species from the prerequisite *Z* enolate such that we could bias the stereoselection in favor of the syn (erythro) diastereoisomers and, perhaps more specifically, the 24*S*,25*R* component.[15,16] A cross-aldol reaction between the lithium enolate derived from **8** and the aldehyde **13** was effected under time and temperature controlled conditions to afford a mixture of two diastereomeric products **14**, $[\alpha]_D$ −17.16°, in 76% yield (Scheme IV), in which the desired 24*S*,25*R* syn isomer was a major component (>7:3).

At this juncture, it was therefore of paramount importance to secure an appropriate degradation product of rifamycin S that contained the intact C19–C29 segment and to be able to establish the constitutional and configurational identity of the aldol product **14**. Degradation of rifamycin S is known to provide a dienic ester fragment **20**.[17] This was further manipulated[18] to give the acetal **17**, mp 73–74 °C, $[\alpha]_D$ +20°, and the pentaacetate derivative **19**, $[\alpha]_D$ ~0°,[19] which were suitable compounds for our correlation. Reduction of the C23 carbonyl function with diisobutylaluminum hydride proceeded with high stereoselectivily (>10:1) to give the desired **15**. Catalytic hydrogenolysis produced major compound **16**,[20] $[\alpha]_D$ −3.2°, which was further transformed into the crystalline hemiacetal and syrupy pentaacetate derivatives **17** and **19**, respectively, and found to be identical in all respects with samples obtained from **20** (TLC, $[\alpha]_D$, 400 MHz and two-dimensional ^1H NMR, mass spectroscopy).

Since intermediates such as **16** and **18** can be easily converted to one of Kishi's advanced intermediates, our approach as reported herein represents a formal synthesis of the optically active antibiotic.[21,22]

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Registry No. 2, 75879-81-1; **2**, acetyl derivative, 82707-13-9; **3**, 82707-02-6; **3**, α-OH derivative, 82731-51-9; **3**, keto derivative, 82731-52-0; **4**, 82707-03-7; **5**, 82707-04-8; **6**, 82707-05-9; **6**, debenzyl derivative, 82731-53-1; **6**, aldehyde derivative, 82707-14-0; **7**, 82769-13-9; **7**, didehydro derivative, 82768-70-5; **8**, 82707-06-0; **8**, α-OH, detrityl derivative, 82707-15-1; **8**, α-OH derivative, 82707-16-2; **9**, 64526-83-6; **10**, 64526-85-8; **11**, 82707-07-1; **11**, β-chloro derivative, 82707-17-3; **12**, 82731-48-4; **13**, 82707-08-2; **13**, hydroxy derivative, 82707-18-4; **14**, 82707-09-3; **15**, 82707-10-6; **16**, 82707-11-7; **17**, 82731-49-5; **18**, 82707-12-8; **19**, 82731-50-8; (+)-rifamycin S, 13553-79-2.

Supplementary Material Available: NMR spectral data and physical constants for selected intermediates (13 pages). Ordering information is given on any current masthead page.

(15) Heathcock, C. H.; Pirrung, M. C.; Lampe, J.; Buse, C. T.; Young, S. D. *J. Org. Chem.* **1981**, *46*, 2290–2300 and references cited therein. Heathcock, C. H.; Young, S. D.; Hagen, J. P.; Pirrung, M. C.; White, C. T.; Van Der Veer, D. *Ibid.* **1980**, *45*, 3846–3856.

(16) The selectivity in the aldol condensation can be rationalized based in part on a coordinated transition state[15] involving the benzyloxy group.

(17) Kinoshita, M.; Tatsuta, K.; Nakata, M. *J. Antibiot.* **1978**, *31*, 630–632.

(18) The following steps were involved: (a) O_3; (b) $NaBH_4$; (c) Ac_2O, DMAP, AcOEt; (d) n-Bu_3SnH, AIBN, toluene; (e) TsOH, aqueous MeOH; (f) $NaBH_4$; (g) 2,2-dimethoxypropane, CSA.

(19) The structure and identity of **19** and complete chemical shift assignments were further confirmed by a completed ^1H NMR decoupling experiments and two-dimensional NMR in the C-Me region at 400 MHz (supplementary material available).

(20) Chromatographic separation on silica gel with CH_2Cl_2–EtOH (96:14) as the eluant.

(21) During the course of this work, another carbohydrate-based approach to the aliphatic segment of rifamycin S was reported by using a different strategy; see ref 3b.

(22) For a highly stereocontrolled syntheses of the optically active form of the aliphatic segment of rigamycin S, see: Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873–3888.

Additions and Corrections

General Methods of Synthesis of Indole Alkaloids. 14.[1,2] Short Routes of Construction of Yohimboid and Ajmalicinoid Alkaloid Systems and Their ^{13}C Nuclear Magnetic Resonance Spectral Analysis [*J. Am. Chem. Soc.* **1976**, *98*, 3645]. ERNEST WENKERT,* CHING-JER CHANG, H. P. S. CHAWLA, DAVID W. COCHRAN, EDWARD W. HAGAMAN, JAMES C. KING, and KAZUHIKO ORITO.

Page 3650, Table II: The δ value of C(3) of compound **24** should read "59.6".

Total Synthesis of the Yohimbines [*J. Am. Chem. Soc.* **1979**, *101*, 5370]. ERNEST WENKERT,* TIMOTHY D. J. HALLS, GERHARD KUNESCH, KAZUHIKO ORITO, RICHARD L. STEPHENS, WAYNE A. TEMPLE, and JHILLU YADAV.

Page 5376, reference 2 (missing fourth line): R. N. Guthikonda, *J. Am. Chem. Soc.*, **94**, 5109 (1972); (d) L. Töke, K. Honty, ...

Reactions of Metal–Metal Multiple Bonds. 8. Forming Mo–Mo Quadruple Bonds by Reductive Elimination (Alkyl Group Disproportionation) in the Reactions of 1,2-$Mo_2R_2(NMe_2)_4$ Compounds (M≡M) with Carbon Dioxide and 1,3-Diaryltriazines [*J. Am. Chem. Soc.* **1982**, *104*, 2138]. M. J. CHETCUTI, M. H. CHISHOLM,* K. FOLTING, D. A. HAITKO, and J. C. HUFFMAN.

Page 2144, last sentence in **Preparation of $Mo_2(O_2CNMe_2)_4$**: The sentence should read as follows—Anal. Calcd: C, 26.48; H, 4.41; N, 10.29. Found: C, 26.48; H, 4.25; N, 10.09.

Coordination Chemistry of Metal Surfaces. 3.[1] Benzene and Toluene Interactions with Nickel Surfaces [*J. Am. Chem. Soc.* **1981**, *103*, 773]. C. M. FRIEND and E. L. MUETTERTIES.*

Page 777, Figure 8: The scale for the abscissa was incorrect. Figure 8 should be: