Alternate Self-Regeneration of Stereocenters: Enantioselective Generation of a C_2-Symmetric Chiral Nitroxide and Its Reduction to the Corresponding, Highly Sterically Hindered Amine

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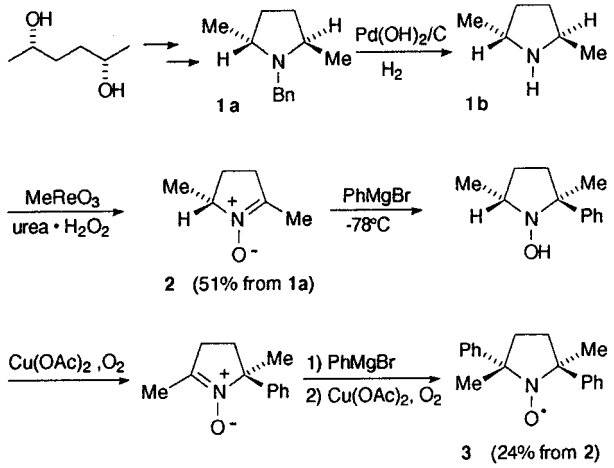
Nitroxides continue to play a central role among organic stable free radicals. They have been, and are still, extensively used as spin labels[1] and in spin trapping experiments,[2] but many other promising applications have emerged more recently: they are now studied as spin sources for the elaboration of organic magnetic materials,[3] as precursors of highly selective oxidants,[4] or as capping agents for the control of "living" free-radical polymerization processes.[5] Chiral nitroxides have attracted a special interest in very recent years due to their potential applications as enantioselective oxidation catalysts, for the development of paramagnetic chiral liquid crystals, or in stereoselective coupling reactions with prochiral radicals.[6] Moreover, chiral nitroxides can be reductively transformed into the corresponding, potentially valuable, chiral amines by very simple and mild chemical processes.[2a] In this context, C_2-symmetric chiral nitroxides appear to be valuable synthetic targets, owing to the well-recognized importance of C_2 chiral auxiliaries in asymmetric synthesis.[7] Up to now, although several C_2-symmetric nitroxide have been described in their racemic form,[5c,8a−e] examples of optically active C_2 nitroxides remain scarce. Müllen[8f] and Sogah[5c] prepared racemic *trans*-2,5-dimethyl-2,5-diphenylpyrrolidin-1-oxy radical **3**. Müllen separated its enantiomers on a half gram scale by chiral HPLC. However, the absolute configurations of the stereocenters remained unknown. We describe herein an enantioselective approach to nitroxide **3**, starting from readily available optically active *trans*-2,5-dimethylpyrrolidine (**1b**) (Scheme 1).

Scheme 1. Enantioselective Synthesis of C_2-Symmetric (2*S*,5*S*)-2,5-Dimethyl-2,5-diphenylpyrrolidin-1-oxy Radical 3



The principle of the synthesis is very simple: C_2-symmetric optically active pyrrolidine **1b**, bearing two equivalent stereogenic centers, was first oxidized into optically active nitrone **2**. The following synthesis utilized the methodology originally developed by Keana[8a−d] and also used by Mullen[8f] and proceeded via two successive nitrone nucleophilic addition−oxidation sequences. This method was known as allowing an efficient control of the relative stereochemistry of the newly created stereocenters, the nucleophiles being introduced on the most accessible faces of the intermediate nitrones, i.e., in the trans relationship with respect to the bulkiest substituent. When applied to optically active nitrone **2**, an absolute control of the newly created stereocenters was performed, generating optically active, C_2-symmetric nitroxide **3**. Starting from C_2-symmetric pyrrolidine **1**, the whole process can be conceptually related to Seebach's general principle of self-regeneration of stereocenters (SRS).[9] In our case, each stereocenter alternatively plays the role of "chiral memory", the second one being destroyed during oxidation into a nitrone. The remaining stereocenter is, therefore, able to ensure the absolute stereochemical control of the subsequent nucleophilic addition to this nitrone.

