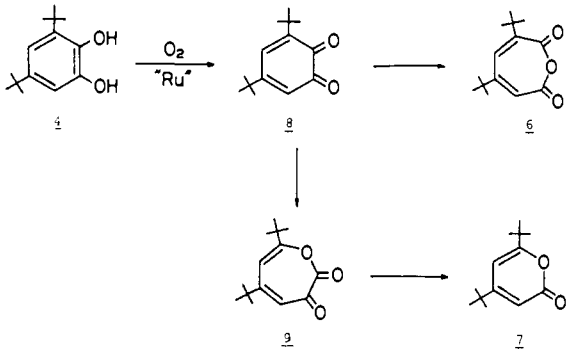
in the periodic table. The characteristic features of the reaction are as follows: (i) the catechols are oxygenated into the Hamilton intermediates **3** (intradiol type) and 2*H*-pyran-2-ones (extradiol type, vide infra), (ii) the oxygenation proceeds through an *o*-quinone intermediate, and (iii) the atom of oxygen molecule is incorporated as the endocyclic oxygen of the products.

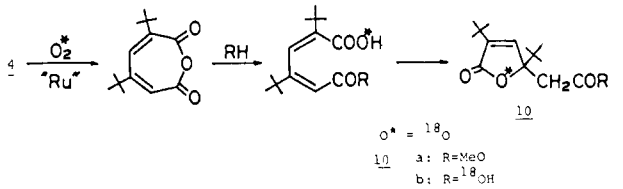
A solution of 3,5-di-*tert*-butylcatechol (**4**) (2 mmol) and $RuCl_2(PPh_3)_3$ (**5**) (0.7 mmol) in 1,1,2,2-tetrachloroethane (TCE) (15 mL) was stirred under an oxygen atmosphere (1 atm) at room temperature for 15 h (about 3 mmol of oxygen was consumed). The resulting dark blue solution was concentrated in vacuo, and the residue was chromatographed on silica gel. Elution with CH_2Cl_2 gave the muconic acid anhydride **6** (26% yield)[9] and the 2*H*-pyran-2-one **7** (64% yield).[10] This oxygenation is significantly different from the Baeyer-Villiger reaction of the quinone **8**, which selectively affords the anhydride **6**.[11]



The GLC analysis following the time course of the oxygenation of **4** disclosed that (i) the quinone **8** was rapidly formed in the early stage of the reaction and then gradually disappeared, (ii) compound **9** in addition to **6**, **7**, and **8** appeared at the midway of the reaction, and (iii) after **4** and **8** disappeared, the pyrone **7** increased, while the compound **9** decreased. The compound **9** was assigned to a seven-membered ring ketolactone from its spectral analyses,[12] though it could not be isolated in pure form because of its instability. These facts suggest that the oxidative cleavage of **4** goes through **8** and that **7** might be formed from the extradiol oxygenation product **9**. This is probably the first example of the extradiol oxygenation of catechols in the nonenzymatic process. the intermediacy of **8** was proved by the following fact. The ruthenium-catalyzed oxygenation of the quinone **8** under similar conditions gave also **6** and **7**, though the reaction rate of **8** was slower than that of **4**.

The oxidation of **4** with $^{18}O_2$ revealed that the endocyclic oxygen of both **6** and **7** is undoubtedly derived from molecular oxygen. The ^{18}O-labeled position of **6** was determined by the mass spectral analysis of **6** and the ester **10a**, obtained by the methanolysis of **6**.[11] It is worth pointing out that the ^{18}O-labeled **6** could be converted into the corresponding muconic acid or its equivalent **10b**, containing two ^{18}O atoms by the hydrolysis with $H_2{}^{18}O$, which formed together with **6** in the oxygenation of **4** with $^{18}O_2$.

In the oxygenation described here, a ruthenium(II) complex having PPh_3 ligands was used as the catalyst. However, phosphine ligands merely supplied a ruthenium(II) catalyst that was easy to handle, but they were not essentially necessary in the oxidation of catechols. This was proved out by the following experiments.



