5,17-Bis(1,1-dimethylethyl)-25,26,27,28-tetrahydroxycalix[4]arene (21). To a solution of boron tribromide (7.0 g, 28 mmol) in CH_2Cl_2 (10 mL) was added a solution of 5,17-bis(1,1-dimethylethyl)1-25,27-dihydroxy-26,28-dimethoxycalix[4]arene[4] (4.0 g, 7.0 mmol) in CH_2Cl_2 (250 mL) for 1 h at −78 °C. After being stirred for 20 h at room temperature, the reaction mixture was quenched by addition of MeOH (50 mL) in order to destroy the excess of boron tribromide. After removal of the solvent the residue was taken up in CH_2Cl_2 (250 mL) and subsequently washed with a concentrated $NaHCO_3$ solution (2 × 50 mL) and with brine (1 × 100 mL). The crude reaction product was recrystallized from CH_2Cl_2/hexane to give pure **21** as a white solid: yield 94%; mp >300 °C; ^1H NMR δ 10.28 (s, 4 H, OH), 7.08 (s, 4 H, Ar 4,6,16,18-H), 7.04 (d, 4 H, J = 3.0 Hz, Ar 10,12,22,24-H), 6.75–6.65 (m, 2 H, Ar 11,23-H), 4.26 and 3.56 (br s, 8 H, $ArCH_2Ar$), 1.27 [s, 18 H, $C(CH_3)_3$]; FAB mass spectrum, m/e 537.0 (M^+, calcd 537.3). Anal. Calcd for $C_{36}H_{40}O_4 \cdot CH_2Cl_2$: C, 71.49; H, 6.81. Found: C, 71.76; H, 6.72.

5,17-Bis(1,1-dimethylethyl)-25,26,27,28-tetrakis(ethoxyethoxy)calix[4]arene (22). To a suspension of sodium hydride (80% in oil, 0.7 g, 23.3 mmol; freed from protective mineral oil by 2 hexane washings) in dry DMF (100 mL) was added **21** (2.14 g, 3.9 mmol). After the mixture was stirred for 20 min 2-bromoethyl ethyl ether (4.0 g, 26.1 mmol) was added, and the solution was heated at 80 °C for 5 h. Excess NaH was destroyed by addition of water (caution!), and then the solvent was evaporated. The residue was taken up in CH_2Cl_2 (200 mL), and the resulting solution was washed with 1 N HCl (2 × 50 mL) and brine (50 mL). The crude reaction product was recrystallized from MeOH to give pure **22** as a white solid: yield 89%; mp 188 °C; ^1H NMR δ 7.00 (s, 4 H, Ar 4,6,16,18-H), 6.28 (m, 2 H, Ar 11,23-H), 6.16 (d, 4 H, J = 7.5 Hz, Ar 10,12,22,24-H), 4.46 and 3.10 (AB q, 8 H, J = 13.3 Hz, $ArCH_2Ar$), 4.21 [t, 4 H, J = 6.6 Hz, Ar(p-H)-OCH_2], 3.96 [t, 4 H, J = 5.2 Hz, Ar(p-t-Bu)-OCH_2], 1.31 [s, 18 H, $C(CH_3)_3$]; ^{13}C NMR δ 155.3, 154.8 (s, Ar 25,26,27,28-C), 144.5 (s, Ar 5,17-C), 127.4, 125.5, 122.3 (d, all ArC-H), 34.0 [s, $C(CH_3)_3$], 31.7 [q, $C(CH_3)_3$], 31.1 (t, $ArCH_2Ar$); FAB mass spectrum, m/e 825.4 (M^+, calcd 825.5). Anal. Calcd for $C_{52}H_{72}O_8$: C, 75.69; H, 8.79. Found: C, 75.85; H, 8.75.

Acknowledgment. We thank T. W. Stevens for recording the mass spectra and A. M. Montanaro-Christenhusz for performing the elemental analyses.

