of lithiated amides from 3 and 4 with acetone as compared to deuterioacetone probably reflect the operation of a deuterium isotope effect on enolization which is competitive with the addition. An example of the use of this approach to provide α-hydroxyalkylation of an amine is outlined for pyrrolidine in Scheme II. A similar sequence with piperidine proceeds in yields of 77%, 72%, and 53% for the steps shown. The 2,2-diethylbutyric acid is also recovered in high yield from the hydrolysis and is thereby available to be recycled in the sequence. A typical experimental procedure is given at the end of this communication.

The use of *n*-butyllithium instead of *sec*-butyllithium results in yield which are ca. 20% less than those listed in Table I. Attempted alkylations of α-lithioalkyl amides were not successful and were not pursued because cleavage of the products was anticipated to be difficult; hydrolysis of **3** required heating in 50% sulfuric acid at 130 °C for 30 h.

Steric hindrance of the carbonyl group in the 2,2-diethylbutanamides provides protection of the carbonyl during lithiation but sufficient access for rearrangement and subsequent hydrolytic cleavage. Exceptional steric hindrance by the triethylcarbinyl group is precedented in Brown's studies of F strain and Newman's "rule of six" and has been recently discussed quantitatively.[8,9] Development of the synthetic potential and understanding of the underlying structure stability relationships of these novel and useful α-heteroatom dipole-stabilized carbanions is a matter of continuing interest.[10]

The procedure was as follows. To a diethyl ether solution (30 mL) containing 0.45 mL (3 mmol) of tetramethylethylenediamine (TMEDA) and 2.3 mL (2.8 mmol) of *s*-BuLi (1.20 M in cyclohexane) was added 494 mg (2.51 mmol) of **3** in 5 mL Et_2O at −78 °C. The reaction mixture was stirred at 0 °C for 45 min, followed by the addition of 0.3 mL (3 mmol) of benzaldehyde at −78 °C. After the solution was allowed to warm to room temperature, 40 mL of Et_2O was added; the ethereal solution was washed with 10% HCl solution and saturated NaCl solution and dried ($MgSO_4$). Removal of solvent gave an oily product which was treated with 30 mL of 2:1 methanol–hydrochloric acid (concentrated) at reflux for 17 h. The cooled solution was extracted three times with CH_2Cl_2; the combined organic layer washed once with saturated NaCl solution and once with 10% NaOH solution and dried ($MgSO_4$). Removal of solvent gave the crude ester from which 547 mg of pure ester (72% yield) was isolated by flash chromatography.

Acknowledgment. We are grateful to the National Institutes of Health, Institute of General Medicine, for support of this work and to Professor A. I. Meyers for disclosing his work prior to publication.

Registry No. 1 (R = H; R′ = $(C_2H_5)_3C$), 78986-71-7; 2 (R = CH_3; R′ = $(C_2H_5)_3C$), 78986-72-8; 3 (R_1R = $(CH_2)_2$; R′ $(C_2H_5)_3C$), 78986-73-9; 4 (R_1R = $(CH_2)_3$; R′ = $(C_2H_5)_3C$), 78986-74-0; 5 (R = CH_3; $R_2C_6H_5$, H; R′ = $(C_2H_5)_3C$), 78986-75-1; 5 (R_1R = $(CH_2)_2$, R_2 = C_6H_5, H, R^1 = $(C_2H_5)_3C$), 78986-76-2; 5 (R, R = $(CH_2)_2$; R_2 = C_6H_{13}, H; R^1 = $(C_2H_5)_3C$), 78986-77-3; 5 (R, R = $(CH_2)_2$; R_2 = $(CD_3)_2$; R^1 = $(C_2H_5)_3C$), 78986-78-4; 5 (R,R = $(CH_2)_2$; R_2 = $(CH_3)_2$; R^1 = $(C_2H_5)_3C$), 78986-79-5; 5 (R,R = $(CH_2)_3$; R_2 = C_6H_5, H; R^1 = $(C_2H_5)_3C$), 78986-80-8; 5 (R, R = $(CH_2)_3$; R_2 = $C_6H_{13}H$; R^1 = $(C_2H_5)_3C$), 78986-81-9; 5 (R, R = $(CH_2)_3$; R_2 = $(CD_3)_2$; R^1 = $(C_2H_5)_3C$), 79005-33-7; CH_3OD, 1455-13-6; $(C_6H_5)_2CO$, 119-61-9; C_6H_5CHO, 100-52-7; $C_6H_{13}CHO$, 111-71-7; $(CD_3)_2CO$, 666-52-4; $(CH_3)_2CO$, 67-64-1; $(C_2H_5)_3CCONCH_3CH_2D$, 78986-82-0; $(C_2H_5)_3CCONCH_3CH_2COH(C_6H_5)_2$, 78986-83-1; $(C_2H_5)_3CCONCHD(CH_2)_3$, 78986-84-2; $(C_2H_5)_3CCONCHC((C_6H_5)_2OH)(CH_2)_3$, 78986-85-3; $(C_2H_5)_3CCONCHD(CH_2)_4$, 78986-86-4.

