(1*R,2*R**)-1-Methyl-2-[1-(*tert*-butyldimethylsiloxy)-2-(*E*)-buten-3-yl]-3-cyclohexene-1-carbaldehyde (36).** A solution of **30a** (320 mg, 1.65 mmol) in dry DMF (1 mL) was treated with *tert*-butyldimethylsilyl chloride (273 mg, 1.81 mmol) and imidazole (283 mg, 4.16 mmol) at room temperature. After 5 min, the solution was diluted with ether (10 mL), washed with aqueous ammonium chloride and brine, dried, and concentrated. The residue was subjected to chromatography (silica gel, 2 g; elution with 1:20 AcOEt–hexane) to afford **36** as an oil (466 mg, 92%): ^{1}H NMR (200 MHz) δ 0.07 (s, 6 H, $SiCH_3$), 0.90 (s, 9 H, t-C_4H_9), 1.12 (s, 3 H, 1-CH_3), 1.45 (dt, J = 13, 5 Hz, 1 H, H-6), 1.55 (br s, 3 H, 3′-CH_3), 1.87 (ddd, J = 13, 8.5, 6 Hz, 1 H, H-6), 2.15 (m, 2 H, H-5), 2.79 (br s, 1 H, H-2), 4.20 (d, J = 6 Hz, 2 H, H-1′), 5.52 (m, 2 H, H-2′ and H-3 or H-4), 5.97 (dm, J = ca. 10 Hz, 1 H, H-3 or H-4), 9.62 (s, 1 H, CHO).

3-[(5*R,10*R**)-3-[(3*R**,4*R**)- and 3-[(5*R**,10*R**)-3-[(3*S**,4*S**)-3-[1-Hydroxy-2(*E*)-buten-3-yl]-4-methylcyclohexen-4-yl)carbonyl]-4-methoxy-2-oxo-1-oxaspiro[4.5]deca-3,7-dien-10-yl]-2-methyl-2(*E*)-propenal (38).** A solution of **11** (197 mg, 0.787 mmol) in dry THF (0.6 mL) was syringed into a cold (−78 °C) stirred solution of lithium diisopropylamide [prepared from n-butyllithium (1.56 M in hexane, 1.26 mL, 1.97 mmol) and diisopropylamine (276 μL, 1.97 mmol) in dry THF (1.2 mL) under nitrogen atmosphere]. After 30 min, to the mixture were added a solution of **36** (291 mg, 0.943 mmol) in dry THF (0.6 mL) and dry HMPT (0.6 mL) over 10 min. The reaction mixture was allowed to warm to room temperature over 2 h and then poured onto a mixture of ether (10 mL) and ice–water (10 mL) containing 12 N HCl (0.83 mL). The phases were separated, and the aqueous phase was extracted with ether. The combined ether phases were washed with saturated brine, dried, and concentrated under reduced pressure. The residual oil (736 mg) was dissolved in dry dichloromethane (0.9 mL), and the solution was added dropwise to a cold stirred solution of chlorodimethylsulfonium chloride, which was prepared by addition of Me_2SO (279 μL, 3.93 mmol) in dichloromethane (0.3 mL) to a solution of oxalyl chloride (127 μL, 1.97 mmol) in the same solvent (1.5 mL) at ca. −70 °C.[15] After being allowed to warm to −35 °C over 30 min, the mixture was treated with triethylamine (1.24 mL, 8.90 mmol) and then brought to room temperature over 25 min. The reaction mixture was diluted with dichloromethane (15 mL), washed with 1% HCl (15 mL) and brine (5 mL), dried, and concentrated under reduced pressure. The residue was subjected to chromatography (silica gel, 26 g; elution with 1:3 AcOEt–hexane) to afford **37** as an oil (186 mg, 43%), R_f 0.56 (1:3 AcOEt–hexane).

A solution of **37** (490 mg, 0.883 mmol, combined with that obtained in a separate run) in 0.2% HF in acetonitrile (14.4 mL) was stirred at room temperature for 30 min. The solution was diluted with ether (20 mL), washed with saturated aqueous $NaHCO_3$ and brine, dried, and concentrated. The residue (442 mg) was subjected to chromatography (silica gel, 8 g; elution with 1:2 AcOEt–chloroform) to give a mixture of **38** and its diastereomer as an oil (270 mg, 69%), R_f 0.53 (1:2 AcOEt–chloroform). These diastereomers were separated by MPLC (10-μm silica gel, elution with 1:3 hexane–ether) to afford less polar isomer (113 mg) and more polar isomer (57 mg), which was crystallized from ether–hexane.

