J = 18.3 Hz, 1 H), 2.16 (dd, J = 5.1, 12.0 Hz, 1 H), 2.00 (d, J = 6.8 Hz, 1 H), 1.91-1.79 (m, 2 H), 1.45 (m, 2 H), 1.10 (s, 3 H), 0.15 (s, 9 H); mass spectrum,m/e (relative intensity) 212 (M^+, 2.0), 197 (18.5), 170 (50.1), 169 (base peak), 155 (21.6), 141 (19), 73 (72.6); HRMS calcd for $C_{11}H_{20}O_2Si$ 212.1233, obsd 212.1238.

4b: yield 96% (310 mg); mp 41-42 °C; IR (KBr) 3328, 2923, 1302, 1245, 834 cm^{-1}; NMR δ 2.14 (d, J = 13.3 Hz, 1 H), 2.11 (1 H), 2.02 (d, J = 13.3 Hz, 1 H), 1.82-1.62 (m, 4 H), 1.39 (m, 2 H), 1.36 (s, 3 H), 0.99 (s, 3 H), 0.15 (s, 9 H); mass spectrum, m/e (relative intensity) (no M^+), 195 (3), 171 (14.5), 170 (80.9), 169 (24.5), 144 (32.7), 143 (base peak), 73 (70.9). Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.16; H, 10.53. Found: C, 62.00; H, 10.34.[13]

5b: yield 99% (149 mg) as a colorless liquid;[15] IR (neat) 2898, 1698 cm^{-1}; NMR δ 3.15 (s, 2 H), 2.51 (t, J = 6.6 Hz, 2 H), 2.27 (t, J = 5.8 Hz, 2 H), 1.91 (m, 2 H), 1.75 (s, 3 H), 1.71 (s, 3 H); mass spectrum, m/e (relative intensity) 138 (M^+, 6.8), 137 (13.2), 111 (10.2), 110 (11.1), 109 (40.2), 108 (14.6), 95 (23.4); HRMS calcd for $C_9H_{14}O$ 138.1045, obsd 138.1013.

2c: yield 88% (2.91 g); mp 35-36 °C; IR (neat) 2932, 1798, 1262, 839 cm^{-1}; NMR δ 3.39 (s, 1 H), 2.48 (m, 2 H), 2.29 (m, 1 H), 1.81-1.66 (m, 2 H), 1.08 (d, J = 7.2 Hz, 3 H), 0.21 (s, 9 H); mass spectrum, m/e (relative intensity) (no M^+), 219 (2.8), 218 (2.0), 2.17 (6.9), 216 (3.7), 170 (1.5), 169 (2.6), 168 (1.2), 156 (2.4), 155 (14.9), 154 (14.9), 73 (base peak). Anal. Calcd for $C_{11}H_{18}O_2SiCl_2$: C, 46.98; H, 6.41. Found: C, 46.41; H, 6.35.[13]

3c: yield 91% (1.08 g) as a colorless liquid; IR (neat) 2933, 1778, 1308, 1248, 836 cm^{-1}; NMR δ 3.24 (dd, J = 5.2, 18.1 Hz, 1 H), 3.08 (br s, 1 H), 2.96 (dd, J = 2.9, 18.1 Hz, 1 H), 2.29 (m, 1 H), 2.01-2.16 (m, 2 H), 1.76 (m, 1 H), 1.62 (m, 1 H), 1.03 (d, J = 7.3 Hz, 3 H), 0.17 (s, 9 H); mass spectrum, m/e (relative intensity) 212 (M^+, 5.4), 197 (20.1), 196 (16.8), 195 (24.4), 194 (15.1), 184 (27.4), 183 (17.0), 170 (19.5), 169 (55.1), 168 (39.2), 155 (84), 154 (40.4), 73 (base peak); HRMS calcd for $C_{11}H_{20}O_2Si$ 212.1233, obsd 212.1268.