When a reddish brown solution of **5** in TCE was exposed to an oxygen atmosphere, its color changed immediately to dark green and the phosphine was oxidized into Ph_3PO, as James has reported.[13] It was further cleared by ^{31}P NMR analysis that all the phosphine ligands were oxidized in the solution described above. In this solution, the catechol **4** was similarly oxygenated to **6** and **7**.

Divalent ruthenium complexes such as $RuBr_2(PPh_3)_3$, $Ru(H)Cl(PPh_3)_3$, $Ru(H)SiClPh_2(PPh_3)_3$, and $Ru(H)OAc(PPh_3)_3$ were also effective as the catalyst, but trivalent ruthenium such as $RuCl_3$ was of no use. The ratio of intradiol oxygenation to extradiol oxygenation varied with the ruthenium catalyst used. For example, $Ru(H)OAc(PPh_3)_3$ caused scarcely the extradiol oxygenation. The maximum turnover of the catalyst in these oxygenations was about 20 for the present.

Similar oxygenation of 4-*tert*-butylcatechol and 4-methylcatechol also gave the corresponding muconic acid anhydrides and 2*H*-pyran-2-ones. The details will be reported together with the result of the unsubstituted catechol in the near future.

Although further systematic studies are necessary to clear the mechanism of the reaction and to find a much more effective system for the oxygenation of catechol, it was made clear that ruthenium(II) catalyzed the oxygenation of catechols with molecular oxygen to yield one of the intermediates supposed in biochemical systems and to form the products of the extradiol oxygenation.

Registry No. 4, 1020-31-1; **5**, 40237-23-8; **6**, 24289-60-9; **7**, 70810-35-4; **8**, 3383-21-9; **9**, 80631-09-0; $RuBr_2(PPh_3)_3$, 15709-75-8; $Rh(H)Cl(PPh_3)_3$, 19631-00-6; $Ru(H)SiClPh_2(PPh_3)_3$, 63726-78-3; $Ru(H)OAc(PPh_3)_3$, 55354-87-5.

(9) The anhydride **6** was identified by the comparison of its melting point and spectral data with those of the authentic sample prepared from **8** with *m*-chloroperbenzoic acid.[11]

(10) The pyrone **7** was obtained as colorless granules, mp 113-114 °C, from hexane. The spectral properties were as follows: ^1H NMR ($CDCl_3$) δ 1.19 (s, 9H), 1.26 (s, 9H), 6.01 (s, 2H); ^1H NMR (C_6D_6) δ 0.84 (s, 9H), 1.02 (s, 9H), 5.75 (d, J = 1.7 Hz, 1H), 5.94 (d, J = 1.7 Hz, 1H); ^{13}C NMR (CD_2Cl_2, Me_4Si) 28.1, 29.0, 35.5, 36.2, 98.7, 107.2, 163.4, 167.7, 171.4; IR (KBr) 1710, 1630, 1550, 1255 cm^{-1}; mass spectrum (m/z) 208 (M^+, 29), 180 (14), 165 (65), 151 (100).

(11) Demmin, T. R.; Rogić, M. M. *J. Org. Chem.* **1980**, *45*, 1153.

(12) ^1H NMR (CCl_4) δ 1.16 (s, 9H), 1.25 (s, 9H), 6.34 (br s, 1H), 6.43 (br s, 1H); ^{13}C NMR (CD_2Cl_2, Me_4Si) 29.2, 29.5, 34.7, 36.7, 124.8, 134.0, 134.1, 150.0, 164.0, 190.2; IR (liquid film) 1760 and 1720 cm^{-1}; mass spectrum (m/z) 237 (trace, $M^+ + 1$), 208 (100), 193 (85), 166 (84).

(13) James, B. R.; Markkam, L. D. *Inorg. Chem.* **1974**, *13*, 97.