Less polar **38** (major product): mp 154–155 °C; IR (KBr) 3475, 1750, 1665, 1615 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.32 (s, 3 H), 1.62 (br s, 3 H), 1.76 (d, J = 1.5 Hz, 3 H), 2.75 (br d, J = ca. 18 Hz, 1 H), 3.19 (td, J = 11, 6 Hz, 1 H), 3.27 (br s, 1 H), 3.78 (s, 3 H), 4.05 (dd, J = 11, 7 Hz, 1 H), 4.16 (dd, J = 11, 7 Hz, 1 H), 5.49 (m, 1 H), 5.59 (br t, J = 7 Hz, 1 H), 5.68–5.94 (m, 3 H), 6.18 (dq, J = 11, 1.5 Hz, 1 H), 9.36 (s, 1 H); MS, m/e 440 (M^+), 147 (base peak). Anal. Calcd for $C_{26}H_{32}O_6$: C, 70.89; H, 7.32. Found: C, 70.70; H, 7.45.

More polar **38** (minor product): mp 137–138 °C; IR (KBr) 3530, 1750, 1680, 1615 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.31 (s, 3 H), 1.60 (br s, 3 H), 1.76 (d, J = 1.5 Hz, 3 H), 2.72 (br d, J = ca. 18 Hz, 1 H), 3.21 (td, J = 11, 6 Hz, 1 H), 3.45 (br d, J = ca. 5 Hz, 1 H), 3.69 (s, 3 H), 4.06 (dd, J = 11, 7 Hz, 1 H), 4.15 (dd, J = 11, 7 Hz, 1 H), 5.49 (m, 1 H), 5.62 (br t, J = 7 Hz, 1 H), 5.68–5.94 (m, 3 H), 6.22 (dq, J = 11, 1.5 Hz, 1 H), 9.35 (s, 1 H); MS, m/e 440 (M^+), 147 (base peak). Anal. Calcd for $C_{26}H_{32}O_6$: C, 70.89; H, 7.32. Found: C, 70.84; H, 7.51.

3-[(5*R,10*R**)-3-[(3*R**,4*R**)- and 3-[(5*R**,10*R**)-3-[(3*S**,4*S**)-3-[1-Chloro-2(*E*)-buten-3-yl]-4-methylcyclohexen-4-yl)carbonyl]-4-methoxy-2-oxo-1-oxaspiro[4.5]deca-3,7-dien-10-yl]-2-methyl-2(*E*)-propenal (39).** Dimethyl sulfide (23 μL, 0.313 mmol) was syringed into a cold (0 °C) stirred solution of N-chlorosuccinimide (38 mg, 0.285 mmol) in dichloromethane (1.3 mL) under nitrogen atmosphere. After 3 min, the solution was cooled to −25 °C, and a solution of the major isomer of **38** (113 mg, 0.257 mmol) in dichloromethane (0.2 mL) was introduced. The mixture was then stirred at the ice–water temperature for 25 min. The reaction mixture was diluted with ether, washed with cold saturated brine, dried, and concentrated under reduced pressure. The residue was subjected to chromatography (silica gel, 10 g; elution with 1:3 AcOEt–hexane) to afford a chloride (27 mg, 23%) as an amorphous solid, which decomposed on attempted crystallization: IR (film) 1765, 1695, 1615 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.26 (s, 3 H), 1.76 (d, J = 1.5 Hz, 3 H), 1.81 (s, 3 H), 2.75 (br d, J = ca. 18 Hz, 1 H), 3.21 (td, J = 10, 6 Hz, 1 H), 3.53 (br s, 1 H), 3.78 (s, 3 H), 4.12 (d, J = 8 Hz, 2 H), 5.46–5.64 (m, 2 H), 5.64–5.93 (m, 3 H), 6.20 (dq, J = 10, 1.5 Hz, 1 H), 9.39 (s, 1 H); MS, m/e 423.2198 (M^+ − Cl, calcd 423.2172), 422.2069 (M^+ − HCl, calcd 422.2091), 147 (base peak).

The minor diastereomer of **38** (57 mg) was also chlorinated by the same procedure to give the corresponding chloride (14 mg, 24%) as a solid: IR (film) 1765, 1695, 1625 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.31 (s, 3 H), 1.65 (s, 3 H), 1.78 (d, J = 1.5 Hz, 3 H), 2.72 (br d, J = ca. 18 Hz, 1 H), 3.21 (td, J = 10, 6 Hz, 1 H), 3.55 (br d, J = ca. 5 Hz, 1 H), 3.70 (s, 3 H), 4.04 (dd, J = 8, 2 Hz, 2 H), 5.42–5.54 (m, 1 H), 5.60–5.93 (m, 4 H), 6.23 (dd, J = 10, 1.5 Hz, 1 H), 9.37 (s, 1 H); MS, m/e 423.2129 (M^+ − Cl, calcd 423.2169), 147, 91 (base peak).