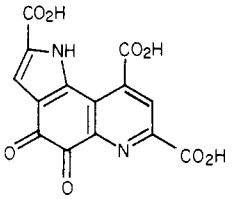
David B. Reitz*
Monsanto Agricultural Products Company
Research Department
St. Louis, Missouri 63166

Peter Beak,* Anthony Tse
Roger Adams Laboratory
University of Illinois
Urbana, Illinois 61801
Received April 13, 1981

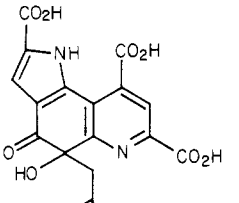
Total Synthesis of Methoxatin, the Coenzyme of Methanol Dehydrogenase and Glucose Dehydrogenase

Summary: The first total synthesis of the bacterial coenzyme methoxatin has been successfully completed starting from readily available 2,3-dimethoxytoluene.

Sir: Methylotrophic bacteria are organisms capable of utilizing C_1 compounds such as methane and methanol as their sole source of cellular carbon.[1] A promising commerical process has been developed for synthesis of single-cell protein from methanol by such a microorganism.[2] These bacteria each contain a methanol dehydrogenase that is capable of oxidizing both primary alcohols and formaldehyde.[3] Recently these bacterial methanol dehydrogenases have all been found to contain an unusual, low molecular weight coenzyme[4,5] for which the name methoxatin has been suggested.[5] Methoxatin has been assigned the unique pyrroloquinoline quinone structure 1 on the basis of limited spectral data[4a] and by an X-ray



1



2

(7) The formation of an ammonium salt which drives the N to O migration has been used by Seebach et al. in a similar case,[5e] and has precedent in the literature. See: D. A. Evans and L. R. McGee, *J. Am. Chem. Soc.*, **103**, 2876 (1981); A. Rüegger, M. Kuhn, H. Lichti, H.-R. Loosli, R. Huguenin, C. Quiquerez, and A. von Wartburg, *Helv. Chim. Acta*, **59**, 1075 (1976); L. V. Pavlova and F. Y. Rachinskii, *Usp. Khim. (Engl. Transl.)* **37**, 587 (1968).

(8) J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley, New York, 1975, pp 229–234; M. S. Newman, "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, pp 201–248; A. Panaye, J. A. MacPhee, and J.-E. Dubois, *Tetrahedron Lett.*, 3485 (1980).

(9) C. Lion, J.-E. Dubois, J. A. MacPhee, and Y. Bonzougou [*Tetrahedron*, **35**, 2077 (1979)] have recently reported that sterically hindered esters with substitution comparable to 1-4 undergo dealkylation on treatment with *n*-propyllithium at 0 °C.

