7.1 Hz, OCH_2CH_3), 1.59 (d, $J = 0.5$ Hz, C-11 CH_3), 1.67 (d, $J = 0.5$ Hz, H-12), 2.46 (s, C-3 CH_3), 4.08 (q, $J = 7.1$ Hz, OCH_2CH_3), 4.95–5.04 (d overlapping t, H-4, H-10); ^{13}C NMR ($CDCl_3$) δ 14.17 (OCH_2CH_3), 17.61 (C-11 CH_3), 18.65 (C-7 CH_3), 19.57 (C-3 CH_3), 25.41 (C-6), 25.87 (C-12), 35.20 (C-7), 35.88 (C-9), 37.21 (C-8), 47.64 (C-5), 59.95 (OCH_2CH_3), 60.36 (C-2), 89.75 (C-4), 99.75 (C-3), 124.39 (C-10), 131.31 (C-11), 207–212 (br, $Fe(CO)_3$); HRMS (70 eV), m/z (relative intensity) 404.1290 (2, $C_{20}H_{28}O_5Fe$), 320.1462 (11), 210.0362 (5), 139.0761 (3), 68.9941 (100), calcd for $C_{20}H_{28}O_5Fe$ 404.1278, found 404.1290.

Ethyl (2*E*,4*E*)-3,7,11-Trimethyl-2,4-dodecadienoate–Fe(CO_3) (5). A solution of tris(triphenylphosphine)rhodium(I) chloride (Wilkinson's catalyst; 115 mg, 0.12 mmol) in 1 mL of dry benzene was degassed four times and flushed with hydrogen gas. The catalyst was vigorously stirred under a hydrogen atmosphere for 4 h until the solution turned from red-brown to yellow-orange. The iron carbonyl complex 4 (15 mg, 0.037 mmol) in 0.5 mL of benzene was added to the charged catalyst, and the reaction was stirred under hydrogen for 15 h. The reaction mixture was concentrated to a paste and the residue was suspended in 5 mL of 2% EtOAc–hexane and filtered (florisil–silica gel) to give 14 mg (0.034 mmol) of the 10,11-dihydro iron carbonyl complex **5** (93% yield): TLC, R_f 0.65; ^1H NMR ($CDCl_3$) δ 0.82 (d, $J = 6.6$ Hz, C-7 CH_3), 0.85 (d, $J = 6.6$ Hz, H-12, C-11 CH_3), 1.24 (t, $J = 7.1$ Hz, OCH_2CH_3), 2.46 (s, C-3 CH_3), 4.08 (q, $J = 7.01$ Hz, OCH_2CH_3), 4.98 (d, $J = 7.8$ Hz, H-4); HRMS (70 eV), m/z (relative intensity) 406.1424 (1), $C_{20}H_{30}O_5Fe$), 322.1596 (27), 210.0317 (52), 139.0740 (100), 68.9952 (91), calcd for $C_{20}H_{30}O_5Fe$ 406.1434, found 406.1424.

Ethyl (2*E*,4*E*)-3,7,11-Trimethyldodecadienoate (6). To 14 mg (0.034 mmol) of the 10,11-dihydro iron carbonyl complex in 10 mL of CH_3CN at 0 °C was added 102 mg (0.202 mmol) of ceric ammonium nitrate. The reaction mixture was stirred at 0 °C for 4 h and diluted with 100 mL of 20% EtOAc–hexane. The organics were washed (H_2O–brine), concentrated, and chromatographed (2% EtOAc–hexane) to give 8.4 mg (0.031 mmol) of (7*S*)-hydroprene **6** (93% yield): TLC, R_f 0.65; UV λ_{max} 261 nm (ϵ 32 700); ^1H NMR ($CDCl_3$) δ 0.87 (br d, $J = 6.6$ Hz, C-7 CH_3, C-11 CH_3, H-12), 1.24 (t, $J = 7.1$ Hz, OCH_2CH_3), 2.24 (d, $J = 1.1$ Hz, C-3 CH_3), 4.14 (q, $J = 7.1$ Hz, OCH_2CH_3), 5.64 (m, H-2), 6.06 (m, H-4, H-5).