Oxocyclopentenol Syntheses

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Received April 16, 1985

Metal-assisted decompositions of α-diazo carbonyl compounds in 1,2-dialkoxy-1-alkenes are shown to yield β,β′-dialkoxycyclopropyl carbonyl systems, whose acid hydrolysis produces α-alkoxy-γ-dicarbonyl substances. Intramolecular condensations of the latter lead to oxocyclopentenols. Application of this reaction scheme to the syntheses of a prostaglandin intermediate and of tetrahydropyrethrolone is described.

The three-step reaction scheme of copper-catalyzed reaction between enol derivatives and α-diazo ketones, hydrolysis of the resultant β-oxycyclopropyl ketones, and base-induced aldolization and dehydration of the thus-produced γ-dicarbonyl compounds has constituted for some time the basis of a short, general method of cyclo-

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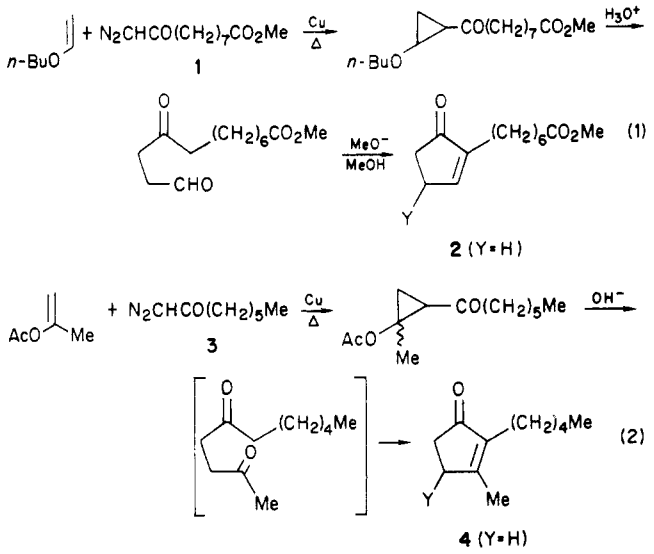
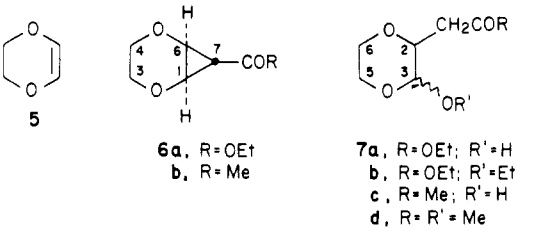
pentenone synthesis,[1] which has been applied inter alia to the construction of the prostaglandin intermediate **2** (eq 1)[2] and dihydrojasmone (**4**) (eq 2).[3] It now became of



interest to discover whether the reaction scheme was applicable also to the formation of oxocyclopentenols, e.g., the prostaglandin intermediate **2** (Y = OH) and tetrahydropyrethrolone (**4**, Y = OH). Since incorporation of a hydroxy group in the end product required the presence of an oxy substituent in the olefinic starting material at the beginning of the reaction sequence, an investigation of the behavior of α-diazo ketones toward enediol derivatives was undertaken.

A Prostaglandin Intermediate.[4] *p*-Dioxene (**5**) served as the starting material of the first few model experiments.[5] Its reaction with ethyl diazoacetate at 80° C over copper bronze yielded cyclopropane **6a**[7] whose acid-catalyzed solvolyses with water and with ethanol gave hemiacetal and acetal esters **7a** and **7b**, respectively. A reaction with diazoacetone under similar conditions, followed by solvolyses with water and with methanol, led to compounds **6b**,[7] **7c** and **7d**, respectively. Thus the first two reactions of the general, three-step method of cyclopentenone synthesis had succeeded in cases emanating from a enediol derivative.[8] Since, however, stripping the masked γ-dicarbonyl



compounds **7** of their undesired ethylene glycol unit proved difficult, all further efforts were devoted to the chemistry of (*Z*)-1,2-dimethoxyethene (**8a**).[9]