"Open-Face" Macrobicycles as Tunable Binucleating Ligands. Design, Synthesis, and Dicopper(II) Complexes

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Metal complexes of binucleating ligands are of much current interest as models[1] for active sites in metallobiomolecules and as unique bimetallic catalysts.[2] In such complexes two metal ions are positioned in close proximity by the ligand framework to promote substrate binding between them. Bimetallic complexes that are particularly attractive for studying interactions of small molecules with transition metals include those formed from binucleating macromonocycles,[3] Schiff bases,[4] "wishbones",[5]

(1) Ibers, J. A.; Holm, R. H. *Science* **1980**, *209*, 223-235.

(2) For example see: Collman, J. P.; Elliot, C. M.; Halbert, T. R.; Tovrog, B. S. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 18-22.

(3) (a) Coughlin, P. K.; Lippard, S. J.; Martin, A. E.; Bulkowski, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 7616-7617. (b) Coughlin, P. K.; Dewan, J. C.; Lippard, S. J.; Watanabe, E. I.; Lehn, J. M. *Ibid.* **1979**, *101*, 265-266. (c) Agnus, Y.; Louis, R.; Weiss, R. J. *Ibid.* **1979**, *101*, 3381-3384.

(4) (a) Drew, M. G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1979**, 481-482. (b) Gagne, R. R.; Kreh. R. P.; Dodge, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6917-6927. (c) Grzybowski, J. J.; Merrell, P. H.; Urbach, F. L. *Inorg. Chem.* **1978**, *17*, 3078-3082. (d) Busch, D. H. *Pure Appl. Chem.* **1980**, *52*, 2477-2484.

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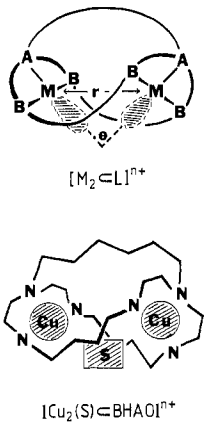

Figure 1.

"earmuffs",[6] macropolycyclic cryptands,[7] and "face-to-face"[2,8] and other porphyrins.[9] Such complexes generally rely on substrate interactions at axial coordination sites to provide bridged species with substrate molecules.

We now wish to introduce a new type of "open-face" binuclear complex, $[M_2 \subset L]^{n+}$, similar to the cryptates[10] but designed to have an accessible two-metal site for substrate binding at cis situated equatorial positions of the coordinated metals.[11] The active site topology can be systematically controlled by changing the ligand structure represented schematically in Figure 1. Thus, varying the length of the bridge B–B results predominantly in changes in r, the intermetal distance, and varying the A–A distance results predominantly in changes in θ, the angle formed from projection of the in-plane $d_{x^2-y^2}$ lobes on each metal. This poised orbital arrangement is especially pertinent to studying substrate interactions at the bimetallic site in metalloproteins such as hemocyanin and tyrosinase.[13] Here we report (i) the general synthetic route to these "open-face" ligands, (ii) the synthesis of one such ligand **11**[14] (see Figure 2) with $n = m = 4$ (molecular models indicate r to be ca. 3–4 Å), and (iii) preliminary results of copper(II) chemistry that give binuclear species $[Cu_2(S) \subset BHAO]^{n+}$.

The synthetic strategy involves formation first of a selectively protected[15] macromonocyclic hexaamine, **7**, which is subsequently partially deprotected to give **8** and then bridged across the diagonally positioned free amines to produce **11** (Figure 2). Control of the size and nature of the macromonocyclic and diagonal bridges provides for the versatility in tuning the ligand structure and

