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Oxidative Free-Radical Cyclization of Allylic α-Chloromalonates. Synthesis of (±)-Avenaciolide.

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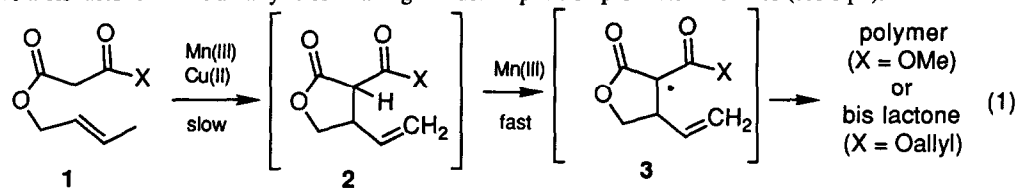
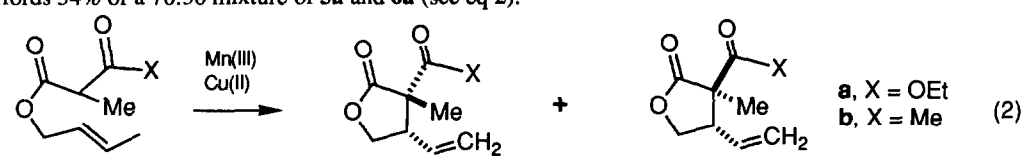
Abstract: Oxidative free-radical cyclization of α-chloromalonate **9** with $Mn(OAc)_3 \cdot 2H_2O$ and $Cu(OAc)_2 \cdot H_2O$ in acetic acid at 75 °C provides 82% of lactones **10a** and **10b**. Hydroboration of **10** followed by oxidation affords acids **12**, which are converted to avenaciolide precursor **15** in 32% overall yield from **9** by decarboxylation and cyclization.

We have recently described Mn(III)-based oxidative free-radical cyclizations which are initiated by oxidation of a β-dicarbonyl compound to a radical by $Mn(OAc)_3 \cdot 2H_2O$ and terminated by oxidative β-hydride elimination from a radical to give an alkene with $Cu(OAc)_2 \cdot H_2O$.[1,2] Most of our studies have addressed the use of this reaction for the formation of carbocyclic ring systems. In an elegant series of studies, Bertrand and coworkers have explored the Mn(III)-based oxidative free-radical cyclizations of malonates leading to γ-lactones.[3] γ-Lactones cannot be obtained from unsubstituted malonate esters. Oxidative cyclization of **1** leads to γ-lactone **2**, which cannot be isolated since it is oxidized more rapidly than **1** to give radical **3** which cyclizes to give a bis lactone if X is an allylic ester and gives decomposition products otherwise (see eq 1).[3]



1 **2** **3**

Oxidative cyclization is generally successful for preparing γ-lactones that do not have an α-hydrogen. For instance, reaction of **4a** with two equiv of $Mn(OAc)_3 \cdot 2H_2O$ and one equiv of $Cu(OAc)_2 \cdot H_2O$ in acetic acid affords 54% of a 70:30 mixture of **5a** and **6a** (see eq 2).[3]