4c: yield 95% (460 mg); mp 44-45 °C; IR (neat) 3291, 2907, 1446, 1244, 833 cm^{-1}; NMR δ 2.20 (dd, J = 3.5, 13.3 Hz, 1 H), 2.18 (1 H), 2.02 (d, J = 13.3 Hz, 1 H), 1.97 (d, J = 3.3 Hz, 1 H), 1.84 (m, 2 H), 1.69 (dd, J = 4.5, 6 Hz, 1 H), 1.51 (m, 1 H), 1.46 (s, 3 H), 1.26 (br s, 1 H), 1.01 (d, J = 7.3 Hz, 3 H), 0.14 (s, 9 H); mass spectrum, m/e (relative intensity) (no M^+), 170 (37.3), 155 (base peak), 144 (33.6), 143 (62.7), 129 (29), 73 (14.6). Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.16; H, 10.53. Found: C, 62.50; H, 10.42.[13]

5c: yield 98% (103 mg) as a colorless liquid; IR (neat) 2897, 1700 cm^{-1}; NMR δ 5.33 (br s, 1 H), 3.22 (d, J = 14.5 Hz, 1 H), 3.09 (d, J = 14.5 Hz, 1 H), 2.60 (m, 1 H), 2.44 (m, 2 H), 1.93-1.70 (m, 2 H), 1.77 (s, 3 H), 1.05 (d, J = 7.0 Hz, 3 H); mass spectrum, m/e (relative intensity) 139 (M^+ + 1, 20) 138 (M^+, 13), 121 (28.5), 109 (10.2), 96 (base peak), 95 (50); HRMS calcd for $C_9H_{14}O$ 138.1045, obsd 138.1030.

2d: as a diastereomeric mixture for 2-methyl; exo:endo = 1.5:1 by gas chromatography; yield 75% (2.11 g) as a colorless oil; IR (neat, mixture) 2926, 1796, 1456, 1248, 854 cm^{-1}; NMR (exo isomer) δ 3.60 (dd, J = 1.9, 7.0 Hz, 1 H), 2.45 (m, 1 H), 2.08 (dd, J = 7.1, 12.0 Hz, 1 H), 1.96-1.83 (m, 2 H), 1.58 (m, 1 H), 1.40 (d, J = 7.2 Hz, 3 H), 0.24 (s, 9 H); (endo isomer) 3.81 (dd, J = 2.7, 9.4 Hz, 1 H, for 5-CH), 1.09 (d, J = 6.7 Hz, 3 H, for 2-CCH_3); mass spectrum, m/e (relative intensity) (no M^+), 219 (1.2), 218 (0.6), 217 (3.7), 170 (5), 169 (5), 155 (2.5), 128 (3.1), 93 (13.8), 73 (base peak).

3d: yield 90% (1.02 g) as a colorless oil; IR (neat, diastereomeric mixture) 2931, 1775, 1455, 1248, 836 cm^{-1}; NMR (exo isomer) δ 3.33 (br s, 1 H), 3.09 (dd, J = 2.2, 18.5 Hz, 1 H), 2.98 (dd, J = 2.9, 18.5 Hz, 1 H), 2.18 (m, 1 H), 1.98-1.81 (m, 3 H), 1.24 (m, 1 H), 1.06 (d, J = 6.2 Hz, 3 H), 0.17 (s, 9 H); (endo isomer) 3.25 (dd, J = 3.4, 18.2 Hz, 1 H for 7-CH), 2.98 (d, J = 18.2 Hz, 1 H for 7-CH), 0.99 (d, J = 7.1 Hz, 3 H), 0.17 (s, 9 H); mass spectrum, m/e (relative intensity) 212 (M^+, 1.3), 197 (6.25), 184 (26.2), 169 (36.2), 155 (20), 142 (15), 127 (10), 73 (base peak); HRMS calcd for $C_{11}H_{20}O_2Si$ 212.1233, obsd 212.1282.

4d: yield 95% (153 mg) as a colorless oil; (spectral data for diastereomeric mixture) IR (neat) 3312, 2925, 1437, 1245, 834 cm^{-1}; NMR 2.32-2.27 (m, 2 H), 2.07-1.53 (m, 6 H), 1.48 (s, 3 H), 1.33-1.25 (m, 1 H), 0.88 (d, J = 6.2 Hz, 1.8 H for exo isomer), 0.86 (d, J = 7 Hz, 1.2 H for endo isomer), 0.15 (s, 9 H); mass spectrum, m/e (relative intensity) 228 (M^+, 12.7), 213 (5), 195 (5), 185 (7), 170 (base peak), 157 (74.5), 144 (60), 129 (41.8), 73 (78.2); HRMS calcd for $C_{12}H_{24}O_2Si$ 228.1539, obsd 228.1522.

