JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Supporting Information for *J. Am. Chem. Soc.*, **1993**, 115(18), 8457-8458, DOI: 10.1021/ja00071a069

WASSERMAN
8457-8458

J. Am. Chem. Soc. v 115
p. 8457 Wasserman

J-8458-M1

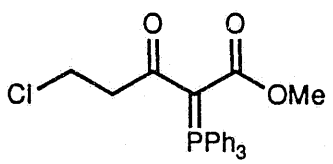
Experimental Section

General Information

Melting points were determined on a Thomas Hoover capillary melting point apparatus and were uncorrected. Infrared spectra were recorded on a Perkin Elmer 1420 Spectrophotometer or Nicolet S-5X FT-IR. Proton and carbon nuclear magnetic resonance spectra were determined in the indicated solvent on a Bruker WM-250 spectrometer. In most cases, trimethyl silane was used as the internal standard (δ 0.00 ppm). Low-resolution mass spectra were recorded on a Hewlett Packard 5985A or 5989A mass spectrometer using electron ionization (20 EV). High-resolution mass spectra, using either electron ionization (EI) or chemical ionization (CI), were performed by Mr. Dan Pentek on a Kratos MS-80RFA at Yale University, Instrument Center. Elemental analyses were performed by Atlantic Microlabs, Norcross, Georgia.

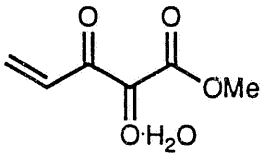
Reactions were generally carried out in oven-dried or flame-dried glassware under a dry nitrogen or argon atmosphere. Flash chromatography was performed on silica gel 60 (230-400 mesh, EM laboratories). All chromatographic solvents were distilled prior to use with the exception of diethyl ether which was obtained in anhydrous form. Thin layer chromatography (TLC) was performed on glass plates pre-coated with silica gel 60 F_{254} (0.25 mm, EM laboratories). Visualization was carried out using UV lamp, iodine, phosphomolybdic acid, or *p*-anisaldehyde stain.

Anhydrous solvents were distilled prior to use as follows: THF was distilled from sodium/benzophenone ketyl; benzene, methylene chloride and hexane were distilled from calcium hydride; ethyl acetate was distilled from K_2CO_3.



J-8458-M2

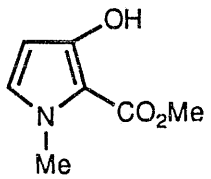
Phosporanylidene. A quantity of 47.6 mL (0.19 mole, 1.8 equivalents) of Bis (trimethylsilyl) acetamide (*BSA*) was added in a dropwise fashion over a period of 5 minutes to a vigorously stirred solution of 37.5 g (0.11 mole, 1.0 equivalent) of methyl (triphenylphosphoranylidene) acetate in 500 mL of benzene at 8° C, followed by 10.5 mL (0.11 mole, 1.0 equivalent) of 3-chloropropionyl chloride. The resulting solution was stirred for an additional 10 min. at 8° C and 30 min. at room temperature. The mixture was then washed 2 X 200 mL of H_2O, the combined aqueous layers were extracted 2 X 200 mL of ether, and the combined organic extracts were washed 1 X 200 mL of brine, dried over anhydrous $MgSO_4$ and solvent removed under reduced pressure. The resulting pale orange solid was washed 3 X 300 mL hexanes which resulted in 41.0 g (88%) of phosporanylidene as a pale yellow solid, mp 114-115° C from ethyl acetate/hexane; ^1H NMR ($CDCl_3$) δ 3.16 (s, 3H), 3.39 (t, J = 7.9 Hz, 2H), 3.81 (t, J = 7.9 Hz, 2H), 7.40-7.58 (m, 9H), 7.61-7.72 (m, 6H); IR (CCl_4) 3060, 2940, 1668, 1432, 1380, 1300, 1110, 1090 cm^{-1}; Anal. Calcd for $C_{24}H_{22}ClO_3P$: C, 67.85; H, 5.22. Found C, 67.73; H, 5.23.



