isomers examined had energies above that of the sulfine: carbonyl *O*-sulfide, 9 kcal/mol; three-membered-ring oxathiirane, 20 kcal/mol; oxathiirane, open form, 33 kcal/mol (small singlet–triplet separation). On the basis of these predictions,[12] oxathiirane **7** can ring open in two ways to give (a) sulfine **2** or (b) carbonyl *O*-sulfide **4**.[13] Loss of sulfur from **4** either spontaneously or by pairwise coupling with another carbonyl *O*-sulfide to eliminate S_2 would lead to the observed enedione **3**.

To intercept the proposed intermediates, **1** was allowed to decompose in the presence of a 10-fold excess of norbornene at room temperature (20 °C) under nitrogen. When all of the thioozonide had reacted, as determined by ^{1}H NMR, analysis of the mixture revealed the formation of the expected products, sulfine (65%) and enediones **3c** and **3t** (13%) as well as norbornene epoxide **8** (12%), thiirane **9** (7%), trisulfide **10** (2%), and elemental sulfur (S_8). The structures of the trapping products were determined by ^{1}H NMR (400 MHz), mass spectral analysis, and comparison with authentic materials.[14] Thiirane and epoxide formation demonstrates the presence of active sulfur- and oxygen-transfer agents. The most likely candidates include a carbonyl *O*-sulfide and oxide, the ring-opened oxathiirane biradical, and for sulfur-transfer alone, sulfur atoms or allotropes. Several investigators have demonstrated the production of carbonyl oxides by the thermolysis of furan endoperoxides[15,16] and the reaction of singlet oxygen with diazo compounds.[17] In the latter case, olefin trapping experiments showed that *cis*- and *trans*-epoxides were generally formed from the corresponding olefins although in low yield.

When thioozonide **1** was allowed to decompose in the presence of an excess of *cis*-2,5-dimethyl-3-hexene, the *cis*-epoxide (cis/trans = 17.5) and *cis*-thiirane (cis/trans = 7.3) were formed with high stereoselectivity and low yield (≤4%). The trans olefin afforded only the *trans*-epoxide and thiirane.[18] The similarity (low yield and specificity) of oxygen and sulfur atom transfer during thioozonide decomposition strongly suggests that carbonyl oxides and sulfides are intermediates.[19] Sulfur radicals would be expected to give larger amounts of the trans isomer via bond rotation and closure.

Typically 1,3-dipoles react with olefins to form 1:1 cycloadducts. The corresponding adduct for carbonyl oxide trapping has been observed during the ozonolysis of methyl vinyl ether.[20] No analogous examples of carbon *O*-sulfide trapping have been reported; although the expected product, a simple 1,2-oxathiolan, has been shown to possess appreciable stability.[21] We have observed no products of this type during decomposition of **1**. This is not surprising in view of the low yield of epoxides and thiirane obtained and the expected thermal lability of the initial cycloadduct (**4** + olefin) due to extended conjugation. Alternatively, the formation of epoxide or thiirane may occur by direct attack of oxygen or sulfur in **6** or **4** on the olefin double bond.

Control experiments show that no thiirane is formed by heating a mixture of norbornene and sulfur in methylene chloride. The apparent trapping of the thermally generated S_3 fragment, perhaps the sulfur analogue of ozone, is unusual and suggests that a concatenation mechanism is involved during the formation of S_8. Other studies are under way to elucidate the nature of the actual sulfur expulsion step.

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Registry No. 1, 67711-62-0; **2**, 28030-87-7; **3c**, 17559-81-8; **3t**, 820-69-9; **5**, 638-02-8; **8**, 3146-39-2; **9**, 39558-58-2; **10**, 23657-27-4; (*Z*)-*i*-PrCH=CHPr-*i*, 10557-44-5; (*E*)-*i*-PrCH=CHPr-*i*, 692-70-6; 2-norbornene, 498-66-8; *cis*-3,4-oxa-2,5-dimethylhexane, 59175-38-1; *cis*-3,4-epithio-2,5-dimethylhexane, 101630-80-2; *trans*-3,4-oxa-2,5-dimethylhexane, 54644-32-5; *trans*-3,4-epithio-2,5-dimethylhexane, 101630-81-3.

(12) This ordering is not analogous to that computed for the three CH_2O_2 isomers where the ring form dioxiirane lies 36 kcal/mol below the carbonyl oxide: Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 7180–7188. This prediction is supported by the observed stability of dioxiiranes: Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847–2853.

