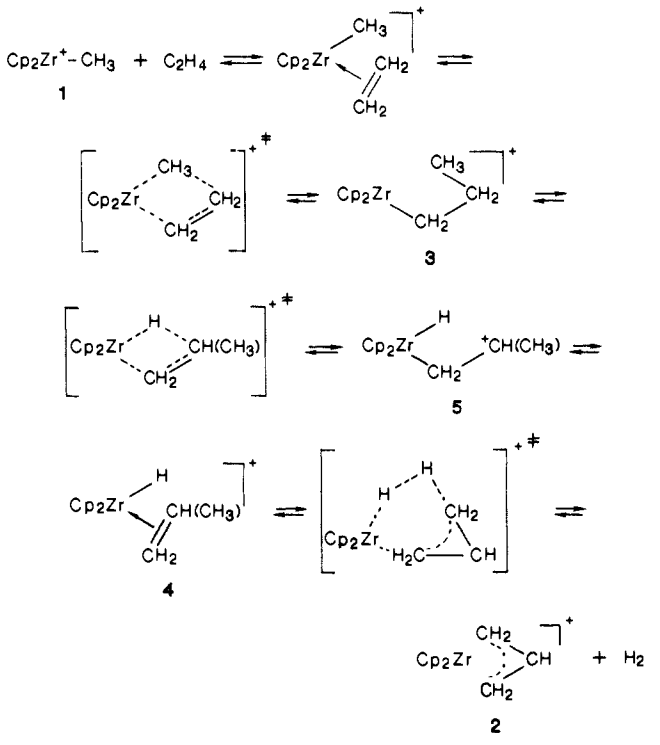
Scheme I



An investigation of mechanistic aspects of the ethylene reaction by using C_2D_4 shows a significant amount of hydrogen–deuterium scrambling, eliminating 11% D_2, 74% HD, and 15% H_2, which is somewhat different from the statistical distribution of 28.6% D_2, 57.1% HD, and 14.3% H_2. A similar experiment with $[Cl_2TiCH_3]^+$ and C_2D_4 was performed by Uppal et al.,[19] and, in contrast to our result, at least 85% HD is lost. Reaction of $[Cp_2ZrD]^+$ with propylene produces a degree of scrambling very close to the statistical distribution of 28.6% HD to 71.4% H_2 loss (eq 3).

$$Cp_2ZrD^+ + C_3H_6 \rightarrow \begin{cases} Cp_2ZrC_3H_5^+ + HD & (23\%) \\ Cp_2ZrC_3H_4D^+ + H_2 & (77\%) \end{cases} \quad (3)$$

A possible mechanism for the reaction of **1** with ethylene to produce **2** is given in Scheme I. Scrambling probably occurs during interconversion of the insertion product **3** and the hydride intermediate **4** possibly via successive hydride shifts along the three-carbon framework of intermediate **5**.

Lack of thermochemical data for the zirconium–carbon and zirconium–allyl bond energies prevents the complete determination of the enthalpies of the proposed insertion reactions and insertion/elimination processes. However, an indication of the relative exothermicities of the insertion reactions is given by the enthalpies for the general reaction $^{\bullet}CH_3 + C_nH_m \rightarrow {}^{\bullet}C_{n+1}H_{m+3}$ ($\Delta H^{0\prime}$).[20] When applied to the reactions of **1** with ethylene and propylene, $\Delta H^{0\prime}$ values are −23.5 and −24.1 kcal mol^{-1}, respectively. The net exothermicity is reduced when H_2 is eliminated, e.g., $^{\bullet}CH_3 + C_2H_4 \rightarrow {}^{\bullet}C_3H_5 + H_2$ (ΔH^0 = −4.6 kcal mol^{-1}), but this is compensated by the expected stability of the zirconium–allyl product.

Our observations suggest that intermediates of polymerization and metathesis reactions also occur in the solvent-free reactions of an electron deficient d^0 transition-metal complex ion. Complexes formed following elimination of H_2 from these chemically activated[22] gas-phase intermediates are possible products of chain termination in the polymerization of alkenes by solvated d^0f^n metal catalysts. In addition, the formation of allyl species in solution and the possible role of this process in introducing unsaturation into polymers warrants further investigation.