Registry No. 1, 105880-81-7; 2, 121935-18-0; 3, 126372-90-5; 4, 137571-04-1; 5, 137571-05-2; 6, 137571-06-3; 7, 121702-03-2; 8, 137594-00-4; 9, 60705-62-6; 10, 137693-26-6; 11, 137571-07-4; 12, 97600-49-2; 13, 137571-08-5; 14, 137571-09-6; 15, 137594-01-5; 16, 137571-10-9; 17, 137571-11-0; 18, 137571-12-1; 19, 137571-13-2; 20, 137571-14-3; 21, 137571-15-4; 22, 137571-16-5; 23, 137571-17-6; 2-bromoethyl ethyl ether, 592-55-2.

A Nitrone-Based Approach to the Enantioselective Total Synthesis of (−)-Anisomycin

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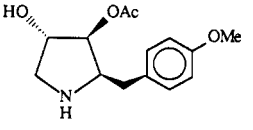
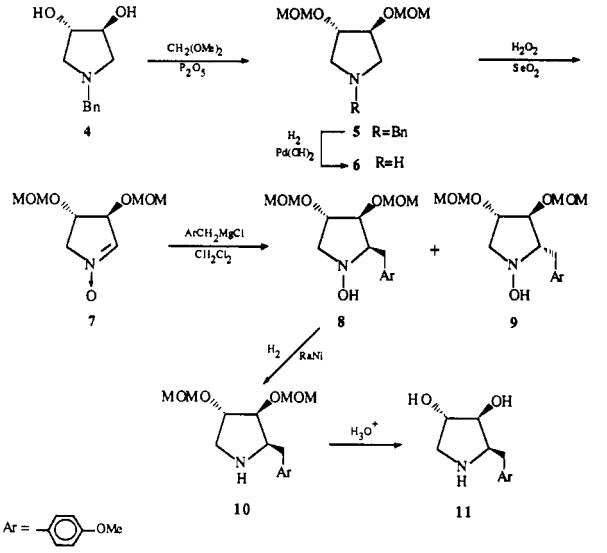
Received June 28, 1991

The antibiotic (−)-anisomycin **1** is a fermentation product of various species of streptomyces[1] which exhibits strong and selective activity against pathogenic protozoa and fungi.[2]



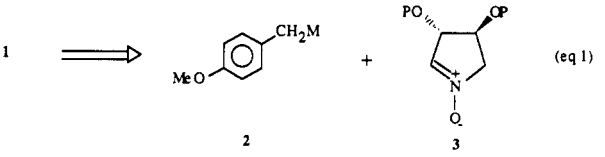
1

Scheme I



It has been shown to act as an inhibitor of protein synthesis,[3] and it finds wide use in the treatment of trichomonas vaginitis and amebic dysentery. Its absolute configuration was definitively established in 1968 by chemical correlation with L-tyrosine.[4] Several chiral syntheses of (−)-anisomycin have appeared in literature for the most part employing naturally occurring starting materials such as carbohydrates,[5] amino acids,[6] and L-tartaric acid or its esters.[7]

Both enantiomers of **1** can be prepared starting from (*R*)- and (*S*)-epichlorohydrin using the method of Takano.[8] Our retrosynthetic analysis[9] as depicted in eq 1 shows that



(eq 1)

2 **3**

by means of a carbon–carbon disconnection two synthons **2** and **3** could be envisaged. The reagent for **2** can be trivially found in the Grignard reagent 4-methoxybenzylmagnesium chloride, less obvious is the substrate corresponding to structure **3**. An electrophilic carbon in the position α to a nitrogen atom can be generated via iminium derivatives,[10] by a carbonyl group (e.g., amide),[11]

(1) Sobin, B. A.; Tanner, F. W. *J. Am. Chem. Soc.* **1954**, *76*, 4053.

(2) Jimenez, A.; Vazquez, D. In *Antibiotics*; Hahn, F. E., Ed.; Springer Verlag: Berlin, 1979.

(3) Grollman, A. P. *J. Biol. Chem.* **1967**, *242*, 3226.

(4) Wong, C. M. *Can. J. Chem.* **1968**, *46*, 1101.