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(18) The identity of the trapping products was confirmed by independent synthesis of all isomers from the corresponding olefins. *trans*-3,4-Oxa-2,5-dimethylhexane: ^{1}H NMR ($CDCl_3$) δ 0.98 (dd, J_{ab} = 28.6, J_{ac} = 6.7 Hz, J_{ac} = 12 H), 1.47 (m, 2 H), 2.48 (d, J = 7.6 Hz), splitting of ring hydrogen ^{13}C satellite = 2.4 Hz; MS, *m/e* (relative intensity) M^+ not observed, 113 (1.6), 73 (23.7), 72 (18.1), 71 (10.5), 57 (28.7), 56 (100.0), 55 (35.2), 43 (47.6), 41 (89.1). *cis*-3,4-Oxa-2,5-dimethylhexane: ^{1}H NMR ($CDCl_3$) δ 1.04 (dd J_{ab} = 44.2 Hz, J_{ac} = 6.6 Hz, 12 H), 1.48 (m, 2 H) 2.62 (m, 2 H), splitting of ^{13}C satellite = 4.4 Hz; MS, *m/e* (relative intensity), M^+ not observed, 113 (1.6), 73 (25.0), 72 (17.3), 71 (9.9), 57 (29.6), 56 (100.0), 43 (43.9), 41 (76.7). *trans*-3,4-Thia-2,5-dimethylhexane: MS, *m/e* (relative intensity) 146 (M + 2, 3.2) 145 (M + 1, 4.8), 144 (M^+, 44.2), 111 (19.0), 101 (35.8), 88 (32.2), 69 (100.0), 55 (81.9), 41 (71.2). *cis*-3,4-Thia-2,5-dimethylhexane: MS, *m/e* (relative intensity), 146 (M + 2, 3.4) 145 (M + 1, 7.3), 144 (64.7), 112 (20.6), 101 (26.7), 88 (61.6), 69 (99.4), 55 (100.0), 41 (82.3).

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Synthesis of (+)-Avermectin B_{1a}

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The avermectins[1-3] are a group of exceedingly potent anthelmintic agents which appear to exert their insecticidal activity by interfering with invertebrate neurotransmission.[4-6] Any aspirations toward a total synthesis of this group of 16-membered macrocyclic lactones with unique structural, functional, and to-