4 **5** **6**

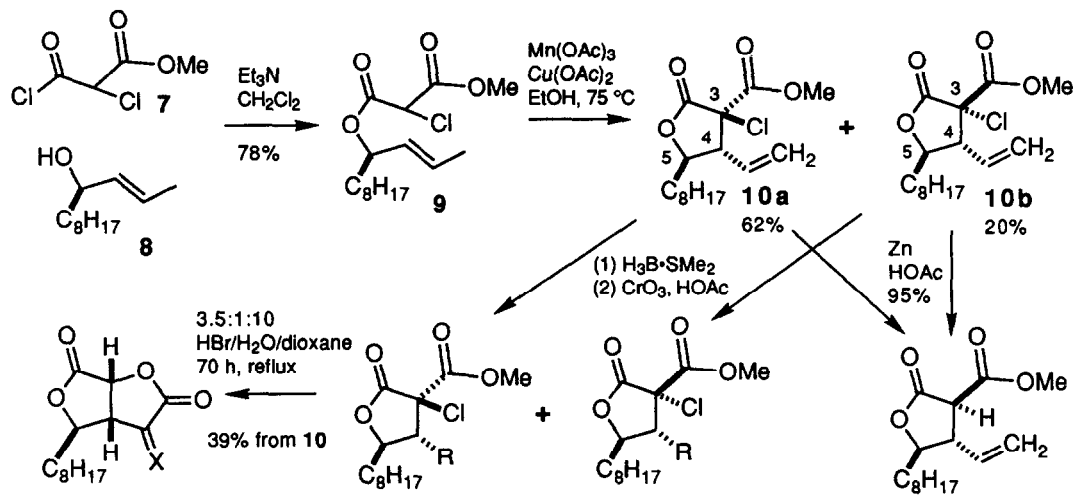
We have had good success forming 5-8 membered ring carbocycles from the oxidative cyclization of α-chloroacetoacetate esters.[1c,f] The chlorine substituent prevents further oxidation of the product as is observed in the conversion of **2** to **3** and is reductively cleaved with zinc to give the α-unsubstituted β-keto ester. Corey and Gross have reported the use of monoethyl α-chloromalonate in intermolecular oxidative Mn(III)-based lactonizations.[4] We decided to examine the oxidative free-radical cyclization of allylic α-chloromalonate esters as a

route to α-unsubstituted lactones such as **2**. We chose to examine the oxidative cyclization of **9** since the products **10** are potential intermediates for the synthesis of avenaciolide (**16**) and asymmetric induction by an alkyl substituent on the carbinol carbon has not been previously examined. All of the examples reported by Bertrand use primary allylic esters.[3]

Results and Discussion

α-Chloro acid chloride **7** has been prepared by Ghosez by chlorination of monomethyl malonate with SO_2Cl_2 followed by formation of the acid chloride with PCl_5.[5] We found that **7** can be prepared more easily in 82% yield by α-chlorination of methyl malonyl chloride with N-chlorosuccinimide by Harpp's procedure.[6] Esterification of 4*E*-dodecen-2-ol (**8**)[7] with **7** (CH_2Cl_2, Et_3N) affords 78% of the desired mixed chloromalonate ester **9**.

Oxidative cyclization of a 0.2 M solution of **9** in EtOH at 75 °C with two equiv of $Mn(OAc)_3 \cdot 2H_2O$ and one equiv of $Cu(OAc)_2 \cdot H_2O$ provides 62% of **10a** and 20% of **10b**. Only two of the four possible stereoisomers of **10** are obtained. Reduction of each diastereomer with zinc in acetic acid affords 91-94% of the same lactone **11** establishing that the isomers of **10** differ in stereochemistry only at the chlorine containing center. The trans stereochemistry of the octyl and ethenyl substituents in **10** and **11** follows from the eventual conversion to avenaciolide (**16**). The trans stereochemistry of both **10a** and **10b** also can be assigned from $J_{4,5}$ = 10.0 and 9.6 Hz, respectively. These coupling constants are similar to those observed for *trans*-3,3,4,5-tetrasubstituted dihydrofuranones and very different from those of the cis isomers.[8] The trans, trans stereochemistry of **11** follows from $J_{3,4}$ = 11.7 Hz and $J_{4,5}$ = 9.5 Hz. These coupling constants are similar to those observed for *trans,trans*-3,4,5-trimethyldihydro-2-furanone and differ markedly from those observed for the other three stereoisomers.[9]



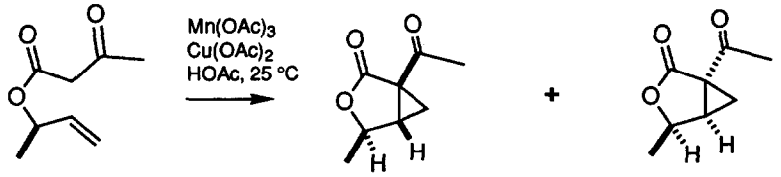
15, X = H_2
16, X = CH_2

12a, R = CH_2CO_2H **12b**, R = CH_2CO_2H
13a, R = CH_2CO_2Me **13b**, R = CH_2CO_2Me
14a, R = COMe **14b**, R = COMe