Copper-assisted decomposition of ethyl diazoacetate in the enediol diether **8a** yielded cyclopropane ester **9a**,[10,11] whose acid-catalyzed hydrolysis or alcoholysis gave difficultly isolable, water-soluble aldehydo ester **10a** and/or its demethanolation product and/or their acetals. However, exposure of cyclopropanecarboxylate **9a** to acidic, ethanolic 2,4-dinitrophenylhydrazine solution led to the aldehyde derivative **10b**, indicating that the first two reactions of the three-step scheme worked as well in the dimethoxyethylene series as in the dioxene field. Cyclopropanation of the starting olefin with 1-diazo-2-octanone (**3**)[3] afforded cyclopropyl ketone **9b**, whose acid hydrolysis produced keto aldehyde **11a**. Whereas all attempts of inducing the latter substance to undergo intramolecular aldolization under base catalysis failed,[12] exposure of the compound to an acidic, aqueous acetone solution gave oxocyclopentenol **12a** (presumably by acid-induced, intramolecular aldolization, followed by acid-induced β-elimination of the methoxy group instead of hydroxy function of the resultant β-hydroxy-β'-methoxycyclopentanone).[13] Isomerization of the cyclopentenolone over basic alumina[13] yielded the desired product (**13a**).

With the synthesis of oxocyclopentenol **13a** serving as a model, the prostaglandin intermediate **13b** was synthesized in the following manner. Copper-catalyzed cyclopropanation of 1,2-dimethoxyethylene (**8a**) with diazo ketone **1** yielded cyclopropyl ketone **9c**, whose interaction with acid in aqueous acetone gave keto ester **12b** (having undergone sequentially cyclopropane unravelling, intramolecular aldolization, and demethanolation). Isomerization of the latter by basic alumina produced the PGE_1 intermediate **13b**.[14,15]

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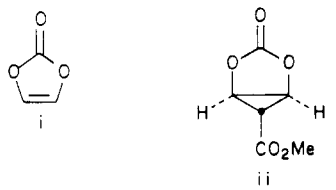
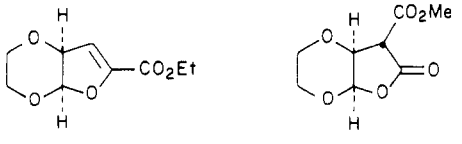
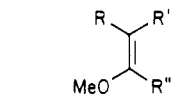
(2) Wenkert, E.; Buckwalter, B. L.; Craveiro, A. A.; Sanchez, E. L.; Sathe, S. S. *J. Am. Chem. Soc.* **1978**, *100*, 1267.
(3) Wenkert, E.; Mueller, R. A.; Reardon, E. J., Jr.; Sathe, S. S.; Scharf, D. J.; Tosi, G. *J. Am. Chem. Soc.* **1970**, *92*, 7428.
(4) Based on M. S. Raju, Ph.D. Dissertation, Rice University, 1978.
(5) The sole previous study of an enediol derivative with an α-diazo carbonyl system prior to the present one[4] involved the transformation of vinylene carbonate i into bicycle ii in less than 10% yield by reaction with ethyl diazoacetate under cuprous cyanide catalysis.[6] Repetition of this reaction, however, under the influence of copper triflate (benzene solution, 0 °C), now has produced carbonate ii in 33% yield.



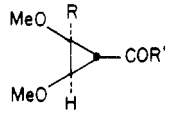
(6) Breitbeil, F. W.; Dennerlein, D. T.; Fiebig, A. E.; Kuznicki, R. E. *J. Org. Chem.* **1968**, *33*, 3389.
(7) The cyclopropanes possessed preponderantly (if not exclusively) the stereochemistry depicted in the formulas. No attempt was made to determine or modify the stereoisomer ratio in view of the destruction of the chiral centers in the next reaction.
(8) Reaction of dioxene (**5**) with ethyl diazopyruvate over (trimethoxyphosphino)copper(I) chloride produced dihydrofuroic ester iii and a similar reaction with dimethyl diazomalonate, followed by mild acid hydrolysis, afforded lactone ester iv (E. Wenkert and M. S. Raju, unpublished observations).



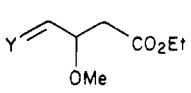
(9) McElvain, S. M.; Stammer, C. H. *J. Am. Chem. Soc.* **1951**, *73*, 915.
(10) The same reaction on 1,2-diethoxyethylene produced the diethoxy equivalent of ester **9a** equally efficiently.
(11) For reactions of dimethoxyethylenes **8a** and **8e** with ethyl diazopyruvate and some reactions of the resultant dimethoxydihydrofuroates, see: Alonso, M. E.; Jano P.; Hernandez, M. I.; Greenberg, R. S.; Wenkert, E. *J. Org. Chem.* **1983**, *26*, 3047.
(12) Under a variety of conditions including those described in (a) ref 2. (b) Ellison, R. A.; Lukenbach, E. R.; Chiu, C. *Tetrahedron Lett.* **1975**, 499. (c) Cooper, G. K.; Dolby, L. J. *Ibid.* **1976**, 4675. (d) Kieczykowski, G. R.; Pogonowski, C. S.; Richman, J. E.; Schlessinger, R. H. *J. Org. Chem.* **1977**, *42*, 175.
(13) Cf. Piancatelli, G.; Scettri, A. *Tetrahedron Lett.* **1977**, 1131 and subsequent papers.