5d: yield 98% (70 mg) as a colorless liquid; IR (neat) 2937, 1701 cm^{-1}; NMR δ 5.55 (t, J = 5.5 Hz, 1 H), 3.20 (d, J = 14.0 Hz, 1 H), 3.08 (d, J = 14.0 Hz, 1 H), 2.67 (m, 1 H), 2.23 (m, 2 H), 1.95 (m, 1 H), 1.79 (s, 3 H), 1.62 (m, 1 H), 1.10 (d, J = 6.9 Hz, 3 H); mass spectrum, m/e (relative intensity) 138 (M^+, 50), 111 (7), 110 (55), 109 (6), 95 (41), 68 (base peak); HRMS calcd for $C_9H_{14}O$ 138.1045, obsd 138.1070.

Registry No. **1a**, 19980-43-9; **1b**, 19980-34-8; **1c**, 81834-51-7; **1d**, 19980-32-6; **1e**, 108643-84-1; **2a**, 66324-01-4; **2b**, 125302-40-1; **2c**, 125302-41-2; *exo*-**2d**, 125302-42-3; *endo*-**2d**, 125409-02-1; **2e**, 125302-43-4; **3a**, 125302-44-5; **3b**, 125302-45-6; **3c**, 125302-46-7; *exo*-**3d**, 125302-47-8; *endo*-**3d**, 125410-63-1; *exo*-**3e**, 125302-48-9; *endo*-**3e**, 125409-05-4; **4a'**, 125302-50-3; *endo*-**4a**, 125302-49-0; *exo*-**4a**, 125409-03-2; **4b**, 125302-51-4; **4c**, 125302-52-5; **4d**, 125302-53-6; *endo*-**4e**, 125302-54-7; *exo*-**4e**, 125409-04-3; **4e'**, 125302-59-2; **5a**, 1121-64-8; **5a'**, 14525-96-3; **5b**, 10479-95-5; **5c**, 125302-55-8; **5d**, 125302-56-9; **5e** (regioisomer 1), 125302-57-0; **5e** (regioisomer 2), 71055-00-0; **5e'**, 125302-58-1; Cl_3OCOCl, 76-02-8.

Supplementary Material Available: ^{1}H NMR spectra of **3a**, **4-5a'**, **2-5b-e**, **4-5e'** and analytical and spectral data for **2-5e**, **4e'**, **5e'** (30 pages). Ordering information is given on any current masthead page.

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An Improved Synthesis of the Taxol Side Chain and of RP 56976

Jean-Noël Denis, Arlene Correa, and Andrew E. Greene*

Université Joseph Fourier de Grenoble, LEDSS, Bât. 52, 38041 Grenoble Cedex, France

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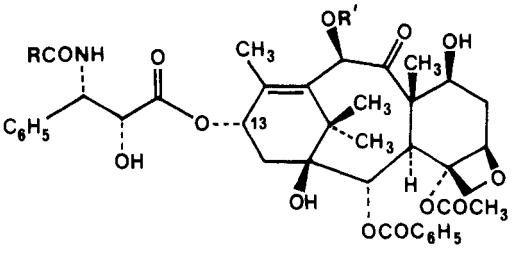
Efforts directed toward the total synthesis of taxol, a highly promising anticancer natural product,[1] continue unabated.[2] In most, if not all, of the numerous approaches recorded to date it would appear that an esterification of the C-13 hydroxyl function of an appropriate taxol precursor with the enantiomerically pure (suitably protected) taxol side chain will ultimately be required to obtain taxol efficiently.[3]