11

The facile preparation of **7** coupled with the efficient two-step procedure, oxidative cyclization of **9** followed by zinc reduction of **10**, makes compounds of type **2** readily available from oxidative free-radical

cyclization. We were also pleasantly surprised to observe that the octyl substituent completely controls the stereochemistry of the cyclization. Only the two stereoisomers with the octyl and ethenyl groups trans are formed. This observation seems to be general since oxidative cyclization of **17** affords 62% of a 10:1 mixture of **18a** and **18b**. The stereochemical assignment follows from vicinal coupling constants of 0 and 6 Hz, respectively. The absence of coupling between the ring hydrogens in **18a** requires that the dihedral angle between the hydrogens is 90 °C. The calculated dihedral angle is 93° in **18a** and 37° in **18b**.[10] Similar selectivity favoring the trans isomer has been observed in the free-radical cyclization of α-bromoacetals.[11]



17 **18a** 56% **18b** 6%

The stereochemistry at C_3 follows from the chemical shift of H_4, which is δ = 3.12, 3.09 and 3.45 for **10a**, **13a** and **14a**, respectively and δ 3.42, 3.32 and 3.88 for **10b**, **13b** and **14b**, respectively. In norbornanes, a carbomethoxy group deshields cis and trans vicinal protons by 0.35 and 0.24 ppm, respectively.[12] A chlorine substituent deshields cis and trans vicinal protons by 0.21 and 0.59 ppm, respectively.[12] Based on these values, H_4 in isomer **10b-14b**, which is trans to a chlorine substituent and cis to a carbomethoxy group, should absorb 0.49 ppm downfield from H_4 in isomer **10a-14a**. This corresponds well with the observed differences of 0.30 ppm for **10b**, 0.23 ppm for **13b** and 0.43 ppm for **14b**. The 3:1 mixture of **10a** and **10b** formed from **9a** is analogous to the 2.3:1 mixture of **5a** and **6a** formed from **4a**. We have found that the stereochemistry varies markedly with the nature of the X substituent on **4**. Oxidative free radical cyclization of acetoacetate **4b** affords 34% of a 1:2 mixture of **5b** and **6b**.

Takeda and coworkers prepared the diethyl esters corresponding to **13a** and **13b** and converted them to the bis lactone avenaciolide precursor **15** in 40% yield by heating in HBr/H_2O/dioxane for 30 h at reflux.[13] This process presumably involves hydrolysis, decarboxylation and intramolecular S_N2 reaction to give **15**. Since **10** is now readily available in two steps and has the same carbon skeleton and stereochemistry as **13**, we explored procedures for conversion of the ethenyl substituent to a carboxymethyl group. Hydroboration of **10** with $BH_3{\cdot}SMe_2$ followed by oxidation with 90% aqueous acetic acid by Brown's procedure[14] gives crude **13** that is cyclized by Takeda's procedure in HBr/H_2O/dioxane at reflux for 70 h to afford 39% of **15** whose spectral data are identical to those of an authentic sample.[15] Methylenation by Johnson's procedure affords avenaciolide (**16**).[16]

The hydroboration-oxidation sequence was examined individually on the two diastereomers of **10**. The major diastereomer **10a** affords, after methylation with diazomethane, 78% of bis methyl ester **13a** and 7% of methyl ketone **14a**, which results from hydroboration to give the more substituted alkylborane. The minor isomer **10b** affords 67% of **13b** and 13% of **14b**.

The results described above indicate that γ-lactones such as **2** and **11** can be prepared by oxidative cyclization of α-chloromalonates followed by zinc reduction and that trans-4,5-disubstituted dihydrofuranones are obtained exclusively. Hydroboration, oxidation and cyclization converts both isomers of **10** into avenaciolide precursor **15**.

Experimental Section

General. NMR were recorded at 300 MHz in $CDCl_3$. Chemical shifts are reported in δ, and coupling constants in Hertz. IR spectra are reported in cm^{-1}. All air sensitive reactions were run under N_2 in flame-dried glassware with magnetic stirring. Reagents were added via oven-dried syringes through septa. 4*E*-dodecen-2-ol (**8**) was prepared by the literature procedure from crotonaldehyde and *n*-octylmagnesium chloride.[6] Methyl malonyl chloride, $Mn(OAc)_3 \cdot 2H_2O$ and $Cu(OAc)_2 \cdot H_2O$ were purchased from Aldrich.