VTC-methyl ester 7. A quantity of 9.0 g (0.021 mole) of **phosporanylidene** in 150 mL of 2:1 CH_2Cl_2/CH_3OH at -78° C was treated with O_3 until a light blue color persisted. The solution was then warmed to room temperature and concentrated under reduced pressure. The residue was dissolved in 100 mL THF and treated, with vigorous stirring, with 70 mL of saturated aqueous $NaHCO_3$ at 0° C for 10 min., and warmed to room temperature for 2.5 hr. The reaction mixture was then diluted with 100 mL of H_2O, extracted 3 X 150 mL ethyl acetate, the combined organic extracts were washed 1 X 100 mL brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was gradient column chromatographed (silica gel, 10% ethyl acetate hexane to 40% ethyl acetate hexane)

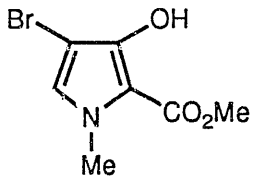
J-84/58-173

to afford 3.0 g (89%) of **VTC-methyl ester 7** as a light yellow oil R_f 0.43 (silica gel, 1:1 ethyl acetate/hexane); ^1H NMR ($CDCl_3$) δ 3.85 (s, 3H), 5.07 (s, 2H), 6.04 (M, 1H), 6.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 53.56, 60.36, 129.02, 133.38, 169.49, 191.33; IR (neat) 3430, 2970, 1750, 1710, 1615, 1440, 1410, 1380, 1270, 1120, 1060, 990 cm^{-1}; Mass Spec (CI) *m/z*, 161 (M^{+1}), 143, 139, 138, 129, 114, 85. Exact Mass Calcd For $C_6H_8O_5$ (hydrate) 161.0449. Found: 161.0450. Exact Mass Calcd For $C_6H_6O_4$ (tricarbonyl) 143.0344. Found: 1143.0342.

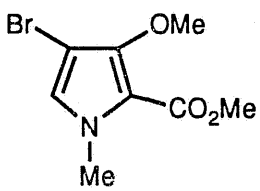


N-methyl-2-methoxycarbonyl-3-hydroxy pyrrole (8). A vigorously stirred solution of 2.0 g (0.0125 mole) of **VTC-methyl ester 7** in 400 mL of CH_2Cl_2 at 0° C was treated in a dropwise fashion over a period of 5 minutes with 1.1 mL (0.0125 mole) 40% methyl amine in H_2O. The resulting solution was stirred for 15 min. at room temperature, at which time no methyl-VTC **7** was visible by TLC, 25 g SiO_2 was added in one portion and stirred for an additional hour. The resulting mixture was filtered through a Celite pad and washed with 200 mL CH_2Cl_2 followed by 200 mL ethyl acetate, the filtrate was concentrated under reduced pressure. The residue was column chromatoghraphed (silica gel, 1:1 ethyl acetate/hexane) to afford 0.6 g (32%) of **N-methyl-2-methoxycarbonyl-3-hydroxy pyrrole (8)** as a light brown solid mp 43-44° C. R_f 0.46 (silica gel, 30% ethyl acetate/hexane); ^1H NMR ($CDCl_3$) δ 3.74 (s, 3H), 3.89 (s, 3H), 5.72 (d, J = 2.8 Hz, 1H), 6.53 (d, J = 2.8 Hz, 1H), 7.98 (bs, 1H): IR ($CHCl_3$) 3500, 2300, 1720, 1660, 1470, 1450, 1410, 1390, 1335, 1120, 1090, 1075 cm^{-1}. Anal. Calcd for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.35; H, 5.92; N, 9.10. Mass Spec (EI, 20 EV) (*m/e*) 155 (M^+), 124, 123, 95, 86, 84; Exact Mass Calcd for $C_7H_9NO_3$ 155.0583. Found 155.0587.