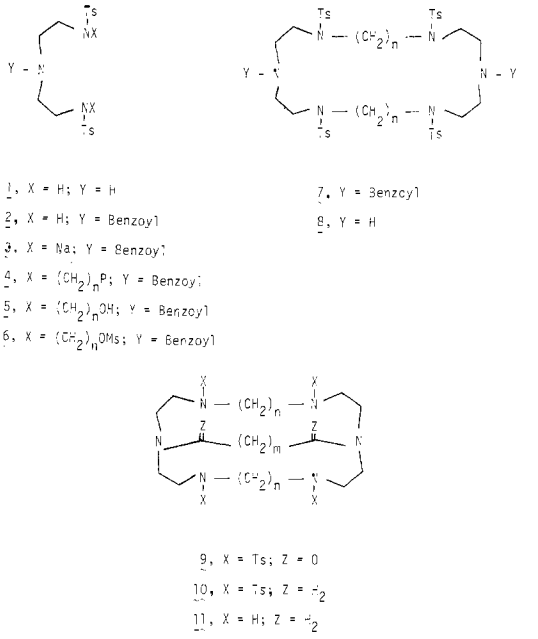

Figure 2.

consequently the bimetallic site.

The key selectively protected macrocyclic precursor **2** was prepared by reaction of benzoyl chloride with **1**. Compound **1** was synthesized by reacting *N*-tosylaziridine with monotosylated ethylenediamine. Reaction of the disodium salt of **2** with two equivalents of the appropriate monotetrahydropyranyloxy-protected mesylated diol gave the ditetrahydropyranyloxy derivative **4**.[16] Acid catalyzed hydrolysis of the tetrahydropyranyl groups provided the diol **5**, which was mesylated to form **6**. Condensation of equimolar quantities of **6** and **3** in DMF at 90 °C for 2 h effected ring closure to give the macromonocycle **7** ($n = 4$ in ca. 20% yield after chromatography). The benzoyl groups were conveniently removed by solvolysis using potassium *tert*-butoxide to give **8** in ca. 85% yield.[17] Compound **8** was reacted with the appropriate diacid halide under high-dilution conditions to give the macrobicycle **9**. This was performed by simultaneous injection of benzene/CH_2Cl_2 solutions of both reactants into a rapidly stirring benzene solution containing Et_3N with use of a syringe pump. Compound **9** ($n = m = 4$) was isolated as a white crystalline solid in 69% yield after chromatography.[18] Compound **9** ($n = m = 4$) was converted to **10** ($n = m = 4$) in 82% yield by reduction with diborane followed by acid hydrolysis and treatment with base. After purification by dry column chromatography (silica, 1:1 THF:hexane), a white crystalline solid was obtained upon recrystallization from CH_2Cl_2/hexane. Detosylation was achieved in 57% yield from 97% H_2SO_4 at 95 °C for 10 h followed by precipitation of the hydrosulfate salt with ether.[19] Passing an aqueous solution of the hydrosulfate salt through a strong-base ion-exchange column in the hydroxide form provided **11** ($n = m = 4$) as a colorless oil after removal of the water and extraction of the solid with CH_2Cl_2. Spectral data are in excellent agreement with the proposed ligand structure.[20]

Dicopper(II) complexes are readily synthesized by addition of the ligand to 2 equiv of Cu(II) salts in methanol. Specifically,

(5) Yuen Ng, C.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1979**, *18*, 2982–2986.

(6) Bulkowski, J. E.; Burk, P. L.; Ludmann, M. F.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 498–499.

(7) (a) Lehn, J. M.; Pine, S. H.; Watanabe, E. I.; Willard, A. K. *J. Am. Chem. Soc.* **1977**, *99*, 6766–6768. (b) Alberts, A. H.; Annunziata, R.; Lehn, J. M. *Ibid.* **1977**, *99*, 8502–8504; (c) Louis, R.; Agnus, Y.; Weiss, R. *Ibid.* **1978**, *100*, 3604–3605.

(8) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027–6036.