Methyl 2,3-Dichloro-3-oxopropanoate (7). A solution of N-chlorosuccinimide (3.47 g, 26 mmol), methyl malonyl chloride (1.41 mL, 13 mmol) and three drops of conc. HCl in thionyl chloride (10 mL) was stirred in a 85 °C bath for 3.5 h.[5] The actual temperature of the reaction mixture was 70 °C. The solvent was removed under reduced pressure and the residue was dissolved in 5 mL of CCl_4. The mixture was filtered to remove the solid succinimide and the filtrate was concentrated under reduced pressure to give 2.53 g of crude **7** as a yellow oil. Evaporative distillation (1 torr, 60 °C) gave 1.83 g (82%) of pure **7**: ^1H NMR 5.17 (s, 1), 3.92 (s, 3); ^{13}C NMR 164.6, 162.9, 62.2, 54.4; IR (neat) 3961, 1840, 1748, 1439, 1310, 1200, 1006, 658.

Methyl 1-(1*E*-Propenyl)nonyl 2-Chloropropanedioate (9). To a cooled solution of alcohol **8** (1.11 g, 6 mmol) and Et_3N (0.9 mL, 6.4 mmol) in 6 mL of CH_2Cl_2 at 0 °C was slowly added a solution of acid chloride **2** (1.54 g, 9 mmol) in 2 mL of CH_2Cl_2. The reaction was stirred at 0 °C for 0.5 h and then at rt for 4 h. Water (20 mL) and 10% HCl (20 mL) were added and the solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with 10% HCl (2 × 20 mL) and NaCl solutions and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave 1.94 g of a yellow oil. Purification by flash chromatography (9:1 hexane-EtOAc) afforded 1.48 g (78%) of **9** as a 1:1 mixture of diastereomers: ^1H NMR 5.78 (dq, 1, *J* = 6.5, 15.1), 5.41 (dd, 1, *J* = 7.6, 15.1), 5.26 (br dt, 1, *J* = 6.1, 7.6), 4.85 (s, 1), 3.84 (s, 3), 1.70 (d, 3, *J* = 6.5), 1.64-1.52 (m, 2), 1.36-1.19 (m, 12), 0.88 (t, 3, *J* = 6.7); ^{13}C NMR (165.0, 164.9), (163.5, 163.6), (130.4, 130.6), (128.3, 128.2), (78.4, 78.3), (55.5, 55.4), 53.53, 34.10, 31.73, 29.33, 29.13, 29.09, (24.9, 24.8), 22.55, 17.63, 13.97; IR (neat) 2927, 2856, 2359, 1794, 1767, 1730, 1436, 1200, 1000, 677. Anal. Calcd for $C_{16}H_{27}ClO_4$: C, 60.27; H, 8.54. Found: C, 59.67; H, 8.62.

Methyl (3α,4β,5α)- and (3α,4α,5β)-3-Chloro-4-ethenyltetrahydro-5-octyl-2-oxo-3-furancarboxylate (10a and 10b). A solution of ester **9** (640 mg, 2 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (1.072 g, 4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (400 mg, 2 mmol) in 10 mL of degassed ethanol was stirred at 75 °C for 2.5 h. The reaction mixture was diluted with water (40 mL) and 10% $NaSO_3$ was added dropwise until the solution turned from brown to light green indicating that all residual Mn(III) had been reduced. The resulting solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with saturated NaCl solution and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave 624 mg of crude **10**. Purification by flash chromatography (20:1 hexane/EtOAc) afforded 128 mg of **10b** (20%) followed by 396 mg of **10a** (62%).

The data for **10a**: ^1H NMR 5.58 (ddd, 1, *J* = 8.1, 10.0, 16.9), 5.41 (br d, 1, *J* = 16.9), 5.39 (br d, 1, *J* = 10.0), 4.52 (ddd, 1, *J* = 3.5, 8.5, 10.0), 3.86 (s, 3), 3.12 (dd, 1, *J* = 8.1, 10.0), 1.76-1.54 (m, 2), 1.24-1.45 (m, 12), 0.88 (t, 3, *J* = 6.7); ^{13}C NMR 168.7, 164.4, 128.2, 123.2, 81.6, 70.7, 60.7, 54.0, 33.2, 31.7, 29.2, 29.1, 29.0, 25.5, 22.5, 14.0; IR (neat) 2926, 2856, 1793, 1766, 1729, 1644, 1457, 1436, 1199, 1000, 938, 677.