Taxol R = C_6H_5, R' = CH_3CO

RP 56976 R = $(CH_3)_3CO$, R' = H

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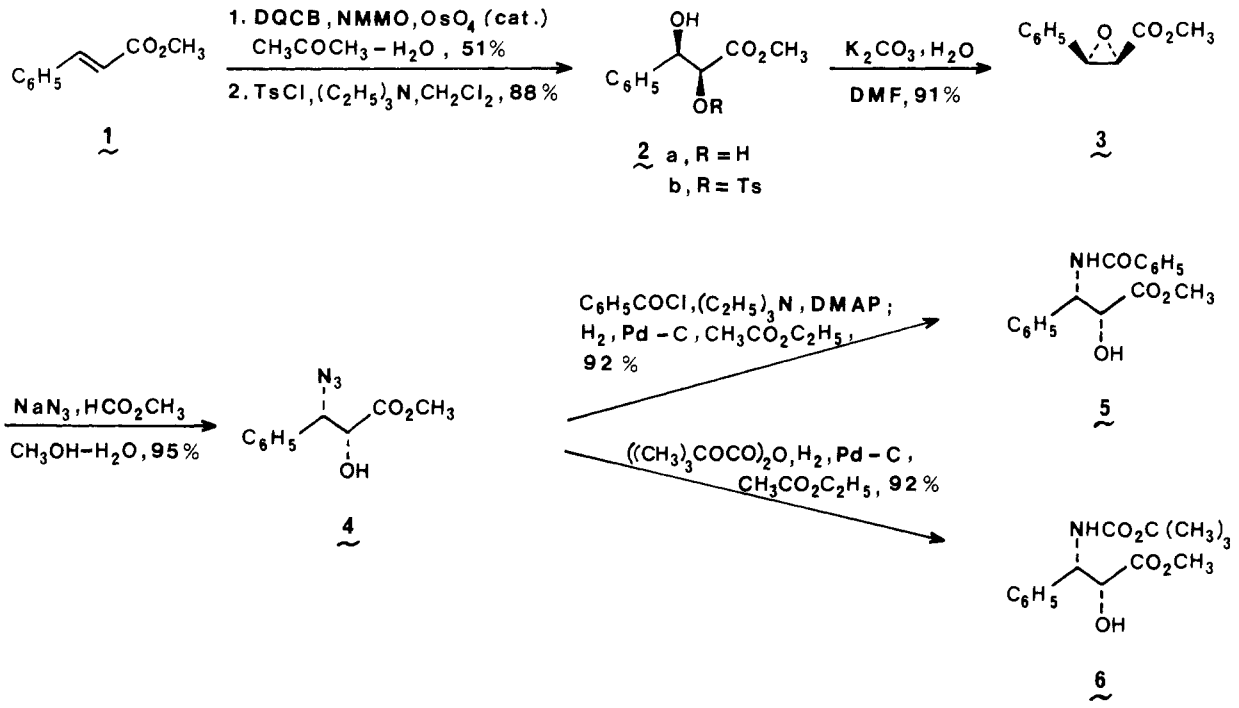
(2) For a compilation of recent references, see: Neh, H.; Kühling, A.; Blechert, S. *Helv. Chim. Acta* **1989**, *72*, 101-109. For earlier work, see ref 5.

0022-3263/90/1955-1957$02.50/0

Scheme I



While our reported[4] synthesis of this phenylisoserine derivative proved adequate for the partial synthesis of taxol[5] and for the preparation of simple analogues,[4,6] it suffered from a number of drawbacks and seemed poorly suited for future needs. In this paper we report a significantly improved preparation that is not only considerably shorter and higher yielding, but also experimentally much simpler. Noteworthy is that the side chain of the CNRS-Rhône-Poulenc taxol analogue RP 56976[7] now also becomes readily available through this improved approach.

Sharpless asymmetric dihydroxylation[8] of inexpensive methyl cinnamate in aqueous acetone with dihydroquinidine 4-chlorobenzoate (DQCB) as the added alkaloid and *N*-methylmorpholine *N*-oxide (NMMO) as the cooxidant produced the expected 2*S*,3*R* diol **2a** (Scheme I) in 82% yield and with an enantiomeric excess of 82%.[9] One recrystallization of this material from dichloromethane–cyclohexane efficiently provided enantiomerically pure (>98% ee[9]) **2a** in 51% yield from 1. Monotosylation of the pure diol in dichloromethane in the presence of triethylamine proved within the limit of NMR detection to be totally C-2 hydroxyl-selective and furnished the desired hydroxy tosylate **2b** in 88% yield. This remarkable selectivity is probably a consequence of intramolecular C-3 hydroxyl–carbonyl hydrogen bonding.[10]