Acknowledgment. This work was supported by a National Science Foundation Grant (CHE-8700765), which is gratefully acknowledged. Additional support was supplied by the Petroleum Research Fund, administered by the American Chemical Society, and the Department of Defense (DOD/University Joint Instrumentation Program, purchase of the Nicolet FTMS-1000). We thank J. Boncella and N. Wong for helpful discussions and D. Straus for providing early samples of zirconium compounds.

(18) Jordan, R. F., private communication.
(19) Uppal, S. J.; Johnson, D. E.; Staley, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 508.
(20) Values for $\Delta H^{0\prime}$ are calculated from published experimental values or are derived from group additivities (Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279. O'Neal, H. E.; Benson, S. W. *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II.
(21) Ballard, D. G. H.; Jones, E.; Medinger, T.; Pioli, A. J. P *Die Makromolekulare Chemie* **1971**, *148*, 175.
(22) (a) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: New York, 1972. (b) Forst, N. *Theory of Unimolecular Reactions*; Academic: New York, 1973.

Palladium-Catalyzed Coupling of Vinyl Epoxides with Organostannanes

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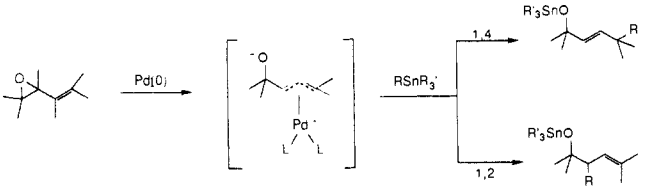
Received February 22, 1988

The palladium-catalyzed alkylation of vinyl epoxides by soft nucleophiles derived from carbon acids is both regioselective (1,4-addition) and stereospecific, with alkylation occurring at the π-allyl face opposite to that bonded to palladium.[1,2] The mild, neutral reaction conditions are ideally suited for the synthesis of a variety of organic compounds.[3] Because 1,3-dienemonoepoxides readily undergo oxidative addition to palladium(0), they should also catalytically couple with organostannanes (eq 1), allowing alkylation by the variety of organic groups available with the tin reagents.[4]



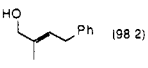
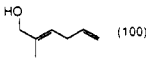
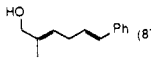
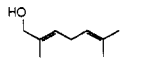
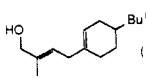
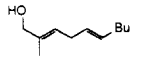
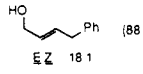
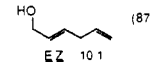
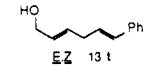
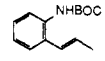
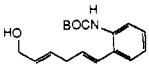
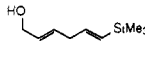
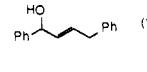
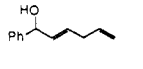
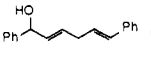
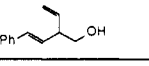
(1)

Indeed this reaction takes place with a weakly ligated palladium catalyst, $(CH_3CN)_2PdCl_2$,[5] in a polar solvent such as DMF at ambient temperature to give good yields of coupled product (Table