J-84/58-M4



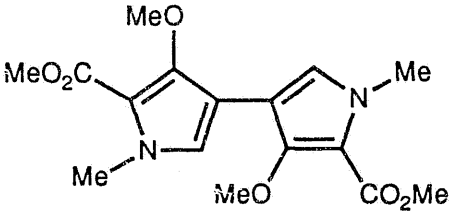
N-methyl-4-bromo-2-methoxycarbonyl-3-hydroxy pyrrole (8a). A vigorously stirred solution of 0.57 g (3.67 mmole) of **N-methyl-2-methoxycarbonyl-3-hydroxy pyrrole (8)** in 40 mL of CH_2Cl_2 at -78° C was treated with 0.58 g (3.30 mmole) of N-bromosuccinimide for 2 hr. The reaction was quenched by addition of 15 mL 10% aqueous Na_2SO_3. The mixture was then warmed to room temperature and extracted 2 X 150 mL CH_2Cl_2, the combined organic extracts were dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and the residue was column chromatographed (silica gel, 20% ethyl acetate / hexanes) to afford 0.64 g (83%) of **N-methyl-4-bromo-2-methoxycarbonyl-3-hydroxy pyrrole (8a)** as a white solid mp 85-87° C. R_f 0.38 (silica gel, 20% ethyl acetate hexane); ^1H NMR ($CDCl_3$) δ 3.75 (s, 3H), 3.91 (s, 3H), 6.59 (s, 1H), 8.05 (bs, 1H): IR (CCl_4) 3495, 2950, 1715, 1664, 1485, 1470, 1450, 1405, 1370, 1335, 1290, 1160, 1110, 1100, 1050 cm^{-1}; Mass Spectrum (EI, 20EV), (*m/e*) 235 (M^+), 233, 203, 201; Exact Mass Calcd for $C_7H_8BrNO_3$ 234.9667. Found: 234.9668. Anal Calcd for $C_7H_8BrNO_3$ C, 35.92; H, 3.45; N, 5.98. Found C, 36.17; H, 3.50; N, 6.08.



N-methyl-4-bromo-2-methoxycarbonyl-3-methoxy pyrrole (8b). A vigorously stirred solution of 0.42 g (1.79 mmole) of **N-methyl-4-bromo-2-methoxycarbonyl-3-hydroxy pyrrole (8a)** in 10 mL of THF at 0° C was treated in one portion with 48 mg (1.96 mmole) of NaH, and the

J-8458.ms

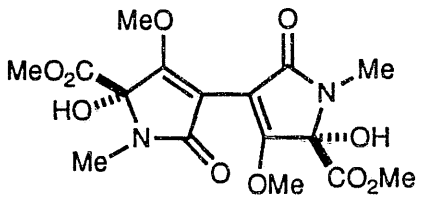
resulting solution was stirred for 5 minutes. At that time 0.2 mL (1.96 mmole) of dimethylsulfate (*DMS*) was added. The resulting solution stirred overnight at room temperature at which time 20 mL of H_2O was added. The reaction mixture was extracted 2 X 100 mL CH_2Cl_2 and the combined organic extracts were dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and residue chromatographed (silica gel, 20% ethyl acetate/hexanes) to afford 0.43 g (99%) of **N-methyl-4-bromo-2-methoxycarbonyl-3-methoxy pyrrole (8b)** as a light yellow solid mp 55-56° C. R_f 0.51 (silica gel, 20% ethyl acetate/hexanes); ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 3.87 (s, 6H), 6.65 (s, 1H); IR (CCl_4) 3000, 2945, 2920, 1700, 1440, 1405, 1360, 1275, 1170, 1105, 1060 cm^{-1}; Mass Spectrum (EI, 20EV), (*m/e*) 249 (M^+), 247, 216, 214, 202, 200; Exact Mass Calcd for $C_8H_{10}BrNO_3$: 248.9824. Found: 248.9829. Anal Calcd for $C_8H_{10}BrNO_3$: C, 38.73; H, 4.06; N, 5.65. Found: C, 38.83; H, 4.07; N, 5.60.