(10) For examples of analogous thioesters and esters see: D. B. Reitz, P. Beak, R. F. Farney, and L. S. Helmick, *J. Am. Chem. Soc.*, **100**, 5428 (1978); P. Beak and L. G. Carter, *J. Org. Chem.*, **46**, 2363 (1981).

(1) For a review, see: Colby, J.; Dalton, H.; Whittenbury, R. *Ann. Rev. Microbiol.* **1979**, *33*, 481.

(2) Windass, J. D.; Worsey, M. J.; Pioli, E. M.; Pioli, D.; Barth, P. T.; Atherton, K. T.; Dart, E. C.; Byrom, D.; Powell, K.; Senior, P. J. *Nature (London)* **1980**, *287*, 396 and references cited.

(3) Anthony, C.; Zatman, L. J. *Biochem. J.* **1967**, *104*, 960 and references cited.

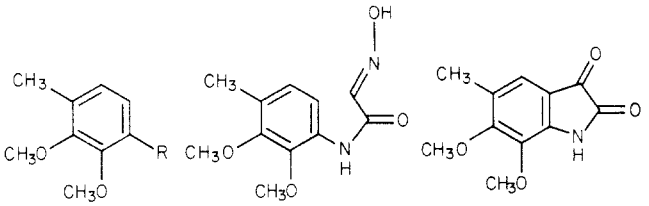
(4) (a) Duine, J. A.; Frank, J.; Verwiel, P. E. *Eur. J. Biochem.* **1980**, *108*, 187. (b) Duine, J.; Frank, J. *Biochem. J.* **1980**, *187*, 213. (c) Duine, J. A.; Frank, J. *Ibid.* **1980**, *187*, 221.

(5) Salisbury, S. A.; Forrest, H. S.; Cruse, W. B. T.; Kennard, O. *Nature (London)* **1979**, *280*, 843.

0022-3263/81/1946-4317$01.25/0

crystal structure determination on its acetone condensation product **2**.[5] It appears that this same coefactor is also present in glucose dehydrogenase isolated from *Acinetobacter calcoaceticus*.[6] Lack of substantial quantities of **1** have to date hindered attempts to reconstitute the holoenzyme from apoenzyme and coenzyme, to determine the mechanistic role of the coenzyme in the oxidation process, and to establish the biosynthesis of methoxatin.[7,8] We now describe the first total synthesis of methoxatin by a route that confirms the original structural assignment and that will make it available for these important studies.

2,3-Dimethoxytoluene was lithiated[9] (*n*-BuLi, TMEDA, hexane, 18 h, room temperature) and subsequently treated with CO_2 to produce acid **3** (66%, mp[10] 121–122 °C).[11] A