† Present address: Instituto de Química Orgánica, CSIC. Juan de la Cierva 3, 28006-Madrid, Spain.
(1) For a survey of π-allyl Pd complexes and reactivity patterns, see: (a) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (b) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, W. E., Eds.; Pergamon Press: New York, 1982; Vol. 8, p 799.
(2) (a) Trost, B. M.; Molander, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5969. (b) Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575.
(3) (a) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1981**, *103*, 5972. (b) Trost, B. M.; Warner, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 6112; **1983**, *105*, 5940. (c) Kabat, M. M.; Wicha, J. *J. Chem. Soc., Chem. Commun.* **1983**, 985. (d) Takahashi, T.; Ootake, A.; Tsuji, J. *Tetrahedron* **1985**, *41*, 5747. (e) Trost, B. M.; Angle, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 6123. (f) Deardorff, D. R.; Myles, D. C.; MacFerrin, K. D. *Tetrahedron Lett.* **1985**, *26*, 5615. (g) Trost, B. M.; Scanlan, T. S. *Tetrahedron Lett.* **1986**, *27*, 4141. (h) Tsuda, T.; Tokai, M.; Ishida, T.; Saegusa, T. *J. Org. Chem.* **1986**, *51*, 5216. (*i*) Deardorff, D. R.; Shambayati, S.; Linde, R. G.; Dunn, M. M. *J. Org. Chem.* **1988**, *53*, 189. (j) Trost, B. M.; Kuo, G.-H.; Benneche, T. *J. Am. Chem. Soc.* **1988**, *110*, 621.
(4) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.
(5) This catalyst was prepared by a procedure analogous to that for the benzonitrile complex: Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216.

0002-7863/88/1510-4039$01.50/0

Table I. Palladium-Catalyzed Coupling of Vinyl Epoxides with Organostannanes

Entry	Epoxide	$RSnR'_3$ R	R'	1,4-Product (1,4:1,2)	Yield (%)[a]
1		Ph	Me	 (98 2)	85
			Bu		85
2			Me	 (100)	77
			Bu		80
3		Ph	Me	 (87 13)	63
			Bu		65
4			Me	 (100)	72
5		^{t}Bu	Me	 (100)	79
6		Bu	Me	 (100)	63
7		Ph	Me	 (88 12) E:Z 18 1	83
8			Me	 (87 13) E:Z 10 1	77
9		Ph	Me	 (88 12) E:Z 13 t	65
10			Bu	 (82 18)	68
11		Me_3Si	Bu	 (88 12)	100
12		Ph	Me	 (100)	75
13			Me	 (98 2)	80
14		Ph	Me	 (100)	55
15			Bu	 (9 91)	83

[a] Isolated purified products.

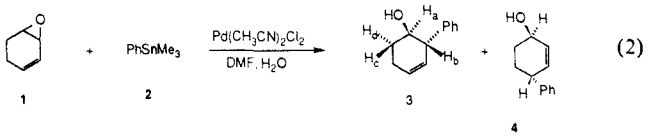
I). Although the palladium-catalyzed coupling reaction of organostannanes with other electrophiles are relatively insensitive to water, surprisingly, the presence of water (10 equiv based on the vinyl epoxide) gave higher yields of coupled product than when the reaction was run under anhydrous conditions. Furthermore, in the presence of water the reaction was more selective, both with respect to 1,4:1,2-addition and E/Z product ratios. Other additives, including Lewis acids and bases, protic acids (e.g., CH_3CO_2H), or protic solvents (e.g., EtOH) were less effective than water in improving the yields. The role of water is not understood.

Coupling with the organotin reagent was rapid enough such that the competing palladium-catalyzed isomerization of the vinyl epoxides to α,β-unsaturated carbonyl compounds was not observed.[6] In a competitive coupling reaction of isoprene monoepoxide with equal molar quantities of phenyltrimethylstannane and diethyl malonate, only a single allylic alcohol, 4-phenyl-2-methylbut-2-en-1-ol; was isolated, diethyl malonate being recovered unchanged from the reaction.

(6) (a) Suzuki, M.; Oda, Y.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 1623. (b) Suzuki, M.; Watanabe, A.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 2095.

In general, acyclic vinyl epoxides gave better yields of coupled allylic alcohols than cyclic vinyl epoxides.[7] Vinyl, phenyl, and styryl groups on the stannane were readily transferred, both trimethyl- and tributylstannanes participating equally well in the transmetalation reaction (entries 1–3). High regioselectivity to yield the 1,4-allylic alcohol product was observed, the ratio of allylic to homoallylic (1,4:1,2) alcohols being affected by the substitution pattern on the vinyl epoxide (entries 2, 8, 13, 15). The geometry of the migrating double bond was not as clean with the E isomer predominating (E/Z = 1–3).[8] In certain examples (entries 7–9, 12–14) high E/Z ratios (>10:1) were observed.