(9) (a) Elliot, C. M. *J. Chem. Soc., Chem. Commun.* **1978**, 399. (b) Gunter, M. J.; Mander, L. N.; McLaughlin, G. M.; Murray, K. S.; Berry, K. J.; Clark, P. E.; Buckingham, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 1470–1473. (c) Chang, C. K. *Ibid.* **1977**, *99*, 2819–2822.

(10) We use "*open-face*" to emphasize the *accessibility* of the two-metal site as opposed to *cryptate*, which was coined to designate metals *hidden* within a ligand cavity.[11]

(11) $[M_2 \subset L]$ represents a two-metal site M_2 contained ($\subset$) within a ligand L cavity; $Cu_2(S)$ represents a substrate S-bridged bicopper site.

(12) Dietrich, B.; Lehn, J. M.; Sauvage, J. P. *Tetrahedron Lett.* **1969**, 2889–2892.

(13) (a) Eickman, N. C.; Himmelwright, R. S.; Solomon, E. I. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2094–2098. (b) Himmelwright, R. S.; Eickman, N. C.; LuBien, C. D.; Lerch, K.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 7339–7344.

(14) Abbreviations: BHAO = bicyclo[10.10.6]-1,4,7,12,15,18-hexaazaoctacosane or **11** ($m = n = 4$); Ts, tosyl; Ms, mesyl; P, tetrahydropyranyloxy; DMF, dimethylformamide; S, substrate.

(15) Martin, A. E.; Ford, T. M.; Bulkowski, J. E. *J. Org. Chem.*, in press.

(16) Martin, A. E.; Bulkowski, J. E. *J. Org. Chem.*, in press.

(17) Gassman, P. G.; Hodgson, P. K. G.; Balchunis, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 1275–1276.

(18) Elemental analysis: Anal. Calcd for $C_{50}H_{68}N_6O_{10}S_4$: C, 57.67; H, 6.58; N, 8.02; mol wt 1041. Found: C, 57.86; H, 6.77; N, 7.52; mol wt (vapor pressure osmometry, CH_2Cl_2) 1075. ^1H NMR ($CDCl_3$, Me_4Si internal standard) δ 7.53 (dd, 16H), 3.28 (n, 28H), 2.41 (s, 12H), 1.55 (br m, 12H). IR (KBr pellet): 1645 cm^{-1} (s, CO). mp 172.5–174.5 °C (uncorrected).

(19) Atkins, T. J.; Richman, J. E.; Oettle, W. F. *Org. Synth.* **1978**, *58*, 86–97.

(20) Chemical ionization mass spec: Calcd for $C_{22}H_{48}H_6$: m/e 397 (m + 1); found, m/e 397. NMR ($CDCl_3$, Me_4Si internal standard): ^1H, δ 2.57 (m, 32H), 1.48 (m, 16H); ^{13}C, δ 55.6, 54.8, 49.2, 47.6, 27.6, 27.5 (all s).

the slow addition of 2.5 mL of a 50 mM solution of BHAO in methanol to 5.0 mL of a 50 mM solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in methanol yielded a deep blue solution characterized by electronic absorptions at 282 and 630 nm (ϵ = 9700 and 100 L mol^{-1} cm^{-1}, respectively). Upon the addition of a trace of aqueous NaOH, a new electronic absorption spectrum was observed with three bands, at 292, 465, and 630 nm (ϵ = 12,700, 270, and 300). A deep blue-violet precipitate was isolated either by allowing the solution to stand for several days or by slow infusion of $CHCl_3$ into the Cu-containing solution. The analytical data[21] were consistent with the formulation of this compound as a monohydrated[22] hydroxy-bridged perchlorate complex, $[Cu_2(OH)\subset BHAO](ClO_4)_3 \cdot H_2O$. The IR spectrum (Fluorolube mull) had a weak OH stretch at 3580 cm^{-1} (superimposed on a broad OH absorption), which is close to the OH band positions observed[23,24] for some recently reported monohydroxy-bridged dicopper(II) complexes. Preliminary magnetic susceptibility data with the solid compound indicate a strong antiferromagnetic exchange interaction.[25] This magnetic behavior is consistent with a hydroxide bridge between the copper centers as has been recently found for structurally characterized monohydroxy-bridged dicopper(II) compounds.[24,26,27]

