h, 45 °C, 20 min, 62% from **12**; (f) 2.0 equiv of Ph_3P, 6 equiv CCl_4, CH_2Cl_2, 24 °C, 10 h, 99%; (g) 25% aqueous HCO_2NH_4/THF 2:15, 10% Pd/C, 0 °C, 2.5 h, 97%; (h) 3 equiv of NaH, THF, 0 to 24 °C, 2 h, 93%.

Page 5826. Legend for Scheme III: (a) For **21a**, 1.4 equiv of NaH, 1.4 equiv of **19**, THF–DMF (9:1), 24 °C, 12 h, 53%; for **21b**, 1.4 equiv of NaH, 1.6 equiv of **19**, DMF, 24 °C, 17 h, 73%; (b) for **22a**, 2.2 equiv of Bu_3SnH, 0.6 equiv of AIBN, benzene, 80 °C, 16 h, 75%; for **22b**, 2.2 equiv of Bu_3SnH, 0.2 equiv of AIBN, benzene, 80 °C, 12 h, 75%; (c) see text; (d) 1.3 equiv of NaH, 3.0 equiv of $BrCH_2CH{=}CH_2$, DMF, 24 °C, 1.5 h, 95%; (e) 1.3 equiv of NaH, 3.0 equiv of $BrCH_2CH{=}CMe_2$, DMF, 0 to 24 °C, 8 h, 94%; (f) for **23a**, O_3/O_2, CH_3OH, 0 °C, 10 min; Me_2S (excess), 0 to 24 °C, 4 h, 58%; for **23b**, O_3/O_2, CH_2Cl_2, −78 °C, 10 min; Me_2S (excess), −78 to 25 °C, 20 h, 88%; (g) see text.

Legend for Scheme IV: (a) 3 N anhydrous HCl/EtOAc, 24 °C, 20 min, 100%; (b) for **29**, 3 equiv of EDCI, 1.0 equiv of **27**, DMF, 24 °C, 8 h, 69%; for **30**, 3 equiv of EDCI, 1.0 equiv of **28**, DMF, 24 °C, 5 h, 78%; (c) for **7**, 3 equiv of NaH, THF–DMF (6:1), 0 °C, 1 h, 74%; for **8**, 2 equiv of NaH, THF–DMF (2:1), 0 °C, 1 h, 84%.

Page 5827. Legend for Scheme V: (a) 1.5 equiv of (−)-(*R*)-*O*-acetylmandelic acid, 1.7 equiv of EDCI, 0.1 equiv of 4-DMAP, CH_2Cl_2, 24 °C, 1 h, 81%; (b) 5 equiv of 4 N aq LiOH, CH_3OH–THF (2:3), 24 °C, 1 h, 97%; (c) 2.0 equiv of Ph_3P, 6.0 equiv of CCl_4, CH_2Cl_2, 24 °C, 10 h, 99%; (d) 25% aqueous HCO_2NH_4–THF (2:15), 10% Pd/C, 0 °C, 2.5 h, 97%; (e) see Scheme II, eq 1, and Scheme IV.