The stereochemistry of the reaction was determined (eq 2) by the coupling of 1,3-cyclohexadiene monoepoxide **1** and phenyltrimethylstannane **2** to give a mixture of alcohols **3** and **4**.



(2)

The phenyl and alcohol groups in both the homoallylic **3** and allylic **4** alcohol were trans. The trans stereochemistry for **3** was assigned from the proton NMR spectrum (270 MHz) in which H_a couples with H_b (J = 10.5 Hz), H_c (J = 7.7 Hz) and H_d (J = 3.1 Hz) giving a ddd pattern, while H_b was observed as a dm pattern coupling with H_a (J = 10.5 Hz). The trans stereochemistry of alcohol **4** was not obvious from the proton NMR spectrum alone. However, **4** was hydrogenated (Pd/C; H_2) to yield *trans*-4-phenylcyclohexan-1-ol which exhibited the same physical and spectroscopic properties as an authentic sample of the saturated alcohol.[9] This anti stereochemistry is the opposite to the syn alkylation observed with a soft anion.[1,2] This difference can be attributed to internal delivery of the R group of the stannane to palladium followed by reductive elimination from palladium with retention of configuration at carbon σ-bonded to palladium.

Acknowledgment. This research was supported by a Grant (CHE-8703218) from the National Science Foundation. Antonio M. Echavarren acknowledges the receipt of a NATO Fellowship. Palladium was provided under the Johnson-Matthey Metal Loan program.

Registry No. 1, 6705-51-7; **2**, 934-56-5; **3**, 114467-53-7; **4**, 71911-76-7; $CH_2OC(CH_3)CH{=}CH_2$, 1838-94-4; $CH_2OCHCH{=}CH_2$, 930-22-3; $PhCHOCHCH{=}CH_2$, 20248-57-1; (*E*)-$PhCH{=}CHCHOCH_2$, 89368-01-4; $PhSnBu_3$, 960-16-7; $CH_2{=}CHSnMe_3$, 754-06-3; $CH_2{=}CHSnBu_3$, 7486-35-3; (*E*)-$PhCH{=}CHSnMe_3$, 7422-28-8; (*E*)-$PhCH{=}CHSnBu_3$, 66680-88-4; $(CH_3)_2C{=}CHSnMe_3$, 20484-24-6; (*E*)-$BuCH{=}CHSnMe_3$, 17421-54-4; (*E*)-BOCN(H)-*o*-$C_6H_4CH{=}CHSnBu_3$, 114467-54-8; (*E*)-$Me_3SiCH{=}CHSnBu_3$, 58207-97-9; (*E*)-$(CH_3)(HOCH_2)C{=}CHCH_2Ph$, 52497-56-0; $CH_2{=}CHC(Ph)(CH_3)CH_2OH$, 114467-55-9; (*E*)-$(CH_3)(HOCH_2)C{=}CHCH_2CH{=}CH_2$, 114467-56-0; (*E,E*)-$(CH_3)(HOCH_2)C{=}CHCH_2CH{=}CHPh$, 114467-57-1; (*E*)-$(HOCH_2)(CH_3)C(CH{=}CH_2)CH{=}CHPh$, 114467-58-2; (*E*)-$(HOCH_2)(CH_3)C{=}CHCH_2CH{=}C(CH_3)_2$, 43161-20-2; (*E,E*)-$(CH_3)(HOCH_2)C{=}CHCH_2CH{=}CH(CH_2)_3CH_3$, 114467-59-3; (*E*)-$HOCH_2CH{=}CHCH_2Ph$, 49676-93-9; $HOCH_2CH(Ph)CH{=}CH_2$, 6052-63-7; (*E*)-$HOCH_2CH{=}CHCH_2CH{=}CH_2$, 28465-64-7; $HOCH_2CH(CH{=}CH_2)_2$, 54962-87-7; (*E,E*)-$HOCH_2CH{=}CHCH_2CH{=}$

(7) All compounds have been fully characterized by IR, ^1H, ^{13}C NMR spectroscopy. Elemental composition was determined by high-resolution mass spectroscopy and/or combustion analysis.