The data for **10b**: ^1H NMR 5.80 (ddd, 1, *J* = 8.3, 10.3, 17.1), 5.38 (br d, 1, *J* = 10.3), 5.32 (br d, 1, *J* = 17.1), 4.43 (ddd, 1, *J* = 3.1, 8.7, 9.6), 3.85 (s, 3), 3.42 (dd, 1, *J* = 8.3, 9.6), 1.74-1.59 (m, 2), 1.28-1.21 (m, 12), 0.88 (t, 3, *J* = 6.7); ^{13}C NMR 168.2, 165.2, 128.8, 123.1, 82.2, 69.4, 56.1, 54.4, 32.0, 31.8, 29.3, 29.2, 29.1, 25.6, 22.6, 14.1; IR (neat) 2927, 2855, 1793, 1766, 1738, 1644, 1457, 1436, 1271, 1204, 991, 660. Anal. Calcd for $C_{16}H_{25}ClO_4$: C, 60.66; H, 7.95. Found: C, 60.80; H, 7.95.

Methyl (3α,4β,5α)-4-Ethenyltetrahydro-5-octyl-2-oxo-3-furancarboxylate (11). A solution of alkene **10a** (32 mg, 0.1 mmol) and Zn dust (32.5 mg, 0.5 mmol) in 1 mL of HOAc was stirred at rt for 10 h.

The reaction mixture was filtered to remove solid Zn and the filtrate was diluted with water (10 mL). The solution was extracted with ether (3 × 10 mL) and the combined organic extracts were washed with saturated $NaHCO_3$ and NaCl solutions and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave 30 mg (94%) of **11**: ^{1}H NMR 5.70 (ddd, 1, J = 8.0, 10.2, 17.1), 5.28 (br d, 1, J = 17.1), 5.24 (br d, 1, J = 10.2), 4.15 (ddd, 1, J = 3.6, 8.5, 9.5), 3.81 (s, 3), 3.52 (d, J = 11.7), 3.23 (ddd, 1, J = 8.0, 9.5, 11.7), 1.75-1.68 (m, 2), 1.33-1.24 (m, 12), 0.88 (t, 3, J = 6.7); ^{13}C NMR 170.6, 167.5, 133.3, 119.9, 83.2, 53.2, 53.0, 50.4, 33.1, 31.8, 29.3, 29.2, 29.1, 25.7, 22.6, 14.1; IR (neat) 2926, 2855, 1783, 1742, 1645, 1458, 1437, 1273, 1164, 994, 926.

A similar reduction of **10b** (32 mg, 0.5 mmol) under the same conditions also gave **11** (29 mg, 91%) as the only product.

4-Chloro-4-(methoxycarbonyl)tetrahydro-2-octyl-5-oxo-3-furanacetic Acid (12). To a 3:1 mixture of alkenes **10a** and **10b** (316 mg, 1.0 mmol) in 2 mL of CH_2Cl_2 was added a 1.0 M solution of BH_3•SMe_2 in CH_2Cl_2 (0.4 mL, 0.4 mmol). The reaction was heated at reflux for 3 h. The solution was then cooled to 0 °C and a freshly prepared solution of CrO_3 (600 mg, 6.0 mmol) in 9:1 HOAc-water (5 mL) was slowly added by the procedure of Brown.[14] The mixture then stirred for 12 h at rt. Water was added (50 mL) and the acid was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with saturated NaCl solution and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave 342 mg (98%) of crude **12** which was used for the next step without purification. The acids were characterized after conversion to the methyl esters **13**.