Ethyl [10,11-$^3H_2$]-(2*E*,4*E*)-3,7,11-Trimethyl-2,4-dodecadienoate–Fe$(CO)_3$ (5a). The same procedure and quantities were used as for compound **5** above, except that the reaction was conducted with carrier-free tritium gas and the product purified by chromatography (2.5% EtOAc–hexane on silica gel). The radiolabeled iron complex was stored in heptane–toluene below –20 °C after HPLC.

Ethyl [10,11-$^3H_2$]-(2*E*,4*E*)-3,7,11-Trimethyldodecadienoate (6a). To 3 mg (0.0074 mmol) of the 10,11-ditritio iron carbonyl complex **5a** in a 2 mL CH_3CN at 0 °C was added 22 mg (0.044 mmol) of ceric ammonium nitrate. The reaction mixture was stirred at 0 °C for 4 h and diluted with 5 mL of 20% EtOAc–hexane. The organics were washed with H_2O–brine, dried with $MgSO_4$, and purified by HPLC (0.5% ether–hexane) to give 1.3 mg (0.0049 mmol) of [$^3H_2$]hydroprene **6a** (66% yield). The total radioactivity was 321 mCi giving a specific activity of 65.5 Ci/mmol: TLC, R_f 0.65; λ_{max} 261 nm (ϵ 32 500); ^1H NMR ($CDCl_3$) δ 0.87 (br d, $J = 6.6$ Hz, C-7 CH_3, C-11 CH_3, H-12), 1.29 (t, $J = 7.2$ Hz, OCH_2CH_3), 2.28 (d, $J = 1.1$ Hz, C-3 CH_3), 4.18 (q, $J = 7.2$ Hz, OCH_2CH_3), 5.70 (br s, H-12), 6.09 (m, H-4, H-5).

(*S*)-(–)-[6,7-$^3H_2$]Dihydrocitronellyl Acetate (8). To 60 mg (0.303 mmol) of citronellyl acetate (**7**) in 20 mL of EtOAc was added 20 mg of 10% Pd/C catalyst. The mixture was degassed three times, flushed with tritium gas, and stirred under a tritium atmosphere for 1 h. The mixture was filtered (Florisil), concentrated, and chromatographed (5% EtOAc–hexane) to give 45 mg (0.225 mmol) of the radiolabeled acetate **8**, specific activity >60 Ci/mmol (74% yield). Autoradiography of TLC plates indicated that the radioactivity comigrated with radioinert dihydrocitronellyl acetate: TLC; R_f 0.72.

(*S*)-(–)-[6,7-$^3H_2$]Dihydrocitronellol (9). To 3.0 mg (0.014 mmol) of **8** in 1 mL of MeOH was added 0.5 mL of a 3 N NaOH solution. The mixture was stirred at room temperature for 4 h or until hydrolysis was complete (TLC). The reaction mixture was poured into 10 mL of a 1:1 ether–water solution, washed (water–brine), dried ($MgSO_4$), concentrated, and chromatographed (10% EtOAc–hexane) to give 1.3 mg (0.008 mmol) of the labeled alcohol **9** (60% yield). RTLCS indicated that the radioactivity comigrated with radioinert dihydrocitronellol (>90% ^3H radiochemical purity): TLC, R_f 0.27.

(*S*)-(–)-[6,7-$^3H_2$]Dihydrocitronellal (10). To 1.3 mg (0.008 mmol) of **5** in 1 mL of CH_2Cl_2 at ambient temperature was added 6 mg (0.016 mmol) of pyridinium dichromate (PDC). The reaction was stirred for 4 h and diluted with 20 mL of ether. The organics were filtered through Florisil, concentrated and chromatographed (10% EtOAc–hexane) to give 0.72 mg (0.0046 mmol) of the labile labeled aldehyde **10** (55% yield). RTLCS indicated that the radioactivity comigrated with radioinert dihydrocitronellal (>90% ^3H radiochemical purity): TLC, R_f 0.42.