Improved methods are known for the synthesis of optically active *trans*-2,5-dimethylpyrrolidine.[10] One of the most convenient methods, reported by Masamune,[11] starts from optically pure (2*S*,5*S*)-2,5-hexanediol,[12] now

(1) (a) Keana, J. F. W. *Chem. Rev.* **1978**, *78*, 37−64. For recent examples see: (b) Bossmann, S. H.; Ghatlia, N. D.; Ottaviani, M. F.; Turro, C.; Dürr, H.; Turro, N. J. *Synthesis* **1996**, 1313−1319. (c) Ulrich, G; Turek, P.; Ziessel, R.; De Cian, A.; Fischer, J. *Chem. Commun.* **1996**, 2461−2462.

(2) (a) Aurich, H. G. in *Nitrones, Nitronates and Nitroxides*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons, Inc.: New York, 1989; pp 313−399. For a recent example, see: (b) Sankuratri, N.; Janzen, E. G.; West, M. S.; Poyer, J. L. *J. Org. Chem.* **1997**, *62*, 1176−1178 and references therein.

(3) See, for example: (a) Chiarelli, R.; Novak, M. A.; Rassat, A.; Tholence, J. L. *Nature* **1993**, *363*, 147−149. (b) Cirujeda, J.; Mas, M.; Molins, E.; Lanfranc de Panthou, F.; Laugier, J.; Park, J. G.; Paulsen, C.; Rey, P.; Rovira, C.; Veciana, J. *J. Chem. Soc., Chem. Commun.* **1995**, 709−710. (c) Inoue, K.; Hayamizu, T.; Iwamura, H.; Hashizume, D.; Onashi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 1803−1804.

(4) (a) Einhorn, J.; Einhorn, C.; Ratajczak, F.; Pierre, J. L. *J. Org. Chem.* **1996**, *61*, 7452−7454. For a review see: (b) de Nooy, A. E. J.; Besemer, A. C.; van Bekkum, H. *Synthesis* **1996**, 1153−1174.

(5) (a) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185−11186. (b) Hawker, C. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1456−1459. (c) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1996**, *29*, 3323−3325. (d) Connolly, T. J.; Scaiano, J. C. *Tetrahedron Lett.* **1997**, *38*, 1133−1136.

(6) (a) Ma, Z.; Huang, Q.; Bobbitt, J. M. *J. Org. Chem.* **1993**, *58*, 4837−4843. (b) Rychnovsky, S. D.; McLernon, T. L.; Rajapakse, H. *J. Org. Chem.* **1996**, *61*, 1194−1195. (c) Tamura, R.; Susuki, S.; Azuma, N.; Matsumoto, A.; Toda, F.; Kamimura, A.; Hori, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 878−879. (d) Tamura, R.; Susuki, S.; Azuma, N.; Matsumoto, A.; Toda, F.; Ishii, Y. *J. Org. Chem.* **1995**, *60*, 6820−6825. (e) Braslau, R.; Burrill, L. C., II; Mahal, L. K.; Wedeking, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 237−238.

(7) Review: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581−1590.

(8) (a) Lee, T. D.; Birrel, G. B.; Keana, J. F. W. *J. Am. Chem. Soc.* **1978**, *100*, 1618−1619. (b) Keana, J. F. W.; Seyedrezai, S. E.; Gaughan, G. *J. Org. Chem.* **1983**, *48*, 2644−2647. (c) Keana, J. F. W.; Cuomo, J.; Lex, L.; Seyedrezai, S. E. *J. Org. Chem.* **1983**, *48*, 2647−2654. (d) Keana, J. F. W.; Prabhu., V. S. *J. Org. Chem.* **1986**, *51*, 4300−4301. (e) Einhorn, J.; Einhorn, C.; Ratajczak, F.; Pierre, J. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1029−1030. (f) Benfaremo, N.; Steenbock, M.; Klapper, M.; Müllen, K.; Enkelmann, V.; Cabrera, K. *Liebigs Ann.* **1996**, 1413−1415.

(9) Review: Seebach, D.; Sting, A. R.; Hoffmann, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2708−2748.

(10) For a review on the synthesis of 2,5-disubstituted pyrrolidines see: Pichon, M.; Figadère, B. *Tetrahedron: Asymmetry* **1996**, *7*, 927−964.

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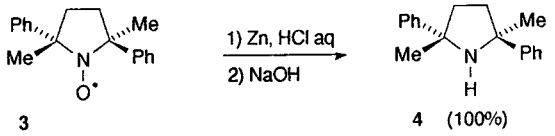
commercially available. Transformation of the diol into dimesilate and double nucleophilic displacement with benzylamine furnishes (2*R*,5*R*)-1-benzyl-2,5-dimethylpyrrolidine (**1a**) with high enantiopurity. In our hands, **1a** proved to be an easy-to-store, protected form of pyrrolidine **1b** itself: N-debenzylation of **1a** to **1b** and subsequent oxidation of **1b** into nitrone **2** has thus been conducted without the need of the highly volatile **1b** to be isolated. The choice of the proper oxidation method of **1b** into **2** was crucial: oxidation of amines to nitrones can efficiently be performed with H_2O_2 catalyzed by Na_2WO_4.[13] Applied to optically active **1b**, this method gave somewhat erratic results with variable degrees of racemization of nitrone **2**. A better alternative is the recently described oxidation method using methyltrioxorhenium/urea·H_2O_2 complex.[14] In this case, the enantiomeric purity of nitrone **2** consistently reflects that of amine **1a**.[15] The following synthesis was straightforward: reaction of optically active nitrone **2** (96% ee) with phenylmagnesium bromide, at −78 °C, followed by a reaction sequence similar to that developed by Keana,[8a−d] gave nitroxide **3** *with an enantiomeric excess of 93%* (measured after column chromatography purification on silica gel).[16,17] The absolute configuration of nitroxide **3** can be correlated to that of the starting amine **1b**: (2*R*,5*R*)-2,5-dimethylpyrrolidine furnishes (2*S*,5*S*)-2,5-dimethyl-2,5-diphenylpyrrolidin-1-oxy radical. The enantiomeric purity of nitroxide **3** could be raised from 93% to 99.8% by two recrystallizations from hexane. This sample had a specific rotation $[\alpha]^{21}_D$ −170.5 (*c* 1.04, EtOAc) and melted at 132.5−133 °C (lit.[8f] $[\alpha]^{25}_D$ 174.4 (*c* 0.108, hexane), mp 130 °C). The spectral properties were in accordance with literature data.[8f] Optically pure **3** is thus available from commercial optically active 2,5-hexanediol without any intermediate enantiomeric enrichment.

Nitroxide **3** was next reduced to the corresponding amine **4**. Attempts to perform the reduction by catalytic hydrogenation using various catalysts were disapointing, leading to extensive degradation. Gratifingly, reduction by zinc in aqueous hydrochloric acid[18] followed by an alkaline workup gave amine **4** with a quantitative yield

Scheme 2. Reduction of Nitroxide 3 to Amine 4



3 4 (100%)

(Scheme 2). Starting from a sample of **3** with an ee of 99.8%, amine **4** had a specific rotation $[\alpha]^{21}_D$ −119.7 (*c* 2.61, EtOAc). Attempts to determine the enantiomeric purity of this amine directly by chiral HPLC or by using NMR techniques[19] have failed so far. It was, however, possible to oxidize amine **4** back into nitroxide **3** with Oxone.[20] Recovered nitroxide **3** had an unchanged enantiomeric purity, confirming that, as expected, both reduction and reoxidation occurred without any loss of enantiomeric purity. Optically active **4** should find interesting applications, for example, by transformation into its lithium amide, as a C_2-symmetric chiral equivalent of lithium 2,2,6,6-tetramethylpiperidide (LiTMP).[21]

Experimental Section

General Methods. (2*S*,5*S*)-2,5-Hexanediol, urea·H_2O_2 complex, Oxone, and methyltrioxorhenium were purchased from Aldrich and used without purification. THF was distilled over sodium/benzophenone prior to use. Infrared spectra were recorded as liquid fims on NaCl plates or as KBr pellets. ^{1}H NMR spectra were recorded at 250 MHz and ^{13}C NMR at 62.5 MHz; $CDCl_3$ was used as the solvent. Chiral HPLC was performed on a Chiracel OD-H column with a UV−vis spectrometer (254 nm) as the detector. UV−vis spectra were recorded in CH_2Cl_2 solutions in 1 cm quartz cells.