Addition of other anions such as N_3^-, NO_2^-, SCN^-, acetate, and phenolate to the methanolic solution of $[Cu_2\subset BHAO]^{4+}$ resulted in changes in the electronic absorption spectrum indicative of interactions with the Cu centers. For example, addition of N_3^- gave a new spectrum with absorptions at 282, 390, and 582 nm (ϵ = 9500, 3200, and 200); addition of phenolate gave bands at 267, 300, and 675 nm (ϵ = 10,000, 4000, and 80). Preliminary examination of X-band EPR spectra (frozen glasses of 1:1 CH_3OH:toluene) of the dicopper complex in the presence of potentially bridging anions such as those listed above provided axial spectra with equivalent Cu's. The values found for the dicopper complex and added phenolate are typical with $g_\parallel \approx 2.21$, $g_\perp \approx 2.01$, and $A_\parallel$ = 184 G.

In summary, these new "open-face" macrobicycles offer promise for systematically studying substrate interactions at binuclear sites. The unique structural aspects of these systems may be particularly useful for enforcing unusual bridging modes (e.g., a single terminal N of N_3^- bridging two Cu's) which are relevant to elucidation of the nature of substrate interactions with bimetallic metalloproteins[28] and the design of new catalysts.[29] Future efforts will be directed toward structural characterization of such species and relating the structures to their physical and chemical properties.

Acknowledgment. This work was partially supported by the Center for Catalytic Science and Technology at the University of Delaware. We also acknowledge the National Science Foundation (Grant CHE 7803312) for funds used to purchase the Varian E-109E EPR spectrometer.

Registry No. 9 ($n = m = 4$), 80631-47-6; **11** ($n = m = 4$), 80631-48-7; $[Cu_2(OH)\subset BHAO](ClO_4)_3$, 80642-28-0; $[Cu_2(N_3)\subset BHAO]^{3+}$, 80642-29-1; $[Cu_2OPh)\subset BHAO]^{3+}$, 80642-30-4; $[Cu_2\subset BHAO]^{4+}$, 80642-31-5.

(21) Elemental analysis: (a) Anal. Calcd for $Cu_2C_{22}H_{51}N_6Cl_3O_{14}$ (from CH_3OH upon standing): C, 30.83; H, 6.00; N, 9.80. Found: C, 30.85; H, 5.91; N, 9.71. (b) Anal. Calcd for $Cu_2C_{22}H_{51}N_6Cl_3O_{14} \cdot CHCl_3$ (from CH_3OH with infusion of $CHCl_3$): C, 28.29; H, 5.37; Cu, 13.01. Found: C, 28.40; H, 5.42; Cu, 13.01.

(22) Dicopper(II) complexes of perchlorate salts typically form monohydrates upon crystallization in the presence of H_2O.[3a,23]

(23) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chim. Acta* **1978**, L121-122.

(24) Haddad, M. S.; Wilson, S. R.; Hodgson, D. J.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1981**, *103*, 384-391.

(25) Sinn, E., private communication.

(26) Burk, P. L.; Osborn, J. A.; Youinou, M. T.; Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1273-1274.

(27) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 3228-3229.

(28) Himmelwright, R. S.; Eickman, N. C.; LuBien, C. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5378-5388.

(29) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Guastini, C. *J. Am. Chem. Soc.* **1981**, *103*, 185-186.