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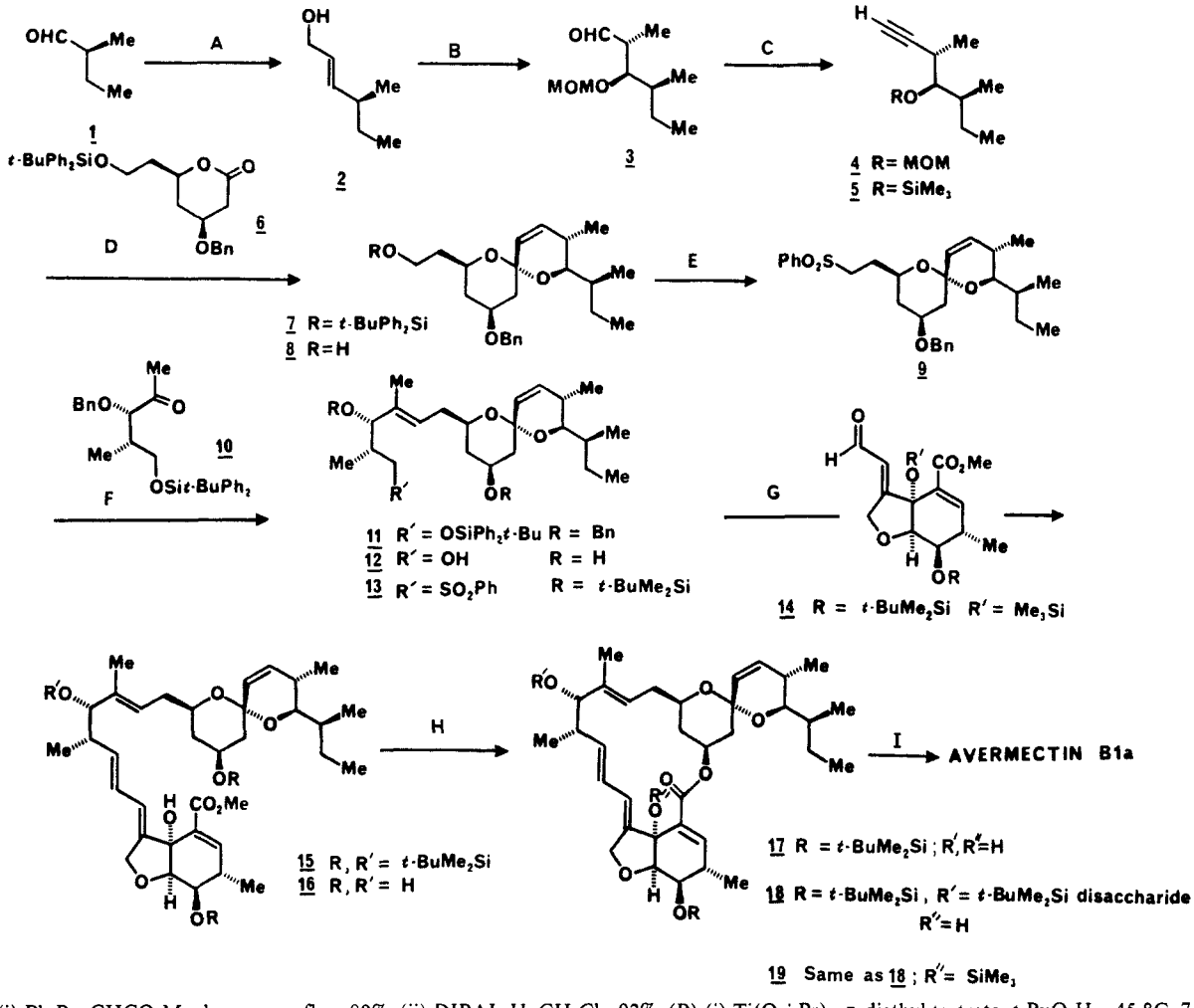
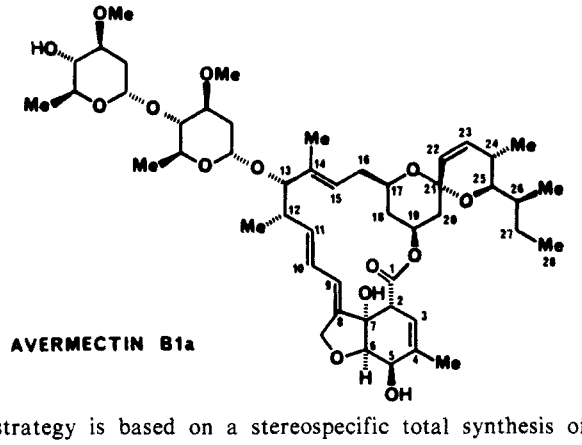
Scheme I[a]



[a] (A) (i) $Ph_3P{=}CHCO_2Me$, benzene, reflux, 89%; (ii) DIBAL-H, CH_2Cl_2, 92%; (B) (i) Ti(O-*i*-Pr)$_4$, D-diethyl tartrate, *t*-BuO_2H, −45 °C, 74%; (ii) $Me_2Cu(CN)Li_2$, Et_2O, 0 °C, 96%; (iii) *t*-$BuPh_2SiCl$, imidazole, CH_2Cl_2, −10 °C, 95%; (iv) MOMCl, *i*-Pr_2NEt, DMAP, 94%; (v) *n*-Bu_4NF, THF, 98%; (vi) PCC, 4-Å sieves, CH_2Cl_2, 78%; (C) (i) Ph_3P, CBr_4, CH_2Cl_2; (ii) *n*-BuLi, THF, 77%, (two steps); (iii) Me_3SiBr, CH_2Cl_2, −30 °C; (iv) Me_3SiCl, Et_3N, DMAP, CH_2Cl_2, 85% (two steps); (D) (i) *n*-BuLi, Et_2O, −78 °C; add lactone **6**; then PPTS, 82%; (ii) Pd/$BaSO_4$-C, H_2, EtOAc, pyr; (iii) $BF_3{\cdot}Et_2O$, THF, 80% (two steps); (iv) *n*-Bu_4NF, THF, 87%; (E) (i) PhSSPh, Ph_3P, THF, 85%; (ii) *m*-CPBA, CH_2Cl_2, −10 °C, 90%; (F) (i) *n*-BuLi, THF, −78 °C; add ketone **10**, 40% (95% based on recovered sulfone); (ii) Na−Hg, MeOH, THF, KH_2PO_4, 40%; (iii) *n*-Bu_4NF, THF, 95%; (iv) Li/NH_3, 75%; (v) *t*-BuCOCl, Et_3N, CH_2Cl_2, 78%; (vi) *t*-$BuMe_2SiCl$, imidazole, DMAP, DMF, 90%; (vii) NaOMe, MeOH, CH_2Cl_2, 80%; (viii) PhSSPh, *n*-Bu_3P, THF, 83%; (ix) *m*-CPBA, CH_2Cl_2, 96%; (G) (i) *n*-BuLi, THF, −78 °C; add **14**, 47% (77% based on recovered sulfone); (ii) $SOCl_2$, pyr; Na−Hg, MeOH; 35%; (iii) *n*-Bu_4NF, THF, 85%; (H) (i) aqueous KOH, THF; then Dowex 50 (H^+), 72%; (ii) DCC, DMAP, CH_2Cl_2, 30%; (iii) *t*-$BuMe_2SiCl$, imidazole, DMF, 91%; (iv) 2-pyridyl thioglycoside in CH_2Cl_2, add AgOTf in toluene, chromatography, 72%; (v) Me_3SiCl, Et_3N, DMAP, CH_2Cl_2, 96%; (I) (i) LDA, Me_3SiCl, THF, −78 °C; then AcOH, THF, −78 °C to room temperature, 31% (72% based on recovered **18**); (ii) *n*-Bu_4NF, THF, 90%.