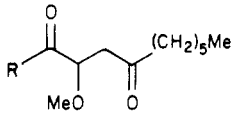
8a, R=OMe; R'=R"=H
b, R=OMe; R'=Me, R"=H
c, R=OMe; R'=*n*-Bu, R"=H
d, R=R"=H; R'=OMe
e, R=*n*-Bu; R'=OMe; R"=H
f, R=OMe; R'=Me; R"=*n*-Bu



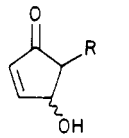
9a, R=H; R'=OEt
b, R=H; R'=$(CH_2)_5Me$
c, R=H; R'=$(CH_2)_7CO_2Me$
d, R=Me; R'=$(CH_2)_5Me$



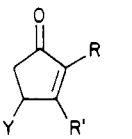
10a, Y=O
b, Y=$NNHC_6H_3(NO_2)_2$-2,4



11a, R=H
b, R=Me



12a, R=$(CH_2)_4Me$
b, R=$(CH_2)_6CO_2Me$



13a, R=$(CH_2)_4Me$; R'=H, Y=OH
b, R=$(CH_2)_6CO_2Me$; R'=H; Y=OH
c, R=$(CH_2)_4Me$; R'=Me; Y=OMe
d, R=$(CH_2)_4Me$; R'=Me; Y=Br
e, R=$(CH_2)_4Me$; R'=Me; Y=OH

Tetrahydropyrethrolone.[16] The tetrahydro alcohol unit of the major pyrethrin ester insecticides being the 3-methyl analogue of the above oxocyclopentenol model **13a** made the present reaction scheme ideally suited for the synthesis of tetrahydropyrethrolone (**13e**). Since this plan necessitated the use of the enediol diether **8b** as starting material and since a simple preparation of the latter could be envisioned to involve methylation of 1,2-dimethoxyethylene,[17] a short study of the feasibility of alkylation of the simplest dioxyethylenes was undertaken.[18]

Metalation of (*Z*)-1,2-dimethoxyethene (**8a**) with *tert*-butyllithium and treatment of the monolithiated olefin with methyl iodide and *n*-butyl bromide yielded enediol diethers **8b** and **8c**, respectively. Lithiation of (*E*)-1,2-dimethoxyethene (**8d**)[9] and treatment of the metalated intermediate with *n*-butyl bromide gave diether **8e**, whose thermolysis induced its transformation into the *Z* isomer **8c**. Introduction of a second alkyl group into the dioxyethylene system proved to be difficult. However, lithiation of diether **8c** in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and subsequent treatment with methyl iodide led to diether **8f**.

With dimethoxypropylene (**8b**) on hand it was possible to initiate the tetrahydropyrethrolone synthesis. However, the first step, the copper-assisted cyclopropanation of the enediol diether with a diazo ketone, ran afoul of the thermal instability of the enol derivative[19] at the elevated temperature needed for the diazo ketone decomposition. Hence this cyclopropanation was carried out with the use of dirhodium tetraacetate, a catalyst known to be active at room temperature or below.[11] The thus-catalyzed reaction between 1-diazo-2-octanone (**3**) and the enediol diether **8b** gave dimethoxycyclopropyl ketone **9d**[7], which in aqueous acid underwent regiospecific ring opening forming γ-diketone **11b**. Base-catalyzed, intramolecular aldol condensation of the latter resulted in the production of the methyl ether (**13c**) of tetrahydropyrethrolone.[20,21] Exposure of the ether to boron tribromide yielded bromo ketone **13d**, whose transformation (by bromide displacement with silver acetate, followed by hydrolysis of the resultant ester) into tetrahydropyrethrolone (**13e**)[22] has been reported some time ago.[21]

Experimental Section

Melting points were determined on a Reichert micro hotstage apparatus and are uncorrected. Infrared spectra of CCl_4 solutions (unless noted otherwise) were recorded on Beckman IR-8, Perkin-Elmer 137, and Pye Unicam 3-200 spectrophotometers. Ultraviolet spectra of methanol solutions were obtained on a Perkin-Elmer 550 spectrophotometer. ^1H NMR spectra of $CDCl_3$ solutions were observed on Varian EM-390 and XL-100-15 spectrometers and a 360-MHz instrument with a highly modified Varian HR-220 console, Oxford magnet, and Nicolet 1180-E computer system. ^{13}C NMR spectra of $CDCl_3$ solutions were acquired on a Varian XL-100-15 spectrometer, operating at 25.2 MHz in the Fourier transform mode, and on a wide-bore, broad-band Nicolet NT-200 spectrometer, operating with an Oxford magnet at 50.3 MHz in the Fourier transform mode. The carbon shifts are listed in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. All extracts were dried over anhydrous Na_2SO_4. Unless noted otherwise, column chromatography was carried out on 70–230-mesh EM or Davisil 62 silica gel. TLC was performed with EM or Merck, precoated, 0.25-mm silica gel 60 (F-254) plates and MPLC on Merck Lobar A, B, or C columns connected to a Fluid Metering, Inc. pump.