(5) (a) Verheyden, J. P. H.; Richardson, A. C.; Bhatt, R. S.; Grant, D. B.; Fitch, W. L.; Moffatt, J. G. *Pure Appl. Chem.* **1978**, *50*, 1363. (b) Buchanan, J. G.; McLean, K. A.; Wightman, R. H.; Paulsen, H. *J. Chem. Soc. Perkin Trans. I* **1985**, 1463. (c) Baer, H. H.; Zamkanei, M. *J. Org. Chem.* **1988**, *53*, 4786.

(6) (a) Meyers, A. I.; Dupre, B. *Heterocycles* **1987**, *25*, 113. (b) Shono, T.; Kise, N. *Chem. Lett.* **1987**, 697. (c) Jegham, S.; Das, B. C. *Tetrahedron Lett.* **1989**, *29*, 4419.

(7) (a) Wong, C. M.; Buccini, J.; Chang, I.; Te Raa, J.; Schwenk, K. *Can. J. Chem.* **1969**, *47*, 2421. (b) Felner, I.; Schenker, K. *Helv. Chim. Acta* **1970**, *53*, 754. (c) Iida, A. I.; Yamazaki, N.; Kibayashi, C. *J. Org. Chem.* **1986**, *51*, 1069.

(8) Takano, S.; Iwabuchi, Y.; Ogasawara, K. *Heterocycles* **1989**, *29*, 1861.

(9) For an authoritative presentation of this strategy, see: (a) Warren, S. *Organic Synthesis: The Disconnection Approach*; Wiley: New York, 1982. (b Hanessian, S. *Total Synthesis of Natural Products: The Chiron Approach*; Pergamon: Oxford, 1983. (c) Corey, E. J.; Cheng, X. M. *The Logic of Chemical Synthesis*; Wiley: New York, 1989.

0022-3263/92/1957-1316$03.00/0

or from a nitrone functionality.

Nitrones represent a versatile class of compounds in organic synthesis since they are useful 1,3 dipoles suitable for cycloaddition reactions.[12] Furthermore, the α carbon atom of the nitrone system is electrophilic enough to undergo attack by a variety of nucleophiles, including Grignard reagents.[12,13]

The stereochemical features of nitrone **3** immediately suggested the possibility of using L-tartaric acid as a precursor. L-Tartaric acid was converted to pyrrolidine **4** (Scheme I) by condensation with benzylamine and then reduction with $NaBH_4/BF_3{\cdot}Et_2O$.[14] Protection of the hydroxy groups as methoxymethyl ethers was carried out by reaction of **4** with dimethoxymethane in the presence of P_2O_5.[15] Removal of *N*-benzyl protection from **5** by hydrogenation in the presence of 20% $Pd(OH)_2$ on carbon[16] afforded the amine **6** in 45% yield from L-tartaric acid. The conversion of pyrrolidine **6** into the desired nitrone **7** was carried out by oxidation with 30% H_2O_2 in the presence of SeO_2 as catalyst.[17] Since isolation of nitrone **7** results in partial decomposition, we preferred to use the crude material for the subsequent step.

Reaction of (4-methoxybenzyl)magnesium chloride with **7** at 0 °C in THF produced a chromatographically separable mixture of diastereomers **8** and **9** in a ratio of 2:3 and 60% yield from **6**. Conducting the reaction in the presence of 1 equiv of $MgBr_2{\cdot}Et_2O$ in CH_2Cl_2 effected a change in the diastereoselectivity (**8**/**9** = 7/3). Since the $MgBr_2$ is capable to coordinating with the nitrone oxygen,[18] the magnesium atom of the Grignard reagent would possibly be forced to interact with the acetal oxygen in position 3. This coordination allows the attack to the double bond through a cyclic five-membered-ring transition state giving preferentially a cis addition.

Catalytic hydrogenation of **8** in the presence of Raney Ni produced pyrrolidine **10** in 85% yield. Removal of the methoxymethyl groups (6 N HCl/MeOH (1:1)) gave deacetylanisomycin **11** in 12% overall yield from L-tartaric acid. Since **11** has been efficiently converted into **1**,[7c] this work constitutes a formal total synthesis of natural anisomycin. The nitrone approach as depicted in this specific instance may be potentially useful for the synthesis of other pyrrolidine alkaloids which have assumed a remarkable importance because of their interesting biological activity.