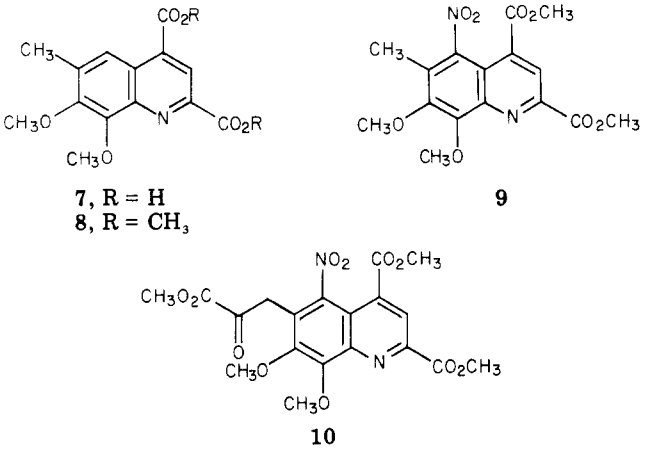


3, R = CO_2H
4, R = NH_2

5 **6**

Curtius rearrangement sequence was applied to **3** [(a) $ClCO_2Et$, Et_3N, NaN_3, $PhCH_3$, reflux; (b) KOH, H_2O; (c) H_3O^+, Δ], producing aniline **4** (60%), and a Sandmeyer isatin synthesis was next used to convert **4** to **6**. Thus, treatment of aniline **4** with chloral hydrate, hydroxylamine hydrochloride, and Na_2SO_4 (H_2O, 50–60 °C) gave oxime **5**.[12] Cyclization of **5** with polyphosphoric acid (100 °C, 10 min) led to isatin **6** in 70% yield (mp 180.5–181.5 °C). Condensation of **6** with pyruvic acid (30% KOH, 95 °C, 6 h) afforded quinoline dicarboxylic acid **7**,[13] which without purification was esterified (CH_3OH, H_2SO_4, reflux), yielding yellow crystalline diester **8** (50% from **6**, mp 133–134 °C).[11]

Our initial strategy was to construct the remaining ring of methoxatin (**1**) by employing a Reissert indole synthesis[14] at this pont. Thus, nitration of **8** (HNO_3/H_2SO_4, 0 °C, 60%) gave the desired precursor **9**. However, all attempts to condense this compound with dimethyl oxalate in the presence of various bases to produce intermediate **10** failed.[15] It was therefore necessary for us to find an alternative route for annulation of the final pyrrole ring onto the quinoline system, and we have successfully developed an "umpolung" variation of the Reissert synthesis.

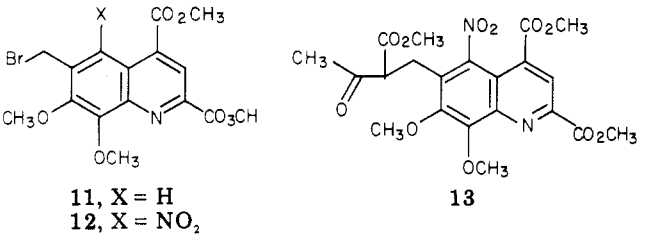


7, R = H
8, R = CH_3

9

10

NBS bromination of **8** (CCl_4, reflux, 3 h) gave **11** (90%,



11, X = H
12, X = NO_2

13

mp 180–181 °C),[11] which was nitrated (HNO_3/H_2SO_4, −20 °C, 1.5 min), affording compound **12** (60%, mp 105–106 °C).[11] A number of unsuccessful attempts were made to combine **12** with various sulfur-based oxalate acyl carbanion equivalents[16] to ultimately produce keto ester **10**. On the other hand, methyl acetoacetate could be nicely alkylated with bromide **12** (NaH, THF, 2 h, room temperature, 92%), affording β-keto ester **13**.[11] The Kozikowski modification[17] of the Japp–Klingemann reaction[18] was used to convert **13** to hydrazone **14**. Thus, treatment of **13** with benzene–diazonium fluoroborate (H_2O/pyridine, −10 °C), followed by addition of methanolic sodium borohydride to the crude product, yielded **14** (70%, mp 169–170 °C).[11] Catalytic hydrogenation of **14** (H_2, 10% Pd/C, HCl, CH_3OH, atmospheric pressure) led directly to tricyclic pyrroloquinoline **15**[11] (62%, mp 218–220 °C). Oxidation of **15** with AgO (HNO_3, THF, 10 min, room temperature)[19] gave quinone **16** (60%, mp 220 °C dec), which had ^1H NMR, UV, and mass spectrum identical with those reported for the compound prepared by methylation of natural methoxatin.[4a,11]

Basic hydrolysis of **16** (LiOH, H_2O/THF, room temperature, 5 h) afforded methoxatin (**1**) as a red-brown solid