Methyl (2α, 3β, 4α)-4-Chloro-4-(methoxycarbonyl)tetrahydro-2-octyl-5-oxo-3-furanacetate (13a). A freshly prepared solution of CH_2N_2 in ether[17] was slowly added dropwise to a solution of crude acid **12a** (139 mg, 0.4 mmol, prepared as described above from pure **10a**) in 1 mL of ether until the color of the reaction solution remained bright yellow. Acetic acid was then added dropwise until the yellow color turned to clear indicating that all excess CH_2N_2 had been quenched. Water (10 mL) and ether (10 mL) were added and the layers were separated. The organic phase was then washed with saturated $NaHCO_3$ (3 × 20 mL) and brine solutions and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave 134 mg of crude **13a**. Purification by flash chromatography (4:1 hexane-EtOAc) afforded 9 mg (7%) of methyl ketone **14a** followed by 109 mg (78%) of **13a**.

The data for **13a**: ^{1}H NMR 4.41 (ddd, 1, J = 3.1, 8.4, 9.7), 3.89 (s, 3), 3.73 (s, 3), 3.09 (ddd, 1, J = 5.8, 7.8, 9.7), 2.66 (dd, 1, J = 5.8, 16.0), 2.41 (dd, 1, J = 7.8, 16.0), 1.72-1.57 (m, 2), 1.33-1.27 (m, 12), 0.88 (t, 3, J = 6.7); ^{13}C NMR 170.2, 168.4, 164.7, 82.8, 69.3, 54.3, 52.3, 51.8, 33.3, 31.8, 31.6, 29.3, 29.2, 29.1, 25.3, 22.6, 14.1; IR (neat) 2955, 2927, 2855, 1790, 1765, 1743, 1437, 1206, 1010, 962, 887, 675.

The data for **14a**: ^{1}H NMR 4.83 (ddd, 1, J = 4.2, 8.0, 9.7), 3.84 (s, 3), 3.45 (d, 1, J = 9.7), 2.37 (s, 3), 1.80-1.60 (m, 2), 1.27-1.24 (m, 12), 0.88 (t, 3, J = 6.7).

Methyl (2α, 3β, 4β)-4-Chloro-4-(methoxycarbonyl)tetrahydro-2-octyl-5-oxo-3-furanacetate (13b). Reaction of crude acid **12b** (87 mg, 0.25 mmol, prepared as described above from pure **10b**) under similar conditions afforded 11 mg (13%) of methyl ketone **14b** followed by 58 mg (67%) of **13b**.

The data for **13b**: ^{1}H NMR 4.22 (ddd, 1, J = 3.1, 8.5, 9.7), 3.92 (s, 3), 3.68 (s, 3), 3.32 (ddd, 1, J = 4.0, 9.7, 10.0), 2.79 (dd, 1, J = 10.0, 17.3), 2.52 (dd, 1, J = 4.0, 17.3), 1.76-1.58 (m, 2), 1.36-1.28 (m, 12), 0.88 (t, 3, J = 6.7); ^{13}C NMR 170.4, 168.5, 165.4, 82.5, 77.2, 54.3, 52.2, 47.5, 32.3, 31.8, 31.1, 29.3, 29.2, 29.1, 25.6, 22.6, 14.1; IR (neat) 2954, 2927, 2855, 1790, 1770, 1741, 1438, 1204, 998, 874, 668.

The data for **14b**: ^{1}H NMR 4.93 (ddd, 1, J = 3.1, 7.8, 10.3), 4.02 (s, 3), 3.88 (d, 1, J = 10.3), 2.17 (s, 3), 1.88-1.76 (m, 2), 1.35-1.27 (m, 12), 0.89 (t, 3, J = 6.7).

(3aα,4α,6aα)-Dihydro-4-octylfuro[3,4-b]furan-2,6(3H,4H)-dione (15). A solution of a 3: mixture of crude acids **12a** and **12b** (175 mg, 0.5 mmol, prepared from 156 mg of a 3:1 mixture of **10a** an **10b**) in 5 mL of a 3.5:1:10 mixture of 48% HBr/water/dioxane was heated at reflux for 70 h by the procedure c Takeda.[13] The reaction was cooled to rt, water (20 mL) was added and the solution was extracted with ether (× 20 mL). The combined organic extracts were washed with saturated $NaCO_3$ and NaCl solutions and drie ($MgSO_4$). Removal of the solvent under reduced pressure afforded 156 mg of crude **15**. Purification by flas chromatography (3:1 hexane-EtOAc) gave 50 mg (39% overall from **10**) of **15**. The ^1H and ^{13}C NMR data ar identical to those previously reported by Schreiber.[15]