Stereocontrolled Total Synthesis of Antibiotic A-23187 (Calcimycin)†

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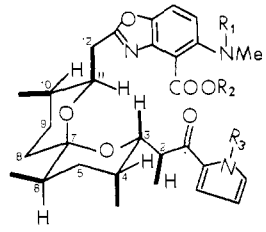
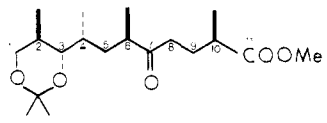
Considerable attention remains focused on antibiotics such as A-23187 (**1**)[1] and X-537A (lasalocid A)[2] because these ionophores



1 $R_1 = R_2 = R_3 = H$



2

17 $R_1 = CF_3CO$, $R_2 = Me$, $R_3 = NMe_2$

represent useful biochemical tools for probing the phenomenon of ion transport.[3] A-23187 (calcimycin), which was isolated from the cultures of *Streptomyces chartreusensis*, is a unique divalent cation ionophore.[1a] Intrigued by the presence of the 1,7-dioxaspiro[5.5]undecane ring system and the accompanying seven centers of chirality, we embarked, a few years ago, on a stereocontrolled total synthesis of **1**. We record below the successful realization of our goal.[4]

Careful analysis of the dioxaspiro[5.5]undecane ring system reveals that each ring oxygen atom bears an axial relationship to the six-membered ring to which it is attached. This arrangement of atoms clearly implies, based on the well-known anomeric effect,[5] that the dioxaspirane unit in A-23187 is in its most stable arrangement. Thus the acyclic keto diol derived from **1**, or its equivalent, emerges as the logical precursor to A-23187 via a thermodynamically controlled acid-catalyzed ring closure. Synthetic efforts reported to date[1b,c] have concentrated on an aldol approach for the elaboration of the chirality at C(2)-C(4). However, the stereochemical problems associated with such an approach led us to pursue an alternate pathway to A-23187 that centered around the stereospecific construction of the C(1)-C(11) segment **2**.

The basic plan for the synthesis of the C(1)-C(11) acyclic portion of A-23187 was performed in two stages (Scheme I): (1) preparation of the C(1)-C(7) segment **7** of **1** from the known bicyclo[2.2.1]heptenone **3**[1c] and (2) elaboration of the remaining C(8)-C(11) carbon atoms bearing the additional chiral center at C(10) onto the C(1)-C(7) segment via the application of the Ireland ester enolate Claisen rearrangement[6] to the propionate

†Dedicated to Professor Gilbert Stork on the occasion of his 60th birthday.

(1) (a) Chaney, M. D.; Demarco, P. V.; Jones, N. D.; Occolowitz, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1932. (b) The first total synthesis of A-23187 was recently reported: Evans, D. A.; Sacks, C. E.; Kleschick, W. A.; Taber, T. R. *Ibid.* **1979**, *101*, 6798. (c) For a formal total synthesis of **1**, see: Grieco, P. A.; Williams, E.; Tanaka, H.; Gilman, S. *J. Org. Chem.* **1980**, *45*, 3537.

(2) (a) Westley, J. W. *Annu. Rep. Med. Chem.* **1975**, *10*, 246. (b) Total syntheses of X-537A have been reported: Nakata, T.; Schmid, G.; Vranesic, B.; Okigawa, M.; Smith-Palmer, T.; Kishi, Y. *J. Am. Chem. Soc.* **1978**, *100*, 2933. Ireland, R. E.; Thaisrivongs, S.; Wilcox, C. S. *Ibid.* **1980**, *102*, 1155. Also see: Ireland, R. E.; McGarvey, G. J.; Anderson, R. C.; Badaud, R.; Fitzsimmons, B.; Thaisrivongs, S. *Ibid.* **1980**, *102*, 6178.

(3) Pfeiffer, D. R.; Taylor, R. W.; Lardy, H. A. *Ann. N.Y. Acad. Sci.* **1978**, *307*, 402. Pressman, B. C. *Annu. Rev. Biochem.* **1976**, *45*, 501. Also see: Wierenga, W.; Evans, B. R.; Woltersom, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1334.

(4) The early stages of this work were presented at the 3rd IUPAC Symposium on Organic Synthesis, Madison, Wisconsin, June 15, 1980.

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