(6) Duine, J. A.; Frank, J.; VanZeeland, J. K. *FEBS Lett.* **1979**, *108*, 443.
(7) Forrest, H. S.; Salisbury, S. A.; Kitty, C. G. *Biochem. Biophys. Res. Commun.* **1980**, *97*, 248.
(8) Dr. H. S. Forrest, personal communication.
(9) Gschwend, H. W.; Rodriquez, H. R. *Org. React.* **1979**, *26*, 1.
(10) Lovie, J. C.; Thomson, R. H. *J. Chem. Soc.* **1961**, 485.
(11) Partial spectral data for selected compounds are as follows. **3**: IR ($CHCl_3$) 3850, 1735, 1605, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.33 (3 H, s), 3.83 (3 H, s), 4.08 (3 H, s), 6.98 (1 H, d, J = 8 Hz), 7.70 (1 H, d, J = 8 Hz), 11.2 (1 H, br s). **4**: IR (film) 3460, 3365 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.13 (3 H, s), 3.78 (3 H, s), 3.81 (3 H, s), 6.33 (1 H, d, J = 8 Hz), 6.65 (1 H, d, J = 8 Hz). **6**: IR (KBr) 3180, 1755, 1730 cm^{-1}; ^1H NMR (acetone-d_6) δ 2.17 (3 H, s), 3.87 (3 H, s), 3.98 (3 H, s), 7.15 (1 H, br s), 10.03 (1 H, br). **8**: IR (KBr) 1725 cm^{-1}; ^1H NMR (CCl_4) δ 2.43 (3 H, s), 3.98 (6 H, s), 4.05 (3 H, s), 4.16 (3 H, s), 8.27 (1 H, br s), 8.38 (1 H, s). **11**: ^1H NMR ($CDCl_3$) δ 4.03 (6 H, s), 4.18 (6 H, s), 4.66 (2 H, s), 8.56 (1 H, s), 8.60 (1 H, s). **12**: IR (KBr) 1730, 1600, 1530, 1355 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (3 H, s), 4.03 (3 H, s), 4.18 (3 H, s), 4.27 (3 H, s), 4.71 (2 H, s), 8.38 (1 H, s). **13**: IR (film) 1740, 1600, 1530, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (3 H, s), 3.42 (2 H, d, J = 6.99 Hz), 3.71 (3 H, s), 3.94 (3 H, s), 4.09 (3 H, s), 4.11 (3 H, s), 4.28 (3 H, s), 8.44 (1 H, s). **14**: IR (KBr) 3320, 1720, 1705, 1600, 1570, 1530, 1350 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.91 (3 H, s), 4.02 (3 H, s), 4.03 (3 H, s), 4.08 (3 H, s), 4.26 (5 H, s), 7.2 (5 H, m), 8.46 (1 H, s), 9.49 (1 H, s). **15**: IR (KBr) 1710, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.01 (3 H, s), 4.09 (3 H, s), 4.13 (3 H, s), 4.17 (3 H, s), 4.33 (3 H, s), 7.51 (1 H, d, J = 2.4 Hz), 8.83 (1 H, s), 12.44 (1 H, br). **16**: ^1H NMR ($CDCl_3$) δ 3.98 (3 H, s), 4.07 (3 H, s), 4.18 (3 H, s), 7.47 (1 H, s), 8.89 (1 H, s); mass spectrum, m/e (relative intensity) 374 (40.7), 372 (7.3), 344 (33.1), 342 (59.6), 314 (41.9), 286 (72.5), 282 (53), 254 (100). **2**: ^1H NMR ($(CD_3)_2SO$) δ 2.01 (3 H, s), 3.59 (1 H, d, J = 17.3 Hz), 4.00 (1 H, d, J = 17.3 Hz), 7.13 (1 H, d, J = 2.2 Hz), 8.41 (1 H, s), 13.40 (1 H, br); UV (H_2O) λ_{max} 360, 318, 252 nm.
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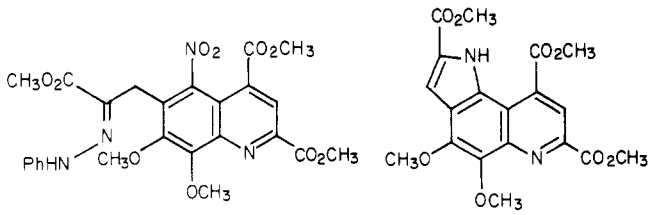
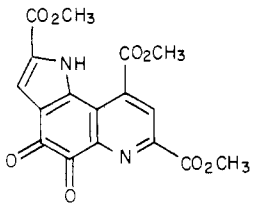
(15) Treatment of **9** with LDA followed by a D_2O quench led to recovery of starting material containing *no* deuterium. This apparent lack of acidity of the aromatic methyl group may be due to the nitro function being twisted out of the plane of the aromatic system due to crowding, thus preventing resonance stabilization of the resulting benzyl carbanion.
(16) Inter alia: Lerner, L. M. *J. Org. Chem.* **1976**, *41*, 2228. Bates, G. S. *J. Chem. Soc., Chem. Commun.* **1979**, 161.
(17) Kozikowski, A. P.; Floyd, W. C. *Tetrahedron Lett.* **1978**, 19.
(18) Phillips, R. R. *Org. React.* **1959**, *10*, 143.
(19) Snyder, C. D.; Rapoport, H. *J. Am. Chem. Soc.* **1972**, *94*, 227.