Ethyl [10,11-H_2]-(2*E*,4*E*)-3,7,11-Trimethyl-2,4-dodecadienoate (6a). To 0.18 mg (0.0012 mmol) of aldehyde **5** in 0.4 mL of dry DMF was added 0.5 mg (0.0019 mmol) of diethyl [3-(ethoxycarbonyl)-2-methyl-2-propenyl]phosphonate and 0.1 mL of a 0.065 M solution of NaOEt in EtOH of 0 °C under nitrogen. The reaction was stirred at room temperature for 1.5 h and then poured into brine. The organics were extracted with 1:1 ether–hexane, dried ($MgSO_4$), and chromatographed (1% ether–hexane) to give a 2:1 mixture of 2*E*,4*E*/2*Z*,4*E* isomers of [$^3H_2$]hydroprene. The two isomers were separated by HPLC (0.5% ether–hexane) to give 0.12 mg (0.000 45 mmol) of pure (2*E*,4*E*)-[$^3H_2$]hydroprene (38% yield) calculated by mass and by UV absorption. The total radioactivity was 51.4 mCi giving a specific activity of 114 Ci/mmol.

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Preparation of 5-Alkyl-2-*tert*-butyl-1,3-dioxolan-4-ones by Trimethylsilyl Triflate Catalyzed Reactions between Bis(trimethylsilyl) Derivatives of α-Hydroxy Carboxylic Acids and Pivaldehyde

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That 5-alkyl-2-*tert*-butyl-1,3-dioxolan-4-ones **1** are useful substrates[1] for self-reproduction of chirality[2] and other applications[3] has been effectively demonstrated. Having a need for some optically pure 2-alkylated derivatives of malic acid, having had some difficulty in preparing the dioxolanone **1a** by the direct acid-catalyzed condensation of malic acid with pivaldehyde,[1] and aware of the useful ketalization method of Noyori involving trimethylsilyl triflate catalyzed reactions of bis(trimethylsilyl) ethers of vicinal diols with ketones,[4] we have studied the analogous transformations of the trimethylsilyl α-[(trimethylsilyl)-oxy]acetate derivatives **2** with trimethylsilyl triflate (Me_3SiOTf) and pivaldehyde. Others have recently described preparations of 1,3-dioxan-4-one acetals[5] and 1,3-dioxolan-4-one ketals[3b,6] by Me_3SiOTf-catalyzed cycliza-

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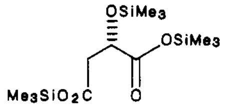
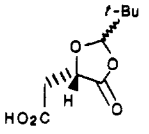
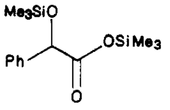
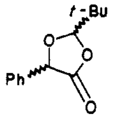
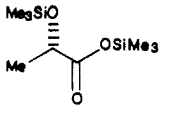
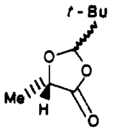
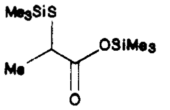
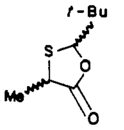
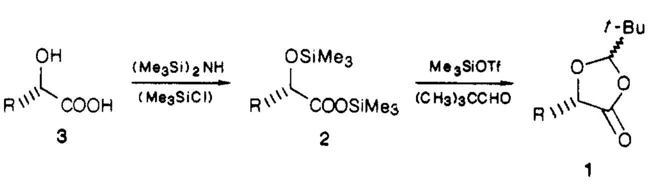
Table I. Summary of Results for Silylations of Acids 3 and for Cyclizations of 2 with Me_3SiOTf and Pivaldehyde

silylation of 3			Me_3SiOTf-catalyzed cyclization of 2			
products	method	yield^g	products	*T* (°C)	yield^a	*cis*-1:*trans*-1
 2a	B	85	 1a	0 −25	70 78	4:1 >100:1
 2b	A	99	 1b	0 −25	74 $(100)^b$	2:1 6:1
 2c	A	43	 1c	0	52	3:1
 2d	A	46	 1d	0	66	4:1