Experimental Section

^1H NMR spectra were recorded at 300 MHz. Mass spectra were performed using the EI technique. Melting points are uncorrected. 4-Methoxymagnesium chloride has been prepared starting from the corresponding chloride in THF and titrated before use.[19] All chemicals used are commercially available (Aldrich Co.). Flash chromatography was performed on Merck silica gel (0.040–0.063 mm).[20]

(3*S*,4*S*)-1-Benzylpyrrolidine-3,4-diol (4). This compund was prepared in 70% yield from L-tartaric acid using the procedure described by Nagel:[14] mp 99 °C; $[\alpha]^{20}_D$ +31.9° (*c* 4, MeOH) [lit.[14] mp 100 °C; $[\alpha]^{20}_D$ +32.4° (*c* 4.2, MeOH).

(3*S*,4*S*)-1-Benzyl-3,4-bis(methoxymethoxy)pyrrolidine (5). A mechanically stirred suspension of compound **8** (4 g, 0.02 mol) in dimethoxymethane was cooled to 0 °C, and P_2O_5 (14.2 g, 0.1 mol) was added in small portions over a period of 1 h. The ice bath was then removed and the suspension was stirred for 2 days at rt. After evaporation of the solvent the solid residue was cooled again to 0 °C and treated with a 20% methanolic KOH (100 mL). The resulting suspension was filtered over a Florisil pad, and the MeOH was evaporated. The crude residue was purified by flash chromatography on silica gel (hexane/ethyl acetate (3:2)) to give **5** (4.22 g, 75%) as a colorless oil: $[\alpha]^{20}_D$ = +11.9° (*c* 2.4, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.55 (dd, 2 H, J = 4.2, 10.2 Hz), 2.95 (dd, 2 H, J = 6.0, 10.0 Hz), 3.34 (s, 6 H), 3.57 (d, 1 H, J = 13.2 Hz), 3.65 (d, 1 H, J = 13.2 Hz), 4.13–4.18 (m, 2 H), 4.63 (d, 2 H, J = 7.0 Hz), 4.72 (d, 2 H, J = 7.0 Hz), 7.22–7.35 (m, 5 H); MS *m*/*e* M^+ 281, 250, 160, 120, 91, 45. Anal. Calcd for $C_{15}H_{23}NO_4$ (281.34): C, 64.03; H, 8.24; N, 4.98. Found: C, 63.94; H, 8.19; N, 4.89.

(3*S*,4*S*)-3,4-Bis(methoxymethoxy)pyrrolidine (6). Pyrrolidine **5** (3 g, 0.01 mol) was dissolved in MeOH (90 mL), and 20% $Pd(OH)_2$ on carbon (0.5 g) was added. The suspension was hydrogenated at rt at 1 atm for 3 h. The catalyst was removed by filtration through a Celite pad and was washed with MeOH (5 × 20 mL). After evaporation of the solvent the crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate/ethanol/30% NH_4OH (4:4:1.8:0.2)) to afford 1.7 g (85%) of pure **6** as a pale yellow oil: $[\alpha]^{20}_D$ −1.51° (*c* 6.4, $CHCl_3$); IR (cm^{-1}, neat 3300; ^1H NMR ($CDCl_3$) δ 2.10 (bs, 1 H), 2.88 (dd, 2 H, J = 3.0, 13.2 Hz), 3.16 (dd, 2 H, J = 5.0, 12.2 Hz), 3.36 (s, 6 H), 4.08–4.14 (m, 2 H), 4.64 and 4.69 (AB, dd, 4 H, J = 6.8 Hz); MS *m*/*e* (M^+ − 1) 190, 160, 130, 114, 101, 68, 45. Anal. Calcd for $C_8H_{17}NO_4$ (191.23): C, 50.24; H, 8.96; N, 7.32. Found: C, 50.18; H, 8.90; N, 7.38.