(5*R*)-3,4-Dihydro-2,5-dimethyl-5*H*-pyrrole 1-Oxide (2). **1a** (6.6 g, 34.3 mmol) (96% ee) was dissolved in 15 mL of MeOH. $Pd(OH)_2$ (2 g) at 20% on carbon was added, and the mixture was vigorously stirred under H_2, at room temperature and atmospheric pressure, until completion of the reaction (TLC on alumina; hexane/EtOAc, 1:1) (5−7 h). The reaction mixture was then filtered on a short path of Celite. Catalyst and Celite were thorougly washed with MeOH (3 × 5 mL) and the washings combined with the filtrate. In a separate flask, 0.185 g of methyltrioxorhenium and 25 g of urea·H_2O_2 complex in 5 mL of MeOH were stirred at room temperature during 10 min and then cooled to 0 °C. The methanolic solution obtained earlier was then added under stirring to this reaction mixture, whose color turned from yellow to dark red. After the mixture has been stirred for 1 h at 0 °C, followed by 12 h at room temperature, the solvent was evaporated in vacuo. The yellowish solid residue was washed with CH_2Cl_2 (3 × 50 mL). The filtrate was concentrated to give a yellow oil. This crude product was purified by column chromatography (silica gel; EtOAc/MeOH, 8:2) to afford 2 g (51%) of pure nitrone **2**: $[\alpha]^{21}_D$ +13.6 (*c* 1.07, EtOAc), ee = 96%.[15] Spectroscopic data are in accordance with those of the literature concerning the racemic compound.[22]

(2*S*,5*S*)-2,5-Dimethyl-2,5-diphenylpyrrolidin-1-oxy Radical (3). Nitrone **2** (2 g, 17.6 mmol) (96% ee) was dissolved in 10 mL of anhydrous THF, under argon, and cooled at −78 °C. To this was added a solution of PhMgBr in THF (1 M, 35 mmol, 35 mL). The temperature was raised slowly to room temperature, and stirring was maintained overnight. The reaction

(11) Short, R. P.; Kennedy, R. M.; Masamune, S. *J. Org. Chem.* **1989**, *54*, 1755−1756.

(12) (2*S*,5*S*)-2,5-Hexanediol is conveniently obtained by bakers' yeast reduction of 2,5-hexanedione: Lieser, J. K. *Synth. Commun.* **1983**, *13*, 765−767. For a recent synthesis of (2*R*,5*R*)-2,5-hexanediol from mannitol, see: Saravanan, P.; Raina, S.; Sambamurthy, T.; Singh, V. K. *J. Org. Chem.* **1997**, *62*, 2669−2670.

(13) (a) Murahashi, S. I.; Mitsui, H.; Shiota, T.; Tsuda, T.; Watanabe, S. *J. Org. Chem.* **1990**, *55*, 1736−1744. (b) Murahashi, S I.; Shiota, T.; Imada, Y. *Org. Synth.* **1991**, *70*, 265−271.

(14) (a) Murray, R. W.; Iyanar, K.; Chen, J.; Wearing, J. T. *J. Org. Chem.* **1996**, *61*, 8099−8102. (b) Goti, A.; Nanelli, L. *Tetrahedron Lett.* **1996**, *37*, 6025−6028.

(15) The enantiomeric purity of optically active nitrone **2** has been estimated by ^{1}H NMR at 200 MHz by adding 3 equiv of enantiomerically pure 2,2′-dihydroxy-1,1′-binaphthyl to a diluted solution of nitrone **2** in $CDCl_3$. Effective splitting of the methyl singlet at 2.04 ppm was observed. See: Toda, F.; Mori, K.; Okada, J.; Node, M.; Itoh, A.; Oomine, K.; Fuji, K. *Chem. Lett.* **1988**, 131−134.

(16) Enantiomeric composition of the optically active nitroxide has been determined by HPLC on a Chiracel OD-H column, elution: ^{i}PrOH/hexane (1/9), 0.5 mL min^{-1}.