^{a}Yields (in percent) of purified product. ^{b}Yield (in percent) of crude product.

tions of bis(trimethylsilyl) derivatives of 3- and 2-hydroxycarboxylic acids, respectively. Analogous substrates that have been cyclized by similar methodology include an α-amino acid (the bis(trimethylsilyl) derivative of proline)[7] and α-hydroperoxy carboxylic acids.[8]



Our results are summarized in Table I. Substrates 2 were prepared by exposure of the α-hydroxy acids 3 to slightly over 1 equiv of hexamethyldisilazane (HMDSH) followed by direct distillation (method A) or exposure to 1 equiv of HMDSH containing 1 equiv of trimethylsilyl chloride (Me_3SiCl) followed by filtration and distillation (method B).[9] The per-trimethylsilyl derivatives 2 were very labile in the presence of moisture but could be stored indefinitely at room temperature in sealed vessels.

The cyclization of 2 was performed in dry methylene chloride in the presence of 5–15 mol % of Me_3SiOTf usually at temperatures between −25 and 0 °C. Reactions were quite fast at 0 °C and could be quenched within a few minutes after mixing, although longer times did not seem to adversely affect the outcome. Preparations of **1–1d** were quenched with water, but the reaction that generated **1a** was quenched with 10% HCl in order to assure hydrolysis and protonation of the unreacted trimethylsilyl ester that remained after dioxolanone formation.

The ratios of cis and trans isomers of 1 were found to be dependent upon the reaction temperature with increasing cis/trans ratios observed at lower temperatures. This is significant since one requires access to a single diastereomer of optically pure 1 if the self-reproduction of chirality ploy[1,2] is to provide access to α-alkylated derivatives of 1 of high optical purity. The temperature dependence was examined the most carefully in the preparation of the malic acid derived dioxolanone (**1a**). At −78 °C in the presence of 9 mol % of Me_3SiOTf, **2a** was converted to **1a** to the extent of only 7% and 21% (by capillary GC) after 0.3 and 2.5 h, respectively. However, at −25 °C **1a** was obtained in 78% yield after recrystallization. Moreover, after conversion of the crude product in this reaction to the corresponding methyl ester with CH_2N_2, no trace of the trans diastereomer (*trans*-**1a**) could be observed as contamination in *cis*-**1a**. A major advantage of the Me_3SiOTf-catalyzed dioxolanone synthesis over the classical acid-catalyzed procedure is the kinetic stereospecificity which can be achieved under the milder reaction conditions of the process described here.

The last entry in Table I demonstrates that α-mercapto carboxylic acids will also serve as substrates for this two-step, silylation/cyclization procedure. Finally, it was found that pivaldehyde is the aldehyde of choice since attempted cyclizations with benzaldehyde and *o*-nitrobenzaldehyde gave lower yields of cyclized products.

Experimental Section

General Methods. Methylene chloride was distilled from CaH_2. HMDSH was used as received. Me_3SiOTf was prepared by the method of Schmeisser.[10] All reactions were performed

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[1] (a) Frater, G.; Muller, U.; Gunther, W. *Tetrahedron Lett.* **1981**, *22*, 4221. (b) Seebach, D.; Naef, R. *Helv. Chim. Acta* **1981**, *64*, 2704. (c) Seebach, D.; Naef, R.; Calderari, G. *Tetrahedron* **1984**, *40*, 1313.

[2] Seebach, D.; Boes, M.; Naef, R.; Schweizer, W. B. *J. Am. Chem. Soc.* **1983**, *105*, 5390.

[3] (a) Mashraqui, S. H.; Kellogg, R. M. *J. Org. Chem.* **1984**, *49*, 2513. (b) Pearson, W. H.; Cheng, M.-C. *J. Org. Chem.* **1986**, *51*, 3746.

[4] Noyori, R.; Tsunoda, T.; Suzuki, M. *Tetrahedron Lett.* **1980**, *21*, 1357.

[5] (a) Schreiber, S. L.; Reagan, J. *Tetrahedron Lett.* **1986**, *26*, 2945. (b) Seebach, D.; Zimmerman, J. *Helv. Chim. Acta* **1986**, *69*, 1147.

[6] Pearson, W. H.; Cheng, M.-C. *J. Org. Chem.*, following note in this issue.

[7] Eschenmoser, A. *Chem. Soc. Rev.* **1976**, *5*, 377.

[8] Jefford, C. W.; Rossier, J.-C.; Richardson, G. D. *J. Chem. Soc., Chem. Commun.* **1983**, 1064.

[9] Wissner, A. *Tetrahedron Lett.* **1978**, 2749.

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in flame-dried glassware under an atmosphere of dry nitrogen.

(*S*)-(−)-Bis(trimethylsilyl) 2-[(Trimethylsilyl)oxy]butanedioate (2a).[11] To (*S*)-(−)-malic acid (20.0 g, 149 mmol) was added HMDSH (34.6 mL, 164 mmol). To the resulting stirred slurry was added dropwise Me_3SiCl (20.8 mL, 164 mmol) at such a rate so as to avoid boiling. The slurry was stirred for 12 h and filtered through sintered glass. The solid was washed with CH_2Cl_2, and the filtrate was distilled (bp 137–140 °C, 11 mmHg) to provide **2a** (44.6 g, 127 mmol, 85.2%) as a colorless liquid: α^{28}_{D} −43.20° (neat): ^1H NMR ($CDCl_3$) δ 4.54 (dd, J = 8.3 and 4.2 Hz, H(2), H_X of ABX), 2.82 (dd, J = 16.1 and 4.2 Hz, H_A of ABX), 2.65 (dd, J = 16.0 and 8.3, H_B of ABX), 0.30 (s, 9 H), 0.29 (s, 9 H), and 0.14 (s, 9 H); IR (neat) 1723, 1254 cm^{-1}. Anal. Calcd for $C_{13}H_{30}O_5Si_3$: C, 44.51; H, 8.86. Found C, 44.76; H, 8.86.

(±)-Trimethylsilyl 2-[(Trimethylsilyl)oxy]-2-phenylethanoate (2b).[12] To a solution of (±)-mandelic acid (10.0 g, 65.7 mmol) in 30 mL of dry CH_2Cl_2 was added HMDSH (15.3 mL, 72.3 mmol) dropwise with formation of a white preciptate. The slurry was stirred overnight and the CH_2Cl_2 was removed by distillation under aspirator pressure with concomitant disappearance of the white precipitate. The residual liquid was distilled (bp 97–98 °C, 0.25 mmHg) to provide **2b** (19.24 g, 99%) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 7.38 (m, Ar H), 5.13 (s, H(2)), 0.20 (s, 9 H), and 0.13 (s, 9 H); IR (neat) 1739 (s), 1715 (m) (presumably split by Fermi resonance), 1254, 849 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_3Si_2$: C, 56.69; H, 8.16. Found: C, 56.84; H, 8.16.

(*S*)-(−)-Trimethylsilyl 2-[(Trimethylsilyl)oxy]propanoate (2c).[13] Following the procedure for the preparation of **2b**, (*S*)-lactic acid (2.09 g, 23.2 mmol) was converted to **2c** (2.63 g, 10.0 mmol, 43.2%) as a colorless liquid (bp 43–48 °C, 3.3 mmHg): α^{29}_{D} −32.6° (neat); ^1H NMR ($CDCl_3$) δ 4.24 (q, J = 6.8 Hz, H(2)), 1.40 (d, J = 6.8 Hz, CH_3), 0.30 (s, 9 H), and 0.14 (s, 9 H); IR (neat) 1738, 1254 cm^{-1}.