General Procedure for the Preparation of Cyclopropanes 6a, 6b, 7a, 7b, and 7c. Ethyl diazoacetate or the requisite diazo ketone was added dropwise to a stirring suspension of copper bronze in 2 or more equiv of *p*-dioxene (**5**) or (*Z*)-1,2-dimethoxyethene (**8a**), kept at 80 °C under nitrogen, and thereafter the stirring and heating was continued for 0.5 h. After removal of the excess enol ether by vacuum distillation the mixture was filtered through Celite. The catalyst was washed with ether and the combined filtrate and washings were evaporated. Distillation of the residue yielded the cyclopropane.

A reaction of 2.85 g (25 mmol) of ethyl diazoacetate with 4.50 g (50 mmol) of *p*-dioxene over 300 mg of copper bronze gave 3.45 g (80%) of colorless liquid ester **6a**: bp 57–59 °C (0.1 torr); IR C=O 1718 (s) cm^{-1}; ^1H NMR δ 1.20 (t, 3, J = 7 Hz, Me), 2.12 (t, 1, J = 3 Hz, COCH), 3.63 (s, 4, 2 OCH_2), 3.89 (d, 2, J = 3 Hz, 2 OCH), 4.07 (q, 2, J = 7 Hz, OCH_2 of OEt); ^{13}C NMR δ 13.9 (Me), 24.4 (C-7), 56.8 (C-1, C-6), 60.0 (OCH_2), 62.5 (C-3, C-4), 170.2 (C=O). Anal. ($C_8H_{12}O_4$) C, H.

A reaction of 2.52 g (30 mmol) of diazoacetone with 8.74 g (90 mmol) of *p*-dioxene over 300 mg of copper bronze gave 2.30 g (54%) of colorless liquid ketone **6b**: bp 50–52 °C (0.15 torr); IR C=O 1687 (s) cm^{-1}; ^1H NMR δ 2.22 (s, 3, Me), 2.50 (t, 1, J = 3 Hz, COCH), 3.63 (s, 4, 2 OCH_2), 3.94 (d, 2, J = 3 Hz, 2 OCH); ^{13}C NMR δ 30.7 (Me), 33.2 (C-7), 60.1 (C-1, C-6), 62.5 (C-3, C-4), 206.4 (C=O); exact mass m/e 142.0630 (calcd for $C_7H_{10}O_3$ m/e 142.0630).

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A reaction of 2.85 g (25 mmol) of ethyl diazoacetate with 4.40 g (50 mmol) of 1,2-dimethoxyethylene (**8a**) over 300 mg of copper bronze gave 3.62 g (83%) of colorless liquid ester **9a**: IR (neat) C=O 1719 (s) cm^{-1}; ^1H NMR δ 1.22 (t, 3, J = 7 Hz, Me), 1.78 (t, 1, J = 3 Hz, COCH), 3.43 (s, 6, 2 OMe), 3.56 (d, 2, J = 3 Hz, 2 OCH), 4.08 (q, 2, J = 7 Hz, OCH_2); ^{13}C NMR δ 14.0 (Me), 27.0 (α-keto C), 59.1 (2 OMe), 60.4 (OCH_2), 64.9 (2 α-oxy C), 170.5 (C=O). Anal. ($C_8H_{14}O_4$) C, H.

A reaction of 8.80 g (57 mmol) of 1-diazo-2-octanone (**3**) with 8.80 g (0.10 mol) of 1,2-dimethoxyethylene (**8a**) over 600 mg of copper bronze gave 8.70 g (71%) of colorless liquid ketone **9b**: IR (neat) C=O 1687 (s) cm^{-1}; ^1H NMR δ 0.89 (t, 3, J = 6 Hz, Me), 1.1–1.9 (m, 8, methylenes), 2.12 (t, 1, J = 3 Hz, COCH), 2.56 (t, 2, J = 7 Hz, $COCH_2$), 3.44 (s, 6, 2 OMe), 3.62 (d, 2, J = 3 Hz, 2 OCH); ^{13}C NMR δ 13.1 (Me), 22.1 (ϵ-keto C), 23.9 (β-keto C), 28.6 (γ-keto C), 31.2 (δ-keto C), 35.1 (c-Pr α-keto C), 43.4 (α-keto C), 58.8 (2 OMe), 67.5 (2 c-Pr oxy-C), 205.4 (C=O). Anal. ($C_{12}H_{22}O_3$) C, H.