4,4'-Dimethoxy-5,5'-dimethoxycarbonyl-1,1'-dimethyl-3,3'-bipyrrole (6a). A solution of 66 mg (0.266 mmole) of **N-methyl-4-bromo-2-methoxycarbonyl-3-methoxy pyrrole (8b)** and 78 mg (0.334 mmole) of $CuBr_2$ (activated by heating with a flame under aspirator vacuum until slight Br_2 evolution occurs and backfilling with N_2, that process repeated 3 times) in 1 mL of THF at -78° C was treated with 0.23 mL (0.346 mmole) 1.51 M *n*-BuLi in pentane. The resulting mixture was stirred at -78° C for 30 min. warmed to 0° C for 1 hr and finally to room temperature for 1 hr. The reaction was quenched by addition of 10 mL dilute aqueous NH_4OH (2 mL conc. NH_4OH in 8 mL H_2O), extracted 3 X 20 mL CH_2Cl_2, the combined organic extracts were dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and residue chromatographed (silica gel, 20% ethyl acetate/hexanes) to afford 37 mg (83%) of **4,4'-Dimethoxy-5,5'-dimethoxycarbonyl-1,1'-dimethyl-3,3'-bipyrrole**

J 8458-m6

(6a) as a white solid mp 172-173° C. R_f 0.25 (silica gel, 20% ethyl acetate/hexanes); ^1H NMR ($CDCl_3$) δ 3.80 (s, 6H), 3.86 (s, 6H), 3.89 (s, 6H), 7.06 (s, 2H); IR (CCl_4) 3000, 2945, 1695, 1440, 1400, 1360, 1350, 1270, 1160, 1100, 1060 cm^{-1}; Exact Mass Calcd for $C_{16}H_{20}NO_6$: 3336.1321. Found: 336.1325.



Isochrysohermidin (5). A quantity of 9.0 g (0.034 mole) of PPh_3 in 150 mL of CH_2Cl_2 at -78° C was treated with O_3 (to generate $PPh_3 \cdot O_3$) until a light blue color persisted. The solution was then purged with N_2 (until the light blue color faded) to remove the excess O_3. The reaction flask was connected through a glass tube to another flask containing 14 mg (0.042 mmole) of **4,4'-Dimethoxy-5,5'-dimethoxycarbonyl-1,1'-dimethyl-3,3'-bipyrrole (6a)** in 20 mL of CH_2Cl_2 at 0° C. N_2 was bubbled through the $PPh_3 \cdot O_3$ solution while it was allowed to warm to room temperature, thus generating singlet oxygen, which was bubbled through the bipyrrole/CH_2Cl_2 solution for 30 min. The solvent was then removed from the bipyrrole/CH_2Cl_2 solution under reduced pressure and the residue chromatographed (silica gel, ethyl acetate) the fractions with R_f 0.2 to 0.5 were collected to afford 7 mg (42%) of a 1:1 mixture of *d,l* and *meso* diastereomers of **isochrysohermidin (5)**. Purification of the *d,l*-**5** isomer was accomplished by selective recrystallization from ethyl acetate to afford 2.9 mg (18%) of pure *d,l*-**5**. Purification of *meso*-**5** was accomplished by column chromatography (silica gel, ethyl acetate) of the mother liquor.

d,l -**5**: mp 264-267° C from ethyl acetate (white needles) lit[5a] mp 265-268° C from ethyl acetate. R_f 0.31 (silica gel, ethyl acetate); ^1H NMR ($CDCl_3$) δ 2.81 (s, 6H), 3.82 (s, 6H), 3.97 (s, 6H); IR (CH_2Cl_2) 3478, 3407, 3186, 1760, 1740, 1700, 1684, 1644, 1393, 1363, 1253, 1147, 1052 cm^{-1};

J- 8458-m7

Mass Spec (EI, 20EV), (*m/e*) 400 (M^+), 368, 341, 323, 277, 236, 196, 129, 83; Exact Mass Calcd for $C_{16}H_{20}N_2O_{10}$: 400.1118. Found: 400.1117.

meso-**5**: mp 207-210° C from ethyl acetate (white needles) lit[5b] mp 207-209° C. R_f 0.21 (silica gel, ethyl acetate); ^1H NMR ($CDCl_3$) δ 2.79 (s, 6H), 3.88 (s, 6H), 3.97 (s, 6H); IR (CH_2Cl_2) 3478, 1750, 1700, 1684, 1644, 1363, 1300, 1253, 1147, 1052 cm^{-1}; Mass Spec (EI, 20EV), (*m/e*) 400 (M^+), 355, 341, 323, 309, 295, 277, 265, 236, 208, 201; Exact Mass (CI) Calcd for $C_{16}H_{20}N_2O_{10}$: 401.1196. Found: 401.1174.