14 15



16

(75%). Since a sample of 1 was not available to us, and since there is only scant spectral data reported[4] for the natural coenzyme, our synthetic material was characterized by clean conversion to acetone adduct 2 (acetone/H_2O/NH_4OH, room temperature, 0.5 h), which was identical in UV, ^1H NMR, and TLC with an authentic sample.[11,20]

Acknowledgment. This research was generously supported by the National Science Foundation (CHE-78-19916). We thank Dr. R. Minard for mass spectra and Mr. A. Freyer and Dr. C. Debrosse for FT NMR spectra.

Registry No. 1, 72909-34-3; 2, 73030-04-3; 3, 77869-39-7; 4, 78891-29-9; 5, 78891-30-2; 6, 78891-31-3; 7, 78891-32-4; 8, 78891-33-5; 9, 78891-34-6; 11, 78891-35-7; 12, 78891-36-8; 13, 78891-37-9; 14, 78891-38-0; 15, 78891-39-1; 16, 74447-88-4; 2,3-dimethoxytoluene, 4463-33-6; pyruvic acid, 127-17-3; methyl acetoacetate, 105-45-3.

(20) We are extremely grateful to Drs. H. S. Forrest and S. A. Salisbury for spectra and a sample of acetone adduct 2, and for their cooperation during the course of this research.

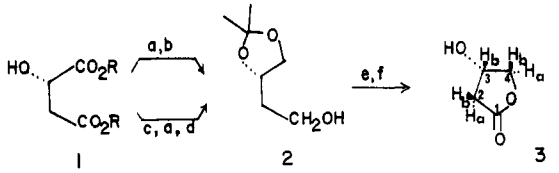
James A. Gainor, Steven M. Weinreb*
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802
Received July 13, 1981

Stereoselective Alkylation and Aldol Reactions of (*S*)-(−)-β-Hydroxy-γ-butyrolactone Dianion

Summary: The dianion of 3 reacts with alkyl halides to give exclusively *trans*-2-alkyl-3-hydroxy lactones and with aldehydes to give 2,3-*trans*-disubstituted lactones which exhibit erythro selectivity in the newly formed aldol moiety.

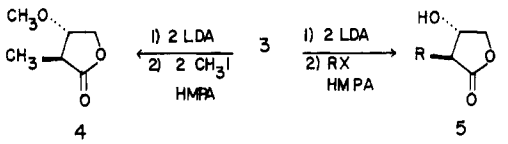
Sir: The dianions of β-hydroxy esters can be alkylated[1] with better than 90% stereoselectivity[2,3] to give threo-type[4] products. We have extended this reaction to include the dianion of a cyclic analogue, (*S*)-(−)-3,4-dihydroxybutanoic acid 1,4-lactone (3), and we report herein that the alkylations proceed with virtually complete threo (trans to O^-) selectivity[5] at C-2 (relative asymmetric induction[6]). Furthermore, both relative and internal asymmetric induction are observed during aldol reactions of this chiral dianion with aldehydes, giving predominately erythro aldols. Variation of the erythro/threo ratios can be rationalized in terms of acyclic vs. cyclic transition-state models.