A reaction of 7.00 g (31 mmol) of methyl 10-diazo-9-oxodecanoate (**1**) with 13.2 g (0.15 mol) of 1,2-dimethoxyethylene (**8a**) over 600 mg of copper bronze gave 6.75 g (76%) of colorless, viscous, liquid keto ester **9c**: IR C=O 1739 (s), 1691 (s) cm^{-1}; ^1H NMR δ 1.1–1.9 (m, 10, methylenes), 2.14 (t, 1, J = 3 Hz, COCH), 2.27 (t, 2, J = 7 Hz, CH_2CO_2), 2.56 (t, 2, J = 7 Hz, $COCH_2$), 3.48 (s, 6, 2 OMe), 3.58 (d, 2, J = 3 Hz, 2 OCH), 3.61 (s, 3, ester OMe); ^{13}C NMR δ 23.3 (β-ketone C), 24.1 (β-ester C), 28.2 (3 central methylenes), 33.1 (α-ester C), 34.6 (c-Pr α-keto C), 42.7 (α-ketone C), 50.3 (ester Me), 58.2 (2 OMe), 66.9 (2 c-Pr oxy-C), 172.7 (ester C=O), 205.3 (ketone C=O); exact mass m/e 286.1779 (calcd for $C_{15}H_{26}O_5$ m/e 286.1780).

2-(Carbethoxymethyl)-3-hydroxy-1,4-dioxane (7a). A mixture of 200 mg of ester **6a** and 2 mL of 2 N hydrochloric acid solution in 10 mL of acetone was stirred under nitrogen at room temperature for 12 h. It then was diluted with 20 mL of ether and filtered through a short column of basic alumina. Evaporation of the filtrate yielded 210 mg (95%) of liquid hemiacetal **7a**: IR OH 3420 (br w), C=O 1720 (s) cm^{-1}; ^1H NMR δ 1.24 (t, 3, J = 7 Hz, Me), 2.3–2.9 (m, 2, $COCH_2$), 3.3–4.1 (m, 5, 2 OCH_2, OCH), 4.12 (q, 2, J = 7 Hz, CO_2CH_2), 4.50 (d, <1, J = 9 Hz, OCHO of one isomer), 4.92 (d, <1, J = 3 Hz, OCHO of other isomer); ^{13}C NMR δ trans isomer 14.5 (Me), 37.4 (α-keto C), 62.7 (Et CH_2), 64.1 (C-5), 65.2 (C-6), 75.0 (C-2), 94.9 (C-3), 174.3 (C=O); cis isomer 14.5 (Me), 37.4 (α-keto C), 57.7 (C-5), 61.1 (Et CH_2), 64.6 (C-6), 73.0 (C-2), 89.7 (C-3), 174.3 (C=O); exact mass m/e 190.0846 (calcd for $C_8H_{14}O_5$ m/e 190.0841).

2-(Carbethoxymethyl)-3-ethoxy-1,4-dioxane (7b). A solution of 200 mg of ester **6a** and 30 mg of p-toluenesulfonic acid in 15 mL of absolute ethanol was stirred under nitrogen at room temperature for 12 h and then diluted with 30 mL of ether and passed through a short column of basic alumina. Evaporation of the solution gave 250 mg (99%) of liquid acetal **7b**: IR C=O 1739 (s) cm^{-1}; ^1H NMR δ 1.16, 1.22 (t, 3 each, J = 7 Hz, 2 Me), 2.2–2.8 (m, 2, $COCH_2$), 3.3–4.2 (m, >5, 2 OCH_2 OCH), 3.72 (q, 2, J = 7 Hz, ethoxy OCH_2), 4.10 (q, 2, J = 7 Hz, ester OCH_2), 4.25 (d, <1, J = 8 Hz, OCHO of one isomer); ^{13}C NMR δ trans isomer 13.8 (ester Me), 14.8 (ether Me), 36.1 (α-keto C), 60.1 (ester OCH_2), 64.2 (ether OCH_2 or C-5), 64.6 (C-5 or ether OCH_2), 65.4 (C-6), 74.5 (C-2), 100.1 (C-3), 170.1 (C=O); cis isomer 13.8 (ester Me), 14.8 (ether Me), 35.8 (α-keto C), 58.1 (C-5), 60.7 (ester OCH_2), 65.0 (ether OCH_2), 66.2 (C-6), 73.1 (C-2), 95.0 (C-3), 170.4 (C=O); exact mass m/e 218.1153 (calcd for $C_{10}H_{18}O_5$ m/e 218.1154).