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References

(1) For leading references see: (a) Kates, S. A.; Dombroski, M. A.; Snider, B. B. *J. Org. Chem.* **1990**, *55* 2427. (b) Dombroski, M. A.; Kates, S. A.; Snider, B. B. *J. Am. Chem. Soc.* **1990**, *112*, 2759. (c Snider, B. B.; Patricia, J. J. Kates, S. A. *J. Org. Chem.* **1988**, *53*, 2137. (d) Curran, D. P.; Morgan, T M.; Schwartz, C. E.; Snider, B. B.; Dombroski, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 6607. (e Snider, B. B.; Merritt, J. E.; Dombroski, M. A.; Buckman, B. O. *J. Org. Chem.* **1991**, *56*, 5544. (f Snider, B. B.; Merritt, J. E. *Tetrahedron* **1991**, *47*, 8663.

(2) For other recent Mn(III)-based oxidative free-radical cyclization studies see: (a) Ernst, A. B.; Fristad, W E. *Tetrahedron Lett.* **1985**, *26*, 3761. (b) Corey, E. J.; Kang, M. *J. Am. Chem. Soc.* **1984**, *106*, 5384 (c) Citterio, A.; Fancelli, D.; Finzi, C.; Pesce, L. *J. Org. Chem.* **1989**, *54*, 2713.

(3) (a) Surzur, J. M.; Bertrand, M. P. *Pure Appl. Chem.* **1988**, *60*, 1659. (b) Oumar-Mahamat, H. Moustrou, C.; Surzur, J.-M.; Bertrand, M. P. *Tetrahedron Lett.* **1989**, *30*, 331. (c) Oumar-Mahama H.; Moustrou, C.; Surzur, J.-M.; Bertrand, M. P. *J. Org. Chem.* **1989**, *54*, 5684. (d) Bertrand, M. P. Surzur, J.-M.; Oumar-Mahamat, H.; Moustrou, C. *J. Org. Chem.* **1991**, *56*, 3089.

(4) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1985**, 26, 4291. *cf.* Fujimoto, N.; Nishino, H.; Kurc sawa, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3161.

(5) Goldstein, S.; Vannes, P.; Houge, C.; Frisque-Hesbain, A. M.; Wiaux-Zamar, C.; Ghosez, L.; Germair G.; Declercq, J. P.; Van Meerssche, M.; Arrieta, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 4616.

(6) Harpp, D. N.; Bao, L. Q.; Black, C. J.; Gleason, J. G.; Smith, R. A. *J. Org. Chem.* **1975**, *40*, 3420.

(7) Mayer, Z.; Obereigner, B.; Lim, D. *J. Polym. Sci., Part C* **1971**, *33*, 289.

(8) (a) Jaime, C.; Segura, C. Dinarés, I.; Font, J. *J. Org. Chem.* **1993**, *58*, 154. (b) Kido, F.; Sinha, S. C Abiko, T.; Yoshikoshi, A. *Tetrahedron Lett.* **1989**, *30*, 1575.

(9) Jaime, C.; Ortuño, R. M.; Font, J. *J. Org. Chem.* **1986**, *51*, 3946.

(10) MM2 calculations were carried out using Model (version KS2.96) obtained from Prof. Kosta Steliou University of Montreal.

(11) Hackmann, C.; Schäfer, H. J. *Tetrahedron* **1993**, *49*, 4559.

(12) Doerffel, K.; Kasper, H.; Zimmermann, G. *J. Prakt. Chem.* **1974**, *316*, 645.

(13) Sakai, T.; Horikawa, H.; Takeda, A. *J. Org. Chem.* **1980**, *45*, 2039.

(14) Brown, H. C.; Kulkarni, S. V.; Khanna, V. V.; Patil, V. D.; Racherla, U. S. *J. Org. Chem.* **1992**, *57* 6173.

(15) Schreiber, S. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1984**, *106*, 7200.

(16) Parker, W.; Johnson, F. *J. Org. Chem.* **1973**, *38*, 2489.

(17) Arndt, F. In *Organic Synthesis, Collective Volume 2*; Blatt, A. H., Ed.; Wiley: New York, 1943; pp 165 167.