Treatment of hydroxy tosylate **2b** with potassium carbonate in wet dimethylformamide gave the 2*R*,3*R* epoxide **3**[4] in 91% yield without the formation of a detectable amount of the 2*S*,3*R* epimer, a serious problem with several other base–solvent combinations. The presence of a small amount of water was found to markedly accelerate this reaction.[11] Epoxide **3** underwent selective cleavage with sodium azide in aqueous methanol–methyl formate[12] to give in 95% yield only the hydroxy azide **4**,[4] which on one-pot benzoylation–hydrogenation in ethyl acetate provided directly the taxol side chain (methyl ester, **5**) in 92% yield.

This efficient synthesis could be readily modified to give also the side chain of RP 56976, a synthetic taxol derivative prepared at the Institut de Chimie des Substances Naturelles of the CNRS and found at Rhône-Poulenc Santé to have significantly greater cancer chemotherapeutic potential than taxol itself.[7] Catalytic hydrogenation of the hydroxy azide **4** in ethyl acetate in the presence of 1.2 equiv of di-*tert*-butyl dicarbonate[13] furnished directly the RP 56976 side chain (methyl ester, **6**) in 92% yield after purification.

The streamlined approach to the side chains presented in this paper should simplify the preparation of both taxol and RP 56976.

Experimental Section

Solvents were generally distilled prior to use: *N*,*N*-dimethylformamide from calcium hydride, dichloromethane from calcium chloride, and ethyl acetate from phosphorus pentoxide.

(3) Although partial kinetic resolution has been observed, it would appear too modest to be preparatively useful. See: Mangatal, L. Ph.D. Dissertation, Université de Paris-Sud, Orsay, 1989.

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(5) Denis, J.-N.; Greene, A. E.; Guénard, D.; Guéritte-Voegelein, F.; Mangatal, L.; Potier, P. *J. Am. Chem. Soc.* **1988**, *110*, 5917–5919.

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(9) The enantiomeric excesses were determined by HPLC analysis of the derived diacetates (Pirkle phenylglycine column and acetonitrile–2-propanol–heptane solvent system). We thank Dr. Mulhauser (Rhône-Poulenc Recherches) for these determinations.

(10) See: Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman and Company: San Francisco, 1960; Chapter 5.

(11) For an explanation of this effect, see: Mouloungui, Z.; Delmas, M.; Gaset, A. *J. Org. Chem.* **1989**, *54*, 3936–3941.

(12) Cf. Behrens, C. H.; Sharpless, K. B. *Aldrichimica Acta* **1983**, *16*, 67–79. Chong, J. M.; Sharpless, K. B. *J. Org. Chem.* **1985**, *50*, 1560–1563.

(13) Saito, S.; Nakajima, H.; Inaba, M.; Moriwake, T. *Tetrahedron Lett.* **1989**, *30*, 837–838.

Thin-layer chromatography was performed on Merck $60F_{254}$ (0.25 mm) sheets, which were visualized with molybdophosphoric acid in ethanol. Merck 70–230 silica gel 60 was employed for column chromatography. A Perkin-Elmer 397 spectrophotometer was used to record the IR spectra (as Nujol films). A Bruker AM 300 spectrometer was employed for the ^1H and ^{13}C NMR spectra ($CDCl_3$ solutions). Mass spectra were obtained on an AEI MS-30 or VG 30F mass spectrometer (90 eV, direct insert probe). Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Melting points were obtained with a Büchi-Tottoli apparatus and are not corrected. Microanalyses were performed by the Central Service of the CNRS.