(±)-Trimethylsilyl 2-[(Trimethylsilyl)thio]propanoate (2d).[14] Following the procedure for the preparation of **2b**, (±)-thiolactic acid (5.98 g, 56.3 mmol) was converted to **2d** (6.54 g, 46%) as a colorless liquid (bp 68 °C, 7 mmHg): ^1H NMR ($CDCl_3$) δ 3.38 (q, J = 7 Hz, H(2)), 1.47 (d, J = 7 Hz, CH_3), 0.35 (s, 9 H), and 0.30 (s, 9 H); IR (neat) 1718, 1253 cm^{-1}. Anal. Calcd for $C_9H_{22}O_2SSi_2$: C, 43.13; H, 8.85. Found: C, 43.04; H, 8.89.

(2*S*,4*S*)-(−)-2-*tert*-Butyl-5-oxo-1,3-dioxolane-4-acetic Acid (*cis*-1a).[1c] The diester **2a** (20.0 mL, 19.4 g, 55.4 mmol) was dissolved in 200 mL of CH_2Cl_2 and cooled to −25 °C. Pivaldehyde (6.9 mL, 63.9 mmol) was added, and the stirred mixture was treated with Me_3SiOTf (1.1 mL, 5.8 mmol). The mixture was stirred at −25 °C for 6 h and then quenched with 1 N HCl. Extraction with CH_2Cl_2, drying ($MgSO_4$), and concentration left crude **1a** as a white solid. Treatment of a portion of this material with ethereal diazomethane and analysis by capillary GC under conditions known to resolve the cis and trans diastereomers of **1a** [obtained after separation (MPLC on silica gel in 6:1 hexane/EtOAc containing 0.5% AcOH) and CH_2N_2 treatment of mixtures of **1** resulting from reactions at higher temperatures] revealed a single peak. The crude **1a** was purified by recrystallization to leave *cis*-**1a** (78% yield, mp 104–105 °C).

General Procedure for Preparation of 1b, 1c, and 1d. The bis(trimethylsilyl) derivatives **2b–d** (0.3 M in CH_2Cl_2) were treated sequentially with 1.1 equiv of *t*-BuCHO and 0.10–0.15 equiv of Me_3SiOTf at −25 or 0 °C. After 10 min to several hours (depending upon substrate and temperature), water was added. Extraction (CH_2Cl_2), drying ($MgSO_4$), concentration, and separation by MPLC on silica gel provided the individual diastereomers of **1b–d** in the yields and ratios indicated in Table I. Spectral data were consistent with those previously descirbed.[1c] In addition: (±)-*trans*-**1b**: colorless oil; IR (neat) 1800, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.47–7.36 (m, 5 H), 5.45 (s, 1 H), 5.39 (s, 1 H), and 1.04 (s, 9 H); (±)-*cis*-**1b**: mp 111–114 °C.

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(10) Schmeisser, M.; Sartori, P.; Kippsmeir, B. *Chem. Ber.* **1970**, *25*, 773.

(11) (a) Petersson, G. *Org. Mass Spectrom.* **1972**, *6*, 565. (b) Kringstad, R.; Bakke, I. L. F. *J. Chromatogr.* **1977**, *144*, 209.

(12) Rubottom, G. M.; Marrero, R. *J. Org. Chem.* **1975**, *40*, 3783.

(13) (a) Ng, K. J.; Andresen, B. D.; Bianchine, J. R. *J. Chromatogr.* **1982**, *228*, 43. (b) Schwarz, G.; Alberts, H.; Kricheldorf, H. R. *Liebigs Ann. Chem.* **1981**, 1257.

(14) Rimpler, M. *Chem. Ber.* **1966**, *99*, 1523.