(8) For a discussion of the factors that may determine E/Z selectivity, see: Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 603; **1978**, *100*, 3435; **1980**, *102*, 4730.

(9) Comparison of the hydrogenated alcohol from **4** with an authentic sample of *trans*-4-phenylcyclohexan-1-ol prepared from 4-phenylcyclohexanone according to Kobayashi et al. (Kobayashi, Y. M.; Lambrecht, J.; Jochimins, J. G.; Burkert, U. *Chem. Ber.* **1978**, *111*, 3442) gave identical results: ^1H NMR ($CDCl_3$) δ 1.35–1.60 (m, 2 H), 1.64 (br s, 1 H), 1.90–1.98 (m, 2 H), 2.05–2.13 (m, 2 H), 2.49 (tt, J = 11.7, 3.4 Hz, 1 H), 3.68 (tt, J = 10.5, 4.4 Hz, 1 H), 7.13–7.32 (m, 5 H); mp 117–118 °C (lit. 118–119 °C; Ungenade, H. E. *J. Org. Chem.* **1948**, *13*, 361). For a detailed NMR study of substituted carbocyclic systems, see: Marino, J. P.; de la Pradilla, R. F.; Laborde, E. *J. Org. Chem.* **1987**, *52*, 4898 and references therein.

CHPh, 83413-35-8; (*E*)-$HOCH_2CH(CH{=}CH_2)CH{=}CHPh$, 83413-27-8; (*E*,*E*)-BOCN(H)-*o*-C_6H_4-$CH{=}CHCH_2CH{=}CHCH_2OH$, 114467-60-6; (*E*)-BOCN(H)-*o*-C_6H_4-$CH{=}CHCH(CH{=}CH_2)CH_2OH$, 114467-61-7; (*E*,*E*)-$HOCH_2CH{=}CHCH_2CH{=}CHTMS$, 114467-62-8; (*E*)-$HOCH_2CH(CH{=}CH_2)CH{=}CHTMS$, 114467-63-9; (*E*)-$PhCH(OH)CH{=}CHCH_2Ph$, 72486-03-4; (*E*)-$PhCH(OH)CH{=}CHCH_2CH{=}CH_2$, 114467-64-0; $PhCH(OH)CH(CH{=}CH_2)_2$, 10544-99-7; (*E*,*E*)-$PhCH(OH)CH{=}CHCH_2CH{=}CHPh$, 114467-65-1; (*E*)-$PhCH(CH{=}CH_2)CH{=}CHCH_2OH$, 114467-66-2; (*E*)-$PhCH{=}CHCH(CH{=}CH_2)CH_2OH$, 83413-27-8; $(CH_3CN)_2PdCl_2$, 14592-56-4; (4-*tert*-butylcyclohexenyl)trimethylstannane, 102073-66-5; (*E*)-4-(1,1-dimethylethyl)-1-(2-methylbut-2-en-1-ol-4-yl)cyclohexene, 114467-52-6; *trans*-1-hydroxy-4-phenylcyclohexane, 5769-13-1.

Total Synthesis of (+)-18-Deoxynargenicin A_1

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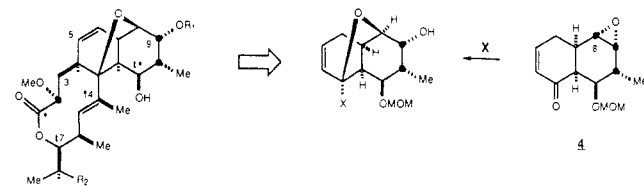
In 1980, workers at Pfizer and Upjohn reported the first examples of a new structural class of antibiotics, the nargenicins. Nargenicin A_1 (**1**), isolated from *Norcardia argentinensis* Huang sp. nov., exhibits in vivo activity against gram-positive bacteria, including drug-resistant strains.[1] Nodusmicin (**2**), a related antibiotic from *Saccharopolyspora hirsuta*, has been characterized by X-ray crystallography and the relationship to **1** demonstrated by synthetic interconversion.[2,3] Other nargenicins,[4-6] including the 18-deoxy congener **3**,[4] have now been isolated. The unique structure and biological activity of these macrolides have fostered considerable interest in their pharmacology[7] and biosynthesis,[3,8] and several groups have described preliminary synthetic studies.[9,10] We now report the first total synthesis of a naturally occurring nargenicin macrolide, (+)-18-deoxynargenicin A_1 (**3**).