(17) When the same sequence was performed with (4-*tert*-butylphenyl)magnesium bromide on another sample of nitrone **2** with ee = 98%, a 79% ee of the corresponding nitroxide was obtained. Benzylmagnesium bromide gave the dibenzyl nitroxide with an ee of only 7%, starting from a 93% enantiopure nitrone **2**. Further studies concerning these dramatic variations in the enantioselectivities as well as improvements of the present method by the use of other organometallics will be reported elswhere.

(18) Rosantsev, E. G.; Sholle, V. D. *Synthesis* **1971**, 401−414.

(19) Parker, D. *Chem. Rev.* **1991**, *91*, 1441−1457.

(20) See: Brik, M. E. *Tetrahedron Lett.* **1995**, *36*, 5519−5522. Brik claimed in situ generated dimethyldioxirane to be the true oxidant in his procedure, as acetone was used as a cosolvent. We have, however, found that when acetone was replaced by ethanol or methanol very similar results were observed, suggesting a more direct involvment of Oxone.

(21) For recent examples of C_2-symmetric amines, see: Woltersdorf, M.; Kranich, R.; Schmalz, H. G. *Tetrahedron* **1997**, *53*, 7219−7230. For applications of C_2-symmetric amines in synthesis see references therein.

(22) Turner, M. J.; Luckenbach, L. A.; Turner, E. L. *Synth. Commun.* **1986**, *16*, 1377−1385.

mixture was then poured into a saturated NH_4Cl solution (100 mL). The mixture was filtrated on a pad of Celite and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product (5.35 g) was dissolved in methanol (66 mL). To this solution were added concentrated ammonium hydroxide (22 wt %, 5 mL) and copper(II) acetate monohydrate (0.57 g, 2.85 mmol). Oxygen was bubbled through the yellow solution so obtained until a persistent deep blue color was observed. The solvent was then removed under reduced pressure and the crude product redissolved in $CHCl_3$ (100 mL). This solution was washed with a saturated $NaHCO_3$ solution (50 mL) and dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product (5.15 g) was dissolved in 50 mL of anhydrous THF and treated with PhMgBr (same quantity and conditions as above). After workup (see above) 6 g of crude product was obtained. It was oxidized by O_2/copper acetate (same quantities, conditions, and workup as above), furnishing 7 g of brown viscous oil. Purification by column chromatography on silica gel (hexane/EtOAc, 98:2) provided nitroxide **3** (1.17 g, 24% yield from **2**, 93% ee), mp 123.5−129 °C. Two recrystallizations from hexane gave 0.71 g of **3** with ee = 99.8%: mp 132.5−133 °C; $[\alpha]^{21}_D$ −170.5° (*c* 1.04, EtOAc); IR (KBr) 1601, 1496, 1444, 1416, 1372, 1269, 1063 cm^{-1}; MS (DCI, NH_3 + isobutane) *m*/*z* 266 (100), 284 (16); UV−vis (0.32 10^{-3} M in CH_2Cl_2) 241 nm (ϵ = 2500), 423 nm (ϵ = 4); ESR (1.3 10^{-3} M in toluene) g = 2.0066, a_N = 13.3 G. Anal. Calcd for $C_{18}H_{20}NO$: C, 81.17; H, 7.56; N, 6.00. Found: C, 81.18; H, 7.72; N, 5.86.

(2*S*,5*S*)-2,5-Dimethyl-2,5-diphenylpyrrolidine (4). A mixture of 0.532 g (2 mmol) of nitroxide **3** (99.8% ee), 12 mL of water, 3 mL of concentrated hydrochloric acid, and 0.94 g (14 mmol) of zinc powder were refluxed under vigorous stirring until the yellow color of the nitroxide had disappeared (1 h). After cooling, the reaction mixture was made alkaline (pH > 12) with concentrated NaOH (30 wt %) and then extracted with Et_2O. The combined extracts were dried over Na_2SO_4; the solvent was removed under reduced pressure to afford 0.502 g of pure **4** as a colorless oil: bp 115 °C (0.5 mmHg). **4·HCl**: mp 165−168 °C; IR (neat) cm^{-1} 3083, 3058, 3024, 2968, 1445, 1094, 1027; ^1H NMR δ (ppm) 1.34 (6H, s), 1.73 (1H, bs), 2.13−2.27 (4H, m), 7.19−7.62 (10H, m); ^{13}C NMR δ (ppm) 32.3, 39.8, 65.4, 125.3, 125.9, 151.3. Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.41; N, 5.57. Found: C, 86.12; H, 8.50; N, 5.58.