Scheme I. Synthesis of Hydroxylactone 3[a]

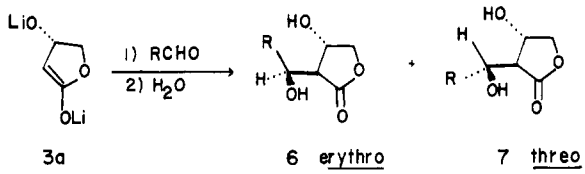


[a] Reagents: (a) $LiAlH_4$, THF; ^-OH; (b) acetone, $ZnCl_2$ or *p*-TsOH; (c) 2-methoxypropene, $POCl_3$; (d) $BF_3{\cdot}Et_2O$; (e) Jones oxidation; (f) H_2O, H_2SO_4.

Scheme II. Alkylation of Dianion 3a



Scheme III. Aldol Condensation of Dianion 3a



The chiral hydroxy lactone 3[7] was prepared[7,8] from (*S*)-(−)-malic acid in 23% overall yield after flash chromatography (Scheme I). Proton shifts and couplings were determined by using $Eu(fod)_3$ and were confirmed by spin simulations.[9] The dianion of 3 was generated in THF at −78 °C by the addition of 2.2 equiv of lithium diisopropylamide and was unstable above −20 °C. Addition of methyl iodide to the dianion solution at −78 °C followed by warming to −45 ± 5 °C for 5 h gave only recovered starting material. However, addition of a variety of alkylating agents (Table I) in THF containing HMPA[2] (to make a 10–20% v/v solution) to the −78 °C solution followed by stirring for 5 h at −45 ± 5 °C gave moderate yields of 4 and 5 in addition to some recovered starting lactone (Scheme II). Reactions run at −45 °C for longer times gave

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(4) We have chosen the R-group-independent convention of Heathcock[5] in naming relative configurations which conflict with Seebach's designations[3] in several cases.

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(9) GLC was performed by using a Varian 3700 gas chromatograph equipped with 2 m × 2 mm i.d. glass columns packed with 3% OV-17. The 80-MHz ^1H NMR and 20-MHz ^{13}C NMR spectra were obtained in $CDCl_3$ solutions on a Varian CFT-20. 3: ^1H NMR δ 2.45 (H-2a, dd, ^2J = 18.4 Hz, $^3J_{H_2H_{2b}}$ = 1.5 Hz), 2.70 (H-2b, dd, ^2J = 18.5 Hz, $^3J_{H_2H_{2b}}$ = 5 Hz), 3.63 (OH), 4.23 (H-4a, dd, ^2J = −10.4 Hz, $J_{H_{4a}H_3}$ < 1 Hz), 4.39 (H-1b, dd, ^2J = −10.4 Hz, $^3J_{H_1H_3}$ = 4.3 Hz), 4.62 (H-3, m); ^{13}C NMR δ 177.35 (C-1), 76.35 (C-3), 67.16 (C-4), 37.62 (C-2). 5a: ^1H NMR δ 4.18 (H-3, H-4, m), 2.44 (OH, br s) 1.62 (dd, *J* = 4.3, 8.0 Hz), 1.04 (CH_2, dq, *J* = 7.2, 8.0 Hz), 0.95 (CH_3, t, *J* = 7.2 Hz); ^{13}C NMR δ 179.30 (C-1), 73.89 (C-3), 71.79 (C-4), 49.94 (C-2), 21.58 (CH_2), 11.42 (CH_3). Full experimental details for 5a–e will be published subsequently. All new compounds gave either microanalyses or high-resolution mass spectra consistent with the proposed structures.

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