pological features must contend with the plethora of asymmetric centers and the delicate balance of strategically situated functionality.[5] In this paper we report the first synthesis of (+)-avermectin B_{1a},[3] the most active avermectin component.[6] The



strategy is based on a stereospecific total synthesis of the "northern" C_{11}–C_{28} segment utilizing chirons derived from (*S*)-malic acid and L-isoleucine followed by coupling with a suitably functionalized "southern" segment, macrolactonization, stereocontrolled glycosylation, and adjustment of functionality.

The allylic alcohol **2**, $[\alpha]_D$ 35.2°, easily obtained from **1** via L-isoleucine,[7] was transformed into the six-carbon chiron **3**, $[\alpha]_D$ −67.3°, by well-established methodology[8-10] (Scheme I). Chain extension[11] to **5** and condensation[12] with the readily available lactone **6**, previously obtained[5c] from (*S*)-malic or D-glucose, led to the spiroacetal subunit **8**, $[\alpha]_D$ 105°. With subunits **8** and **10**[13]

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available in optically pure form, we were ready to address their coupling. We opted for a sulfone anion coupling sequence, based on available precedents[14] and on previous experience within our own laboratory.[15] Direct thioetherification[16] of the alcohol **8**, followed by oxidation gave the sulfone **9**, $[\alpha]_D$ 54.2°. Condensation of the anion of **9** with ketone **10**, followed by reductive cleavage of the intermediate β-hydroxy sulfone cleanly gave the trans olefin **11**, $[\alpha]_D$ 46.7°. Deprotection led to the target triol **12**, $[\alpha]_D$ 52.5°, which was shown by high-field ^1H NMR spectroscopy to be sterochemically pure.

Concurrent with our synthetic studies, we have developed an efficient degradation of the natural product to obtain the "southern" C_1–C_{10} aldehyde subunit **14** in high overall yield.[17,18] As before, we adopted a sulfone anion strategy in which **13**, $[\alpha]_D$ 24.8°, readily prepared from the triol **12**, was coupled with the aldehyde **14**. The desired **15**, $[\alpha]_D$ 141°, was obtained as the only detectable dienic product after reductive cleavage of the β-hydroxy sulfone. Removal of the silyl groups, hydrolysis of the seco acid, and macrolactonization with DCC–DMAP[19] gave the α,β-unsaturated macrocyclic lactone **16**, $[\alpha]_D$ 213°. As anticipated, the tertiary hydroxyl group at C_7 remained unaffected during these operations.

At this juncture, we chose to attach the disaccharide moiety at C_{13} since it also serves as a "protective group". This was effected by a silver triflate mediated stereocontrolled glycosylation of the monosilyl derivative **17**, $[\alpha]_D$ 220°, with the 2-pyridyl thioglycoside derivative of the disaccharide subunit,[20] based on methodology previously developed in our laboratory,[21,22] to give the desired glycoside **18**, $[\alpha]_D$ 144°.