(3*S*,4*S*)-3,4-Bis(methoxymethoxy)-1-pyrroline *N*-Oxide (7). Compound **6** (1.5 g, 7.85 mmol) was dissolved in acetone (15 mL), and SeO_2 (0.043 g, 0.4 mmol) was then added. The mixture was cooled at 0 °C, and 30% H_2O_2 (2.59 g, 23 mmol) was added dropwise under N_2. After 15 min the cooling bath was removed and the mixture was stirred an additional 2 h at rt. The acetone was removed by evaporation, and the aqueous residue was extracted with CH_2Cl_2 (3 × 20 mL) and dried over $MgSO_4$. The crude product obtained by evaporation of the solvent was purified by flash chromatography on silica gel (hexane/ethyl acetate/ethanol (4:5:1)) affording 0.96 g (60%) of nitrone **7** as an oil: IR (cm^{-1}, neat) 1580 (C=N), 1150 (NO); ^1H NMR ($CDCl_3$) δ 3.35 (s, 3 H), 3.36 (s, 3 H), 3.78–3.87 (m, 1 H), 4.26–4.39 (m, 3 H), 4.66 and 4.73 (AB, dd, 2 H, J = 7.0 Hz), 4.68–4.70 (m, 1 H), 4.67 and 4.74 (AB, dd, 2 H, J = 6.9 Hz), 6.90 (d, 1 H, J = 2.5 Hz); MS *m*/*e* M^+ 205, 176, 160, 143, 82, 45.

(2*R*,3*S*,4*S*)-1-Hydroxy-2-(4-methoxybenzyl)-3,4-bis(methoxymethoxy)pyrrolidine (8). The crude compound **7** obtained by oxidation of **6** (1.5 g, 7.85 mmol) was dissolved in dry CH_2Cl_2 (25 mL), and $MgBr_2{\cdot}Et_2O$ (2.58 g, 10 mmol) was added. The mixture was then stirred at rt for 15 min, and 4-methoxybenzylmagnesium chloride (6.5 mol, 7 mL, 1 M in THF) was added dropwise at 0 °C. After additional stirring for 30 min saturated

(10) Shono, T.; Matsumura, Y.; Tsubata, K. *J. Am. Chem. Soc.* **1981**, *103*, 1172. For a recent example see: Roussi, G.; Zhang, J. *Tetrahedron Lett.* **1991**, *32*, 1443.

(11) Yoda, H.; Shirakawa, K.; Takabe, K. *Chem. Lett.* **1991**, 489.

(12) For reviews of properties and utilization of nitrones see: (a) Annunziata, R.; Cinquini, M.; Cozzi, F.; Raimondi, L. *Gazz. Chim. Ital.* **1989**, *119*, 253. (b) Torssell, K. B. G. *Nitrile Oxides, Nitrones and Nitronates in Organic Synthesis*; VCH: New York, 1988. (c) Padwa, A. *1,3 Dipolar Cycloadditions Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 2. (d) Breuer, E. *The Chemistry of Amino, Nitroso and Nitrocompounds*; Patai, S., Ed.; Wiley: New York, 1982; p 459. (e) Tufariello, J. J. *Acc. Chem. Res.* **1979**, *12*, 396. (f) Black, D. St. C.; Crozier, R. F.; Davis, V. C. *Synthesis* **1975**, 205. (g) Hamer, J.; Macaluso, A. *Chem. Rev.* **1964**, 473.

(13) (a) Gossinger, E. *Tetrahedron Lett.* **1980**, *21*, 2229. (b) Gossinger, E.; Witkop, B. *Monat. Chem.* **1980**, *111*, 803. (c) Chang, Z. Y.; Coates, R. M. *J. Org. Chem.* **1990**, *55*, 3464 and references cited therein.

(14) Nagel, U.; Kinzel, E.; Andrade, J.; Prescher, G. *Chem. Ber.* **1986**, *119*, 3326.

(15) Attempts to use different protecting groups (*t*-$BuMe_2Si$ or MEM) gave very low yields of conversion, and furthermore, rather unclean reactions were observed in the nitrone synthesis.

(16) Yoshida, K.; Nakajima, S.; Wakamatsu, T.; Ban, Y.; Shibasaki, M. *Heterocycles* **1988**, *27*, 1167.

(17) Murahashi, S.; Shiota, T. *Tetrahedron Lett.* **1987**, *28*, 2383. Na_2WO_4 can also be used as catalyst but yields of conversion are lower: Murahashi, S.; Mitsui, H.; Shiota, T.; Tsuda, T.; Watanabe, S. *J. Org. Chem.* **1990**, *55*, 1736.