Reoxidation of Amine 4 into Nitroxide 3. Amine **4** (25.1 mg, 0.1 mmol) was dissolved in a mixture of 1 mL of EtOH[20] and 0.3 mL of water. To this solution were added, under stirring, 106 mg (1 mmol) of Na_2CO_3 followed by 361 mg of Oxone (0.46 mmol) in portions of ca. 50 mg every 10 min. At the end of the addition, the mixture was stirred for another 5 h. The solid was then filtered off and washed with ethanol. The combined filtrate and washings were evaporated at reduced pressure, and the residue was chromatographed on silica gel (hexane/EtOAc, 98:2), affording 19.7 mg of nitroxide **3** (74%), ee = 99.8%.[16]

JO971812P

Additions and Corrections

Vol. 60, 1995

Narasimhachari Narayanan, Lucjan Strekowski, Malgorzata Lipowska, and Gabor Patonay*. A New Method for the Synthesis of Heptamethine Cyanine Dyes: Synthesis of New Near Infrared Fluorescent Labels.

Page 2391. L. Strekowski and M. Lipowska should be included as authors for this paper.

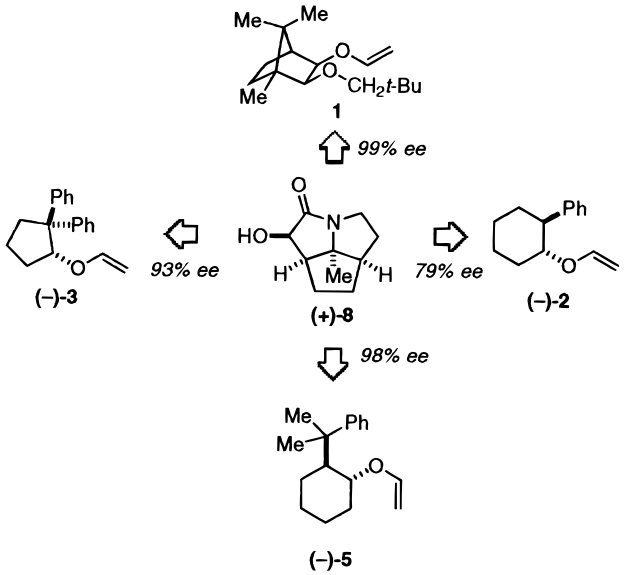
Page 2395, Acknowledgment. This work was supported by a grant from LI-COR, Inc., Lincoln, NE.

JO974022O

Vol. 61, 1996

Scott E. Denmark* and Atli Thorarensen. Tandem [4 + 2]/[3 + 2] Cycloadditions of Nitroalkenes. 10. *trans*-2-(1-Methyl-1-Phenylethyl)cyclohexanol as a New Auxiliary.

Page 6728, Figure 2. Structure **8** in Figure 2 is correctly depicted as the (1*R*) isomer for the intended correlations. However, the (1*R*) isomer is dextrotatory and the sign of rotation shown for **8** is in error, the correct label is (+)-**8**.



Leo Paquette* and Jingsung Tae. Stereocontrolled Preparation of Spirocyclic Ethers by Intramolecular Trapping of Oxonium Ions with Allylsilanes.

Page 7860. The pioneering investigations by Denmark on the stereochemistry and mechanism of allylmetal−acetal additions were inadvertently not cited. The relevant references are as follows.

(1) Denmark, S. E.; Willson, T. M. *J. Am. Chem. Soc.* **1989**, *111*, 3475.
(2) Denmark, S. E.; Willson, T. M. In *Selectivities in Lewis Acid Promoted Reactions*; Schnizer, D., Ed.; Kluwer Academic Publishers: 1989; pp 247−263.