The last major hurdle to overcome depended upon a critical deconjugation[23] of the C_2–C_3 double bond in **18**. Thus, treatment of **19** with LDA and Me_3SiCl,[24] followed by rapid quenching with acetic acid and deprotection of the silyl ethers gave avermectin B_{1a}, $[\alpha]_D$ 52°, which was shown by high-field ^1H NMR spectroscopy to be identical with the natural product except for the absence of signals corresponding to the minor B_{1b} isomer (~15%) which is normally found in the commercially available avermectin complex, $[\alpha]_D$ 55.1° ($CHCl_3$).[3]

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Supplementary Material Available: ^1H NMR, IR, and 2D ^1H NMR spectra (33 pages). Ordering information is given on any current masthead page.

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(17) The alcohol corresponding to **14**, R = *t*-$BuMe_2Si$, R′ = H, $[\alpha]_D$ 111°, can be obtained by controlled ozonolysis of avermectin B_{1a} seco ester (conjugated in 79% yield: Hanessian, S.; Ugolini, A.; Hodges, P. J.; Dubé, D., unpublished results.

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(20) The disaccharide subunit was obtained from avermectin B_{1a} via the following sequence: (a) ozonolysis and isolation of a fragment corresponding to **12** (containing 15% of the B_{1b} component R = protected disaccharide); (b) PCC (90%); (c) $KN(Me_3Si)_2$, THF, −30 °C (85%).

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Effect of Charge on Bond Formation and Cleavage in Main-Group–Transition-Metal Clusters: The Reactions of $Bi_2Fe_3(CO)_9$ with $[Fe(CO)_4]^{2-}$ and $[Co(CO)_4]^-$

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Transition-metal clusters containing p-block elements have been known for some time, but the chemical and structural importance of the main-group element has often been overshadowed by the interest in the transition-metal part of the molecule. The recent discovery of molecules such as $M_2[W(CO)_5]_3$ (M = As, Sb, Bi)[1] and $[Et_4N]_2[Bi_4Fe_4(CO)_{13}]$[2] has prompted a renewed interest in these clusters with an emphasis on the main-group portion. Rauchfuss' recent discovery of hypervalency in $(RC_5H_4)MoFe(Te_2X)(CO)_5$[3] (X = monovalent functionality) is another interesting example. Key aspects of these systems include the formation of direct bonds between main-group elements, the effect of the main-group element on the transition-metal bonding, and the nature of the bonding between the main-group and transition elements.

In efforts to synthesize new Zintl-metal carbonylates, we have examined the reaction of $Bi_2Fe_3(CO)_9$ with the metal carbonyl anions $[Fe(CO)_4]^{2-}$ and $[Co(CO)_4]^-$. These two reactions proceed quite differently, in one case leading to Bi–Bi bond formation and in the other to Fe–Fe bond cleavage. The available information suggests that these differences may be attributed to charge effects.

When $Bi_2Fe_3(CO)_9$ is treated with $[Co(CO)_4]^-$, replacement of an iron vertex occurs with concurrent formation of a Bi–Bi bond as shown by X-ray analysis.[4] The molecule $[Et_4N][Bi_2Fe_2Co(CO)_{10}]$ (**1**) is shown in Figure 1, with selected bond angles and distances in Table I. The incorporation of cobalt and extrusion of iron is confirmed by elemental analysis. The molecule is best

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(4) Excess $Co_2(CO)_8$ (0.16 mmol) was dissolved in 10 mL of tetrahydrofuran (THF) and reduced with 1 mL of 1% Na/Hg. The THF solution was removed via syringe and filtered through Celite onto $Bi_2Fe_3(CO)_9$ (0.24 mmol). The solution was stirred overnight, then the solvent was removed under vacuum, and the product dissolved in methanol. $[Et_4N]Br$ (0.12 g) was added to the methanol solution followed by addition of water to precipitate the product in yields >45%. Anal. Calcd for $[Et_4N][Bi_2Fe_2Co(CO)_{10}]$: Bi, 41.84; Fe, 11.13; Co, 5.90. Found: Bi, 40.53; Fe, 10.65; Co, 5.12. IR (MeOH): 2030 sh, 2025 w, 2000 s, 1980 vs, 1960 s, 1944 m, 1918 mw. Crystal data: triclinic, space group $P\bar{1}$, a = 10.205 (4) Å, b = 11.250 (8) Å, c = 13.125 (6) Å, α = 70.30 (5)°, β = 76.94 (3)°, γ = 76.89 (5)°; V = 1363.1 (14) Å^3; Z = 2, R_1 = 0.083, R_2 = 0.074 for $I > 3\sigma$ and R_1 = 0.064, R_2 = 0.069 for $I > 6\sigma$.

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