J-8458-m8

5,5′-Dimethoxy-3,3′,6,6′-tetramethoxycarbonyl-4,4′-bi-1,2-diazine (11). Mp 124-125°C (Et_2O, pale yellow plates); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.12 (s, 3H, OMe), 3.89 (s, 3H, CO_2Me), 3.82 (s, 3H, CO_2Me); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 164.4 (e, C-3 CO_2Me), 163.8 (e, C6 CO_2Me), 155.9 (e, C-5), 150.4 (e, C-4), 147.3 (e, C-3), 125.8 (e, C-6), 61.6 (o, OMe), 53.7 (o, CO_2Me), 53.4 (o, CO_2Me); UV ($CHCl_3$) λ_{max} 248 nm (ε 58000); IR (KBr) ν_{max} 3745, 1735, 1697, 1438, 1385, 1288, 1249, 1211, 1098, 1054 cm^{-1}; EIMS, *m/e* (relative intensity) 450 (M^+, 4) 378 (14), 377 (95), 325 (35), 211 (91), 179 (39), 59 (base); CIMS (2-methylpropane), *m/e* 451 (M + H^+, base); EIHRMS, *m/e* 450.1021 ($C_{18}H_{18}N_4O_{10}$ requires 450.1023).

Anal. Calcd for $C_{18}H_{18}N_4O_{10}$: C, 48.01; H, 4.03; N, 12.44. Found: C, 47.72; H, 3.93; N, 12.22.

4,4′-Dimethoxy-2,2′,5,5′-tetramethoxycarbonyl-3,3′-bipyrrole (12). Mp 199-200°C (*i*PrOH, colorless needles); ^1H NMR ($CDCl_3$, 500 MHz) δ 9.44 (bs, 1H, NH), 3.98 (s, 3H, OMe), 3.78 (s, 3H, CO_2Me), 3.72 (s, 3H, CO_2Me); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 160.6 (e, C-2 CO_2Me), 160.3 (e, C-5 CO_2Me), 150.7 (e, C-4), 120.6 (e, C-3), 114.1 (e, C-2), 112.6 (e, C-5), 62.0 (o, OMe), 51.8 (o, CO_2Me), 51.8 (o, CO_2Me); UV ($CHCl_3$) λ_{max} 282 nm (ε 46000); IR (KBr) ν_{max} 3315, 3286, 2956, 1727, 1705, 1556, 1491, 1440, 1303, 1267, 1247, 1200, 1143, 1110, 1017, 957, 784 cm^{-1}; EIMS, *m/e* 424 (M^+, base); CIMS (2-methylpropane), *m/e* 425 (M + H^+, base); EIHRMS *m/e* 424.1119 ($C_{18}H_{20}N_2O_{10}$ requires 424.1118).

Anal. Calcd for $C_{18}H_{20}N_2O_{10}$: C, 50.95; H, 4.75; N, 6.60. Found: C, 50.79; H, 4.88; N, 6.54.

4,4′-Dimethoxy-2,2′,5,5′-tetramethoxycarbonyl-1,1′-dimethyl-3,3′-bipyrrole (13). Mp 119-120°C (*i*PrOH, colorless prisms); ^1H NMR ($CDCl_3$, 200 MHz) δ 4.16 (s, 3H, NMe),

J 8458-m9

3.91 (s, 3H, OMe), 3.63 (s, 3H, CO_2Me), 3.60 (s, 3H, CO_2Me); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 161.7 (e, C-2 CO_2Me), 161.4 (e, C-5 CO_2Me), 150.6 (e, C-4), 124.3 (e, C-3), 117.2 (e, C-2), 113.7 (e, C-5), 62.1 (o, OMe), 51.5 (o, CO_2Me), 51.4 (o, CO_2Me), 34.9 (o, NMe); UV ($CHCl_3$) λ_{max} 286 nm (ε 22000); IR (KBr) ν_{max} 2955, 1719, 1483, 1458, 1433, 1414, 1399, 1350, 1283, 1241, 1206, 1116, 1032 cm^{-1}; EIMS, *m/e* 452 (M^+, base); CIMS (2-methylpropane), *m/e* 453 ($M + H^+$, base); EIHRMS, *m/e* 452.1431 ($C_{20}H_{24}N_2O_{10}$ requires 452.1431).