(18) It is known[13c] that the interaction between $MgBr_2$ and the oxygen atoms is more effective in noncoordinating solvents as CH_2Cl_2.

(19) The Grignard is titrated just before use: Bergbreiter, D. E.; Pendergrass, E. *J. Org. Chem.* **1981**, *46*, 219.

(20) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

aqueous NH_4Cl (10 mL) was poured into the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The organic phases were dried over $MgSO_4$. After evaporation of the solvent the crude material was purified by flash chromatography over silica gel (hexane/ethyl acetate/ethanol (6:3:1)) affording 1.08 g (42%) of **8** and 0.46 g (18%) of **9**. Compound **8**: oil; $[\alpha]^{20}_D$ +18° (*c* 2.55, $CHCl_3$); IR (cm^{-1}, neat) 3550; ^1H NMR ($CDCl_3$) δ 2.72–2.82 (m, 1 H), 3.07–3.18 (m, 2 H), 3.15 (s, 3 H), 3.36 (s, 3 H), 3.77 (s, 3 H), 4.08–4.12 (m, 1 H), 4.28 and 4.48 (AB dd, 2 H, J = 6.8 Hz), 4.53 and 4.57 (AB dd, 2 H, J = 7.0 Hz), 6.83 and 7.18 (AB dd, 4 H, J = 8.6 Hz); MS m/e (M^+ − 18) 309, 280, 190, 121, 96, 45. Anal. Calcd for $C_{16}H_{25}NO_6$ (327.37): C, 58.69; H, 7.69; N, 4.27. Found: C, 58.57; H, 7.61; N, 4.32.

(2*R*,3*S*,4*S*)-2-(4-Methoxybenzyl)-3,4-bis(methoxymethoxy)pyrrolidine (10). Compound **8** (0.5 g, 1.52 mmol) was dissolved in MeOH (20 mL) and hydrogenated at 1 atm in the presence of Raney Ni (0.07 g) for 6 h at rt. The catalyst was removed by filtration and washed thoroughly with methanol. After evaporation of the solvent, the crude product was purified by flash chromatography (hexane/ethyl acetate/ethanol/30% NH_4OH (5:3:1.8:0.2)) to give 0.4 g (85%) of amine **10** as an oil: $[\alpha]^{20}_D$ −11.6° (*c* 2.35, MeOH) (lit.[7c] $[\alpha]^{20}_D$ −12.5° (*c* 1.52, MeOH); IR (cm^{-1}, neat) 3300; ^1H NMR ($CDCl_3$) δ 2.02 (bs, 1 H), 2.79 (dd, 1 H, J = 8.0, 17.7 Hz), 2.84 (dd, 1 H, J = 6.2, 13.7 Hz), 2.92 (m, 1 H), 3.29 (s, 3 H), 3.32–3.42 (m, 2 H), 3.39 (s, 3 H), 3.78 (s, 3 H), 3.82 (dd, 1 H, J = 4.7, 1.5 Hz), 4.12 (dt, 1 H, J = 3.4, 1.5 Hz), 4.50 and 4.64 (AB dd, 2 H, J = 6.7 Hz), 4.63 and 4.69 (AB dd, 2 H, J = 6.7 Hz), 6.83 and 7.17 (AB dd, 4 H, J = 8.7 Hz); MS m/e M^+ 312, 304, 190, 121, 96, 68, 45.

(2*R*,3*S*,4*S*)-2-(4-Methoxybenzyl)pyrrolidine-3,4-diol (Deacetylanisomycin, 11). Pyrrolidine **10** (0.15 g, 0.48 mmol) was refluxed in a mixture of MeOH/6 N HCl (1:1) for 24 h. The solution was then concentrated, made alkaline with Na_2CO_3, and extracted with $CHCl_3$ (2 × 30 mL). The aqueous phase was allowed to stand overnight at 5 °C, and the colorless crystals were collected by suction giving 0.08 g (75%) of **11**: mp 171–172 °C (lit.[7c] mp 176–177 °C).