Previous work in our laboratories has resulted in an efficient, stereocontrolled route to the 11-oxatricyclo[4.4.1.$0^{2,7}$]undecene nucleus characteristic of the nargenicins.[9] Our entry to this novel ring system is based on the addition of nucleophilic reagents to ketone **4** (available in 7 steps from benzoquinone);[9a] addition of the resulting alkoxide to the C_8–C_9 epoxide (nargenicin numbering system) establishes the C_8–C_{13} ether bridge (Figure 1). We reasoned that this approach could be extended to the synthesis of an advanced intermediate incorporating the key structural and stereochemical elements of **3**, by addition of a vinyl lithium reagent



1 R_1 = 2-carboxypyrrole R_2 = OH nargenicin A_1
2 R_1 = H, R_2 = OH nodusmicin
3 R_1 = 2-carboxypyrrole R_2 = H 18 deoxynargenicin A_1

Figure 1.

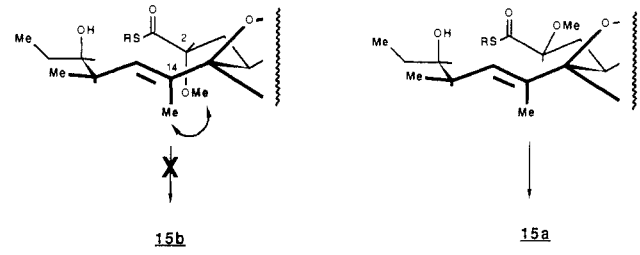


Figure 2.

representing the C_{14}–C_{19} fragment of the nargenicin macrolide system to enone **4**. Iodide (+)-**5a**, possessing the functionality and stereochemistry of the required C_{14}–C_{19} subunit, has been reported by Corey in the context of a total synthesis of erythronolide B.[11] For the present application, we required the methoxymethyl protected derivative (+)-**5b**, readily available from (+)-crotyl epoxide[12] using a modification of the Corey scheme.

Addition of the vinyl lithium reagent derived from (+)-**5b** (2 equiv of *t*-BuLi, Et_2O, −78 °C) to racemic enone **4** gave the expected mixture of diastereomeric products **6**, which were transformed directly to the methoxymethyl-protected derivatives **7** (Scheme I).[13] While **7a** and **7b** were readily separated by flash chromatography, we were unable to unambiguously identify the desired diastereomer by spectroscopic methods; consequently, each diastereomer was *independently* carried through the next synthetic sequence (for clarity, only transformations of diastereomer **7a** are shown). Allylic oxidation of **7** with 3,5-dimethylpyrazole–CrO_3 complex[14] (CH_2Cl_2, −20 °C) afforded enone **8** in modest yield. Introduction of the C_1–C_3 subunit of the nargenicins was accomplished by addition of the mixed cuprate reagent **9**, followed by immediate trapping of the resulting enolate as the enol phosphodiamidate and dissolving metal reduction[15] to afford **10**. The stereochemistry of cuprate addition to **8** is consistent with our observations in related model systems[9b] and is presumably a consequence of initial coordination of the cuprate reagent to the oxygen of the ether bridge. That we had introduced the C_1–C_3 subunit with the desired relative stereochemistry was demonstrated by selective deprotection of **10** and Jones oxidation of the resulting primary alcohol to afford the crystalline acids **11**. X-ray crystallography of one of the diastereomeric acids revealed this material to be **11b**,[16] allowing us to confine our final synthetic transformations to the "natural" diastereomer **11a**.

Introduction of the C_2 methoxyl was accomplished by enolate oxidation[17] of ester **12** (LDA, MoO_5–HMPA–pyridine) and

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0002-7863/88/1510-4041$01.50/0