Scheme III. Hydroboration of the exocyclic methylene function (C-16) with 9-BBN occurred stereospecifically from the β-face of the double bond and on oxidative workup (3 N NaOH/H_2O_2/40 °C/2 h) provided the triol **11** in 85% yield. Direct hydroboration of the β-dicarbonyl compound **9** with 9-BBN furnished the triol **11**; however, the yield was somewhat lower. As shown in Scheme III (structure **11**), 9-BBN has attacked the β-face of the exocyclic methylene function in order to minimize steric repulsion (1,3) between the axial N_b-methyl function and the incoming hydroboration reagent. This is opposite to the stereochemical outcome of the hydroboration at C-16 observed during the synthesis of (±)-suaveoline.[4b]

The optically active triol (−)-**11** was regioselectively cyclized to the desired (−)-tetrahydroalstonerine monol **12** on stirring with tosyl chloride (1 equiv) in pyridine followed by the addition of either triethylamine or potassium hydroxide. This process gave (−)-**12** in 60% yield, accompanied by starting triol **11** (33%), which could be recycled to provide additional quantities of (−)-tetrahydroalstonerine **12**. When monol **12** was stirred with pyridinium dichromate, an 86% yield of (−)-dihydroalstonerine (**3b**) was realized; however, treatment of **12** under modified Swern[9] conditions [$(COCl)_2$/DMSO/CH_2Cl_2/−78 °C → −10 °C/1.5 h; Et_3N] gave (−)-alstonerine (**2a**) (mp 171–172 °C) in 51% yield, accompanied by dihydroalstonerine (**3b**) (31%). The spectral data for (−)-**2a** (^1H NMR, ^{13}C NMR,[10] IR, UV, MS)[2a] were in complete agreement with those published for natural (−)-alstonerine (mp 172–173 °C); moreover, the optical rotation $\{[\alpha]^{25}_{\mathrm{D}}\ -190^\circ$ (*c* 0.32, EtOH)$\}$ of synthetic **2a** indicates that it has been prepared in at least 98% ee.

The synthesis described above represents the first chirally controlled preparation of a member of the macroline-related alkaloids.[11] The stereospecific preparation of tetracyclic ketone **5a**,[4a,b] coupled with the execution of both the Claisen rearrangement (C-15) and the hydroboration process (C-16) in the desired fashion, provides a route for the enantiospecific synthesis of the macroline/sarpagine alkaloids. Further work is in progress to extend this approach to the synthesis of alstophylline (**2b**), as well as a number of bisindole alkaloids,[1-3] including the hypotensive bisindole alkaloid macralstonine (**1**).[1a,b]

Note Added in Proof. Recently, base-catalyzed (NaOMe, CH_3OH, Δ) epimerization of synthetic **3b** gave the epimeric **3a** which had been previously converted into macroline **4** by LeQuesne et al.[3a] Consequently, the synthesis of (−)-**3b** also constitutes a formal total synthesis of **4**, although the yield of this conversion has not been maximized.

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(9) Mancuso, A. J.; Huang, S.-L.; Swern, S. *J. Org. Chem.* **1978**, *43*, 2480.

(10) Ratnayake, C.; Lakshimi, S. R.; Arambewela, K. T.; Silva, D.; Rahman, A.; Alvi, K. A. *Phytochemistry* **1987**, *26*, 868.

(11) The optical purity (>97% ee) of **5a** as well as other intermediates was proven by the use of chiral shift reagents as detailed in the following: Campbell, J. *Aldrichimica Acta* **1972**, *5*, 2. All compounds including (−)-**2a** gave satisfactory NMR, IR, and mass spectral data.

Additions and Corrections

Phosphate Ester and Phosphinate Binding to the (μ-Oxo)diiron(III) Core: Synthesis and Characterization of $[Fe_2O\{O_2P(OC_6H_5)_2\}_2(HBpz_3)_2]$ and $[Fe_2O\{O_2P(C_6H_5)_2\}_2(HBpz_3)_2]$ [*J. Am. Chem. Soc.* **1990**, *112*, 681–690]. PETRA N. TUROWSKI, WILLIAM H. ARMSTRONG, MARY E. ROTH, and STEPHEN J. LIPPARD*

Page 687: The minus sign in eq 2 should be a plus sign. This change does not affect any results of the paper, for which the correct equation was used.

Characterization of (Methylcyclopentadienyl)trimethylplatinum and Low-Temperature Organometallic Chemical Vapor Deposition of Platinum Metal [*J. Am. Chem. Soc.* **1989**, *111*, 8779]. ZILING XUE, M. JANE STROUSE, DAVID K. SHUH, CAROLYN B. KNOBLER, HERBERT D. KAESZ,* ROBERT F. HICKS, and R. STANLEY WILLIAMS

Page 8780: We have learned of new evidence from NOESY spectra that suggests that the assignment of H_a and H_b (Figure 1) and C_a and C_b (Figure 2) in (MeCp)$PtMe_3$ should be *reversed* (private communication from Richard A. Newmark, Larry D. Boardman, and Allen R. Siedle, 3M Corporate Research Laboratories, Bldg. 201-BS-05, Box 33221, St. Paul, MN 55144-1000). Arguments and supporting data that involve a series of compounds including the one mentioned above are being prepared for publication.

X-ray Structures of Cubylcubane and 2-*tert*-Butylcubylcubane: Short Cage–Cage Bonds [*J. Am. Chem. Soc.* **1988**, *110*, 7232]. R. GILARDI,* M. MAGGINI, and P. E. EATON

Page 7232, footnote 3: the *c* dimension should be 13.431 (1) Å rather than 13.341 (1) Å.

Mechanism of Grignard Reagent Formation. The Surface Nature of the Reaction [*J. Am. Chem. Soc.* **1989**, *111*, 1896]. H. M. WALBORSKY* and JANUSZ RACHON

Page 1896: The label for structure **4** should read (*S*)-(+)-**4**.

Evidence for a 1,2-Fluoride Shift in a Gaseous Cation [*J. Am. Chem. Soc.* **1989**, *111*, 6868]. THOMAS A. SHALER and THOMAS HELLMAN MORTON*

Page 6869, Table I: The first entry should be −216.22724 au for ion **5**. Footnote *b* should refer to the following reference: Stams, D. A.; Thomas, T. D.; Maclaren, D. C.; Ji, D.; Morton, T. H. *J. Am. Chem. Soc.* **1990**, *112*, 1427–1434.

Computer Software Reviews

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