Anal. Calcd for $C_{20}H_{24}N_2O_{10}$: C, 53.10; H, 5.35; N, 6.19. Found: C, 52.89; H, 5.50; N, 6.17.

4,4′-Dimethoxy-1,1′-dimethyl-3,3′-bipyrrole-2,2′,5,5′-tetracarboxylic Acid (14). Mp 190-192°C (dec, *i*PrOH-Et_2O, white solid); ^1H NMR (d_6-acetone, 200 MHz) δ 4.14 (s, 3H, NMe), 3.66 (s, 3H, OMe); ^{13}C NMR (CD_3OD, 50 MHz) δ 164.2 (e, C-2 CO_2H), 163.6 (e, C-5 CO_2H), 152.2 (e, C-4), 126.6 (e, C-3), 118.5 (e, C-2), 115.5 (e, C-5), 47.7 (o, OMe), 35.4 (o, NMe); UV (CH_3CN) λ_{max} 288 nm (ε 22700); IR (KBr) ν_{max} 3855, 3745, 3630, 3423, 2966, 2616, 1685, 1526, 1444, 1419, 1352, 1262, 1207, 1114 cm^{-1}; FABHRMS (NBA), *m/e* 397.0810 ($C_{16}H_{16}N_2O_{10} + H^+$ requires 397.0883).

Anal. calcd for $C_{16}H_{16}N_2O_{10}$: C, 48.49; H, 4.07; N, 7.07. Found: C, 48.09; H, 4.44; N, 7.38.

4,4′-Dimethoxy-5,5′-dimethoxycarbonyl-1,1′-dimethyl-3,3′-bipyrrole-2,2′-dicarboxylic Acid (6b). Mp 175-177°C (dec, *i*PrOH-Et_2O, white solid); ^1H NMR (d_6-DMSO, 400 MHz) δ 4.02 (s, 3H, NMe), 3.81 (s, 3H, OMe), 3.52 (s, 3H, CO_2Me); ^{13}C NMR (d_6-DMSO, 100 MHz) δ 161.8 (e, CO_2H), 149.9 (e, CO_2Me), 149.8 (e, C-4), 124.9 (e, C-3), 116.1 (e, C-2), 113.6 (e, C-5), 61.7 (o, OMe), 51.5 (o, CO_2Me), 34.8 (o, NMe); UV (THF) λ_{max} 280 nm (ε 24800); IR (KBr) ν_{max} 3418, 2923, 1720, 1655, 1443, 1384, 1261, 1101, 800 cm^{-1};

J- 8458m10

FABHRMS (NBA), *m/e* 424.1118 ($C_{18}H_{20}N_2O_{10}$ requires 424.1118).

Anal. Calcd for $C_{18}H_{20}N_2O_{10}$: C, 50.95; H, 4.75; N, 6.60. Found: C, 51.30; H, 5.07; N, 6.50.