Acknowledgment. The authors wish to thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica of Italy for financial assistance.

Registry No. **1**, 22862-76-6; **4**, 90365-74-5; **5**, 137945-72-3; **6**, 138051-80-6; **7**, 137945-73-4; **8**, 137945-74-5; **9**, 137945-75-6; **10**, 100449-58-9; **11**, 27958-06-1; (4-methoxybenzyl)magnesium bromide, 38769-92-5.

Additions and Corrections

Vol. 45, 1980

Arthur G. Anderson, Jr.,* Gary M. Masada, and Glenn L. Kao. Electrophilic Trifluoroacetylation of Dicyclopenta[*ef,kl*]-heptalene (Azupyrene).

Page 1313, left column, line 2, should read the 1 position and the latter the 4 position.

Vol. 52, 1987

Arthur G. Anderson, Jr.,* and Edward D. Daugs. Dicyclopenta[*ef,kl*]heptalene (Azupyrene) Chemistry. Electrophilic Monosubstitution: Acetylation, Halogenation, and Thiocyanation. 1-(Ethoxymethyl)azupyrene and Dimethyl (1-Azupyrenylmethyl)malonate. Acetylazupyrene Geometry..

Page 4392, left column. The reference to the ^1H NMR signal for H-2 of 1-(trifluoroacetyl)azupyrene (**10**) should be 3a instead of 7. The references to the ^1H–^{19}F coupling in the analogous 1-(trifluoroacetyl)azulene and phenyl hexafluorobutyl ketone should be 7 and 8, respectively.

Vol. 56, 1991

Arthur G. Anderson, Jr.* and Ralph D. Haddock. The Thermal Isomerization of [2a,11-$^{13}C_2$]Dicyclopenta[*ef,kl*]heptalene (Azupyrene) to Pyrene.

Page 551, right column, Scheme III, above the left-hand arrow should read "$\pi_s^2 + \pi_a^2$". Line 5 under Scheme III should read "also 1- and 2-methylpyrene (**4** and **5**) from 1-methylazupyrene".

Suruliappa Jeganathan and Pierre Vogel*. Highly Stereoselective Total Syntheses of Octoses and Derivatives.

Page 1135. Reference 46 should have the following added: Bilik, V.; Petrus, L.; Aldölfi, J. *Chem. Zvesti* **1976**, *30*, 698.

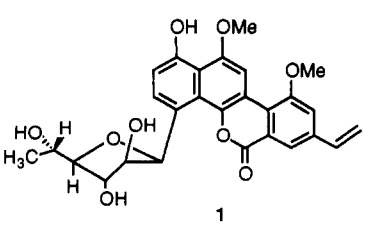
Page 1137, column 2, line 12, should read (−)-(**7**) were obtained as hydroscopic solid materials.

Page 1136, column 1, lines 11 and 13, page 1137, column 1, line 19 and 21, page 1140, column 2, lines 31–35, lines 41–44, and page 1141, column 2, lines 43–46 and lines 52–55: because of the presence of impurities due to incomplete hydrolysis of the acetonide precursors of octoses (−)-**4**, (+)-**5**, (+)-**6**, and (−)-**7**, the ^1H-NMR signal attributions for the anomeric protons of these carbohydrates as well as the proportions given for the corresponding α-furanose, β-furanose, α-pyranose, and β-pyranose forms cannot be considered as definitive.

We thank Professor S. J. Angyal, the University of New South Wales, Australia, for pointing out these problems to us.

Kathlyn A. Parker* and Craig A. Coburn. A Strategy for the Convergent Synthesis of Gilvocarcins via Chromium Carbene Benzannulation. 1-*O*-Methyldefucogilvocarcin V in Seven Steps.

Page 1666. Structure **1** should be



1

James M. Tanko,* N. Kamrudin Suleman, and Joseph F. Blackert. Kinetic vs Thermodynamic Factors in α-Hydrogen Atom Abstractions from Alkylaromatics. 2. Reactivities of α-Alkylnaphthalenes and Several Conformationally Locked Alkylaromatics toward Bromine Atom.

Page 6395. The author name N. Kamrudin should be N. Kamrudin Suleman.