(2*S*,3*R*)-(−)-Methyl 2,3-Dihydroxy-3-phenylpropionate (2a). A mixture of 1.74 g (3.74 mmol) of dihydroquinidine 4-chlorobenzoate (Aldrich) and 2.64 g (22.5 mmol) of *N*-methylmorpholine *N*-oxide in 10 mL of acetone and 1.4 mL of water was stirred under argon for 5 min at 20 °C and then cooled to −7 °C (bath temperature) and treated first with a solution of 30.5 mg (0.12 mmol) of osmium tetroxide in 254 μL of toluene and then over 48 h with a solution of 2.37 g (14.6 mmol) of methyl cinnamate in 4.4 mL of acetone. After the addition, the reaction mixture was stirred for an additional hour and then treated with 4.5 g of solid sodium metabisulfite. After being stirred for 1–2 min at −7 °C and 30 min at 20 °C, the mixture was diluted with dichloromethane, treated with anhydrous sodium sulfate, and then stirred for 30 min. After separation of the solids, the reaction mixture was processed with dichloromethane in the usual manner, and the crude product was purified by silica gel chromatography with 40% ether in hexane to give 2.36 g (82%) of diol **2a**: $[\alpha]^{24}_D$ −8.8° (*c* 1.0, chloroform), which corresponds to an enantiomeric excess of 82%.[9] One recrystallization of this material from dichloromethane–cyclohexane gave 1.47 g (51%) of enantiomerically pure[9] **2a**: mp 85–85.5 °C; $[\alpha]^{24}_D$ −10.7° (*c* 1.1, chloroform); IR 3460, 3375, 3060, 3050, 2950, 1710, 1445, 1438, 1390, 1320, 1300, 1270, 1220, 1200, 1102, 1080, 1040, 1022, 980, 920, 880, 850, 800, 760, 720, 700 cm^{-1}; ^1H NMR δ 2.71 (d, *J* = 7.0 Hz, 1 H), 3.07 (d, *J* = 6.0 Hz, 1 H), 3.81 (s, 3 H), 4.38 (dd, *J* = 2.9, 6.0 Hz, 1 H), 5.01 (dd, *J* = 2.9, 7.0 Hz, 1 H), 7.32–7.42 (m, 5 H); ^{13}C NMR δ 52.59, 74.44, 74.84, 126.20, 127.93, 128.32, 139.91, 173.06; mass spectrum (CI, ammonia–isobutane), *m/e* 254, 236, 214, 197, 196, 179, 168, 159, 151, 119, 107.

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.18; H, 6.18.

(2*S*,3*R*)-(−)-Methyl 3-Hydroxy-3-phenyl-2-((*p*-tolylsulfonyl)oxy)propionate (2b). To a stirred solution of 2.90 g (14.8 mmol) of diol **2a** in 74 mL of dichloromethane at 0 °C under argon was added 3.09 mL (2.24 g, 22.2 mmol) of triethylamine followed by 2.89 g (15.2 mmol) of *p*-toluenesulfonyl chloride. After being stirred for 63 h at 0 °C, the reaction mixture was processed with ethyl acetate and the crude product was purified by silica gel chromatography with 40% ether in hexane to give 4.58 g (88%) of the tosylate **2b**: mp 111–112 °C (dichloromethane–cyclohexane); $[\alpha]^{24}_D$ −47.5° (*c* 1.4, chloroform); IR 3500, 3100, 3050, 2950, 2920, 2850, 1750, 1595, 1490, 1450, 1435, 1360, 1290, 1190, 1175, 1095, 1062, 1030, 1020, 940, 920, 865, 810, 760, 745, 700, 685 cm^{-1}; ^1H NMR δ 2.42 (s, 3 H), 2.59 (s, 1 H), 3.60 (s, 3 H), 4.93 (d, *J* = 4.6 Hz, 1 H), 5.10 (d, *J* = 4.6 Hz, 1 H), 7.20–7.28 (m, 7 H), 7.56–7.60 (m, 2 H).

Anal. Calcd for $C_{17}H_{18}O_6S$: C, 58.27; H, 5.18. Found: C, 58.48; H, 5.08.

(2*R*,3*R*)-(+)-Methyl 3-Phenyloxiranecarboxylate (3). A solution of 2.96 g (8.46 mmol) of tosylate **2b** and 761 μL (42.3 mmol) of water in 42 mL of *N*,*N*-dimethylformamide at 20 °C was treated with 3.50 g (25.4 mmol) of potassium carbonate. After being stirred for 24 h at 20 °C, the reaction mixture was processed with ether in the usual way, and the crude product was purified by silica gel chromatography with 10% ether in hexane to provide 1.37 g (91%) of epoxide **3**: $[\alpha]^{24}_D$ +14° (*c* 1.6, chloroform). The IR and NMR spectra were identical with those previously[4] obtained.