Isocrysohermidin (5). A solution of **6b** (40.0 mg, 0.094 mmol) in collidine (30 mL), H_2O (90 mL), and 2-propanol (15 mL) containing Rose Bengal (800 μg, 7.9 x 10^{-4} mmol, 8 mequiv) in a pyrex tube was treated with a steady stream of O_2 (5 psi). The solution was irradiated with a Hanovia high-pressure mercury lamp (450 W) through a uranium yellow glass filter (transmits > 330 nm) at 22°C for 1 h. The reaction mixture was partitioned between 10% aqueous HCl and EtOAc. The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography (SiO_2, 1 x 10 cm, EtOAc) afforded 35 mg of crude product (R_f 0.2-0.5, EtOAc). The crude product which contained a mixture of d,l- and meso-**5** as well as potential ring opened isomers was dissolved in hot EtOAc which was allowed to slowly concentrate (recrystallization of the mother liquor was repeated two times) to afford d,l-**5** as a white solid (14 mg, 38 mg theoretical, 37%; typically 37-43%). The mother liquor was concentrated and the residue purified by chromatography (SiO_2, 1 x 10 cm, EtOAc, 3x) to afford pure meso-**5** (3 mg, 38 mg theoretical, 8%). For d,l-**5**: mp 266-268°C (EtOAc, colorless needles); lit[6] mp 265-268°C (EtOAc); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.62 (bs, 1H, OH), 3.98 (s, 3H, OMe), 3.83 (s, 3H, CO_2Me), 2.84 (s, 3H, NMe); ^{13}C NMR (d_6-DMSO, 100 MHz) δ 169.7 (e, *C*ONMe), 168.6 (e, *C*O_2Me), 167.9 (e, C-4), 97.2 (e, C-3), 86.8 (e, C-5), 58.8 (o, CO_2*Me*), 53.3 (o, OMe), 24.1 (o, NMe); IR (KBr) ν_{max} 3478, 3408, 3187, 1760, 1740, 1700, 1684, 1644, 1393, 1363, 1253, 1147, 1052 cm^{-1}; FABHRMS (NBA-CsI), *m/e* 533.0178 ($C_{16}H_{20}N_2O_{10}$ + Cs^+ requires 533.0172).

For meso-**5**: mp 207-209°C (EtOAc, white powder); lit[5] mp 207-209°C (1:1, EtOAc-

J-8458-m11

Et_2O); ^1H NMR ($CDCl_3$, 400 MHz) δ 4.65 (bs, 1H, OH), 3.98 (s, 3H, OMe), 3.87 (s, 3H, CO_2Me), 2.78 (s, 3H, NMe); ^{13}C NMR (d_6-DMSO, 100 MHz) δ 169.6 (e, *C*ONMe), 168.5 (e, *C*O_2Me), 167.7 (e, C-4), 97.1 (e, C-3), 86.7 (e, C-5), 58.7 (o, CO_2*Me*), 53.2 (o, OMe), 23.9 (o, NMe); IR (KBr) ν_{max} 3413, 3180, 2954, 1753, 1730, 1706, 1692, 1638, 1440, 1366, 1307, 1253, 1146, 1053, 938 cm^{-1}; FABHRMS (NBA-CsI), *m/e* 533.0172 ($C_{16}H_{20}N_2O_{10}$ + Cs^+ requires 533.0172).

Singlet Oxygen Reaction of **6b**.[a]

solvent	d,l-**5**
*i*PrOH-H_2O (3:1)	---
CH_3CN-H_2O (3:1)	---
*i*PrOH-Pyridine-H_2O (3:1:1)	6%[b] 16%[c]
CH_3CN-Pyridine-H_2O (3:1:1)	5%[b]
*i*PrOH-H_2O-DBU (6:2:1)	---
Pyridine-H_2O (1:1)	10%[b] 23%[c]
Pyridine-H_2O (1:3)	28%[c]
Pyridine-H_2O (3:1)	11%[c]
Collidine-H_2O (1:10)	26%[c]
Collidine-H_2O (1:3)	40%[c]
Collidine-H_2O (1:1)	36%[c]

[a] $^1O_2$ source: rose bengal (8 mequiv), Hanovia high-pressure lamp (450 W), uranium yellow glass filter (transmits > 330 nm), O_2, 22°C, 1 h. [b] Product (R_f 0.39, SiO_2, EtOAc) was isolated by chromatography (SiO_2, EtOAc) and recrystallized (EtOAc) to provide pure d,l-**5**. [c] Product (R_f 0.2-0.5) isolated by chromatography (SiO_2, EtOAc) and recrystallized (EtOAc) to provide pure d,l-**5**. Meso-**5** and isomers of **5** remained in mother liquor.