JO974005Z JO974032P

Vol. 62, 1997

N. André Sasaki,* Michael Dockner, Angèle Chiaroni, Claude Riche, and Pierre Potier. A Novel Stereodivergent Synthesis of Optically Pure *cis*- and *trans*-3-Substituted Proline Derivatives.

Page 766, column 1, lines 6−11, should read "While **5a** exhibits a multiplet centered at 5.70 ppm which is attributed to one of the allylic protons, its counterpart of **5b** appears somewhat downfield centered at 6.08 ppm suggesting *cis* relationship between the allyl and the hydroxymethyl groups."

JO9740249

Shikegi Matsunaga, Toshiyuki Wakimoto, and Nobuhiro Fusetani*. Isolation of Four New Calyculins from the Marine Sponge *Discodermia calyx*.

Page 2640. Structural formulas for compounds **1**−**5** were inadvertently drawn in an enantiomeric form.

JO9740251

Neville P. Pavri and Mark L. Trudell*. An Efficient Method for the Synthesis of 3-Arylpyrroles.

Page 2649. The fourth sentence of the last paragraph should read "A recent report describes the synthesis of **4a** from benzonitrile in four steps and 37% overall yield[5]...".

JO9740150

Dennis P. Arnold* and David A. James. Dimers and Model Monomers of Nickel(II) Octaethylporphyrin Substituted by Conjugated Groups Comprising Combinations of Triple Bonds with Double Bonds and Arenes. 1. Synthesis and Electronic Spectra.

Page 3468, column 1. The electronic spectral data for compound **25** were incorrect. The data should read as follows: vis λ_{max} 408 nm (ϵ 153 000), 442 sh (100 000), 530 (24 400), 567 (30 000), 602 sh (21 000). The spectrum displayed in Figure 6 is correct.

JO974026T

Raymond J. Cvetovich,* Chris H. Senanayake, Joseph S. Amato, Lisa M. DiMichele, Timothy J. Bill, Ji Liu, Sheo B. Singh, Robert D. Larsen, R. F. Shuman, Thomas R. Verhoeven, and Edward J. J. Grabowski. Practical Syntheses of 13-*O*-[(2-Methoxyethoxy)-methyl]-22,23-dihydroavermectin B_1 Aglycon [Dimedectin Isopropanol, MK-324] and 13-*epi*-*O*-(Methoxymethyl)-22,23-Dihydroavermectin B_1 Aglycon [L-694,554], Flea Active Ivermectin Analogues.

Page 3989. Due to an oversight, two names (Ji Liu and Sheo B. Singh) were not included in the list of authors for this paper, for which they are fully deserving.

JO974017K

N. A. J. M. Sommerdijk, P. J. J. A. Buynsters, H. Akdemir, D. G. Geurts, R. J. M. Nolte,* and Binne Zwanenburg*. Aziridines as Synthons for Chiral Amide-Containing Surfactants.

Page 4958−9. The names of compounds **8b**, **8c**, **9b**, and **9c** should read as follows: disodium (2*S*)-3-butanoyl-2-(dodecanoylamino)propan-1-yl phosphate (**8b**), disodium (2*S*)-3-butanoyl-2-(octadecanoylamino)propan-1-yl phosphate (**8c**), disodium (2*R*)-3-butanoyl-1-(dodecanoylamino)propan-2-yl phosphate (**9b**), and disodium (2*R*)-3-butanoyl-1-(octadecanoylamino)propan-2-yl phosphate (**9c**).

JO974027L

Robert B. Grossman* and Melissa A. Varner. Selective Monoalkylation of Diethyl Malonate, Ethyl Cyanoacetate, and Malononitrile Using a Masking Group for the Second Acidic Hydrogen.

Page 5235. A relevant reference (Padgett, H. C.; Csendes, I. G.; Rapoport, H. *J. Org. Chem.* **1979**, *44*, 3492) was inadvertently omitted. The reference describes the use of triethyl methanetricarboxylate as a diethyl malonate surrogate in the alkylation of 1,2-dibromoethane and 1,4-dibromobutane. One ethoxycarbonyl group could be removed from the alkylation product using various acidic or basic conditions. Thanks to Prof. Rapoport for bringing this work to our attention.

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