(2*R*,3*S*)-(+)-Methyl 3-Azido-2-hydroxy-3-phenylpropionate (4). A 1.35-g (7.58-mmol) sample of epoxide **3** in 40 mL of methanol–water (8:1) was treated with 6.3 mL of methyl formate and 2.46 g (37.8 mmol) of sodium azide and then stirred under argon at 50 °C for 46 h. The crude product was isolated with ether in the normal way and then purified by silica gel chromatography with 10% ethyl acetate in hexane to give 1.59 g (95%) of hydroxy azide **4**: mp 56–57 °C (pentane); $[\alpha]^{24}_D$ +142° (*c* 1.1, chloroform). The IR and NMR spectra were identical with those previously[4] obtained.

(2*R*,3*S*)-(−)-*N*-Benzoyl-3-phenylisoserine Methyl Ester (5). A mixture of 1.51 g (6.83 mmol) of hydroxy azide **4**, 1.59 mL (1.93 g, 13.7 mmol) of benzoyl chloride, 2.85 mL (2.07 g, 20.4 mmol) of triethylamine, and 30.2 mg (0.25 mmol) of 4-(dimethylamino)pyridine in 27 mL of ethyl acetate was stirred under argon at 20 °C for 4 h, whereupon 1.4 mL of methanol was added. After being stirred for an additional 3 h, the reaction mixture was treated with 152 mg of 10% palladium on carbon and then placed under a hydrogen atmosphere. The resulting mixture was stirred for 68 h and then processed with dichloromethane in the usual manner to afford the crude product, which was purified by silica gel chromatography with 5% ether in dichloromethane to give 1.88 g (92%) of hydroxy amide **5**: mp 184–185 °C (lit.[1,4] mp 183–185 °C, 184–185 °C); $[\alpha]^{24}_D$ −48° (*c* 1.0, methanol) [lit.[1,4] $[\alpha]^{23}_D$ −49.6° (methanol), $[\alpha]^{26}_D$ −48° (*c* 0.92, methanol)]. The IR and NMR spectra were identical with those previously[4] obtained.

(2*R*,3*S*)-(−)-*N*-(*tert*-Butoxycarbonyl)-3-phenylisoserine Methyl Ester (6). A suspension of 148 mg of 10% palladium on carbon in 3 mL of ethyl acetate was stirred at 20 °C under a hydrogen atmosphere for 10 min, whereupon a solution of 1.75 g (8.02 mmol) of di-*tert*-butyl dicarbonate and 1.48 g (6.70 mmol) of hydroxy azide **4** in 12 mL of ethyl acetate was added. The resulting mixture was stirred under a hydrogen atmosphere for 56 h and then processed with ethyl acetate in the normal manner to afford the crude product, which was purified by silica gel chromatography with 5% ether in dichloromethane to give 1.81 g (92%) of hydroxy carbamate **6**: mp 130.5–131.5 °C (dichloromethane–cyclohexane); $[\alpha]^{24}_D$ −7° (*c* 1.2, chloroform); IR 3500, 3380, 3110, 3060, 3000, 2975, 2930, 1735, 1690, 1518, 1500, 1442, 1390, 1360, 1300, 1250, 1170, 1100, 1050, 1030, 980, 940, 930, 900, 705 cm^{-1}; ^1H NMR δ 1.42 (br s, 9 H), 3.11 (br s, 1 H), 3.84 (s, 3 H), 4.47 (br s, 1 H), 5.21 (~d, *J* = 9.4 Hz, 1 H), 5.36 (~d, *J* = 8.5 Hz, 1 H), 7.26–7.37 (m, 5 H); mass spectrum (CI, ammonia–isobutane), *m/e* 313, 296, 257, 240, 206, 196.

Anal. Calcd for $C_{15}H_{21}O_5N$: C, 61.00; H, 7.17. Found: C, 60.85; H, 7.17.

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An Improved Method for the Synthesis of α-Diazo Ketones

Rick L. Danheiser,* Raymond F. Miller, Ronald G. Brisbois, and Saung Z. Park[1]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Recent work in our laboratory has led to the development of a new aromatic annulation strategy based on the photochemically induced reaction of acetylenes with α,β-unsaturated α′-diazo ketones.[2] During the course of this

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