Synthesis of 1,3-Dioxolan-4-ones. An Improved Procedure

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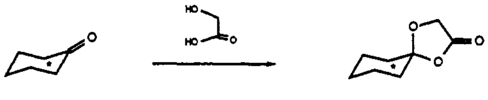
In conjunction with our efforts to develop a new method for the asymmetric synthesis of α-hydroxy acids,[2] we required chiral 1,3-dioxolan-4-ones such as 1, which are formally derived from condensation of glycolic acid with chiral cycloalkanones (eq 1). Although 1,3-dioxolan-4-ones may generally be prepared from carbonyl compounds and branched α-hydroxy acids such as lactic and mandelic acids,[3] those derived from glycolic acid are rare.[3a,4] For example, acid-catalyzed condensation of glycolic acid with cyclohexanone is reported to afford 1,4-dioxaspiro[4.5]decane-2-one **3** in low yield as an oil that is unstable at room temperature.[3a] In this paper we report a new route to such materials that proceeds in good to excellent yield to provide stable dioxolanones.[11] Further, the stereo-



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eq.1

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(1) Recipient of a Dreyfus Foundation Grant for Newly Appointed Faculty in Chemistry, 1984–1989.

(2) Pearson, W. H.; Cheng, M.-C. *J. Org. Chem.* **1986**, *51*, 3746.

(3) (a) Farines, M.; Soulier, J. *Bull. Soc. Chim. Fr.* **1970**, 332. (b) Elderfield, R. C.; Short, F. W. In *Heterocyclic Compounds*; Elderfield, R. C., Ed.; John Wiley: New York, 1957; Vol. 5, Chapter 1, p 1 and 27.

(4) (a) Asabe, Y.; Takitani, S.; Tsuzuki, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 661. (b) Berney, D.; Deslongchamps, P. *Can. J. Chem.* **1969**, *47*, 515. (c) Thomas, H. G.; Schwager, H.-W. *Tetrahedron Lett.* **1984**, *25*, 4471 and references therein. (d) Kammula, S. L.; Tracer, H. L.; Shevlin, P. B.; Jones, M., Jr. *J. Org. Chem.* **1977**, *42*, 2931. (e) Eberle, M. K.; Kahle, G. G. *J. Am. Chem. Soc.* **1977**, *99*, 6038.

(5) Wissner, A. *J. Org. Chem.* **1979**, *44*, 4617.

(6) This approach is related to work by Noyori[6a] on the preparation of dioxolanes and work by Jefford[6b] on the synthesis of 1,2,4-trioxan-5-ones: (a) Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* **1981**, *37*, 3899. (b) Jefford, C. W.; Rossier, J.-C.; Richardson, G. D. *J. Chem. Soc., Chem. commun.* **1983**, 1064. For recent applications of this technique to the synthesis of 1,3-dioxanones, see: (c) Schreiber, S. L.; Reagan, J. *Tetrahedron Lett.* **1986**, *27*, 2945. (d) Seebach, D.; Zimmerman, J. *Helv. Chim. Acta* **1986**, *69*, 1147.

(7) All new compounds were fully characterized by IR, ^1H and ^{13}C NMR, MS, and combustion analysis.

(8) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(9) ^1H NMR spectra were recorded on a Bruker WM-300 or WM-360 spectrometer, using tetramethylsilane as an internal standard. ^{13}C NMR spectra were obtained on a Bruker WM-300 (75 MHz) or WM-360 (90 MHz) spectrometer and are reported relative to deuteriated chloroform as an internal standard. Infrared spectra were recorded on a Nicolet 5-DX (FTIR) or 60-SX (FTIR) spectrometer. Mass spectra were obtained on a Finnigan 4500 GC/MS-EICI system at 70 eV. Elemental analyses were performed by Spang Microanalytical Laboratory at Eagle Harbor, MI, or Galbraith Laboratories, Inc. at Knoxville, TN. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 chromatograph equipped with a fused silica capillary column (Carbowax) and a flame ionization detector. HPLC analyses were performed with Rainin Microsorb SiO_2 or C18 HPLC columns (analytical) or a Rainin Dynamax Macro HPLC SiO_2 column (preparative).

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