2-Acetonyl-3-hydroxy-1,4-dioxane (7c). An ether solution of 200 mg of ketone **6b** was kept adsorbed on a column of 3 g of silica gel for 24 h and then eluted with ether. Evaporation of the eluate yielded 215 mg (95%) of liquid hemiacetal **7c**: IR OH 3420 (br w), C=O 1739 (s) cm^{-1}; ^1H NMR δ 2.15 (s, 3, Me), 2.2–2.8 (m, 2, $COCH_2$), 3.5–4.2 (m, 5, 2 OCH_2, OCH), 4.50 (d, <1, J = 8 Hz, OCHO of one isomer), 4.90 (d, <1, J = 3 Hz, OCHO of other isomer); ^{13}C NMR δ trans isomer: 30.0 (Me), 44.4 (α-keto C), 64.7 (C-5), 65.1 (C-6), 75.3 (C-2), 94.5 (C-3), 206.7 (C=O); cis isomer: 30.3 (Me), 43.9 (α-keto C), 57.6 (C-5), 65.8 (C-6), 72.9 (C-2), 89.5 (C-3), 206.7 (C=O); exact mass m/e 160.0733 (calcd for $C_7H_{12}O_4$ m/e 160.0735).

2-Acetonyl-3-methoxy-1,4-dioxane (7d). A solution of 200 mg of ketone **6b** and 20 mg of p-toluenesulfonic acid in 10 mL of anhydrous methanol was stirred under nitrogen at room temperature for 4 h and then diluted with 20 mL of ether and passed through a short column of basic alumina. Evaporation of the solution gave 240 mg of liquid acetal **7d**: IR C=O 1720 (s) cm^{-1}; ^1H NMR δ 2.17 (s, 3, Me), 2.5–2.8 (m, 2 $COCH_2$), 3.36, 3.42 (s each, 3 total, OMe), 3.5–4.0 (m, 5, 2 OCH_2, OCH), 4.23 (d, <1, J = 7 Hz, OCHO of one isomer), 4.38 (d, <1, J = 2 Hz, OCHO of other isomer); ^{13}C NMR δ trans isomer: 30.4 (Me), 44.7 (α-keto C), 56.1 (OMe), 64.7 (C-5), 65.4 (C-6), 74.2 (C-2), 101.5 (C-3), 205.5 (C=O); cis isomer: 30.7 (Me), 44.4 (α-keto C), 56.1 (OMe), 58.1 (C-5), 66.4 (C-6), 77.7 (C-2), 96.6 (C-3), 206.2 (C=O); exact mass m/e 174.0896 (calcd for $C_8H_{14}O_4$ m/e 174.0892). Anal. ($C_8H_{14}O_4$) C, H.

Ethyl 3-Methoxy-4-oxobutanoate 2,4-Dinitrophenylhydrazone (10b). A solution of 100 mg (0.57 mmol) of ester **9a**, 114 mg (0.57 mmol) of 2,4-dinitrophenylhydrazine, 1 mL of concentrated sulfuric acid, and 1 mL of water in 7 mL of ethanol was stirred at room temperature for 12 h. The resultant precipitate was filtered and crystallized from ethanol, yielding 150 mg (80%) of crystalline, yellow hydrazone **10b**: mp 104–106 °C; IR NH 3307 (w), C=O 1740 (s), C=N 1617 (s), C=C 1596 (s) cm^{-1}; ^1H NMR δ 1.27 (t, 3, J = 7 Hz, Me), 2.75 (d, 2, J = 6 Hz, $COCH_2$), 3.42 (s, 3, OMe), 4.16 (q, 2, J = 7 Hz, OCH_2), 4.35 (dt, 1, J = 6, 6 Hz, OCH), 7.49 (d, 1, J = 6 Hz, CH=N), 7.91 (d, 1, J = 10 Hz, aromatic H-6), 8.30 (dd, 1, J = 10, 2 Hz, aromatic H-5), 9.06 (d, 1, J = 2 Hz, aromatic H-3); exact mass m/e 340.1019 (calcd for $C_{13}H_{16}O_7N_4$ m/e 340.1027).

2-Methoxy-4-oxodecanal (11a). A mixture of 280 mg of ketone **9b** and 8 mL of 2 N hydrochloric acid in 20 mL of dichloromethane was stirred under nitrogen at room temperature for 1 h. The organic layer was separated, diluted with 20 mL of ether, washed with water and saturated sodium bicarbonate and brine solutions, and dried. Evaporation of the solvent left 257 mg (98%) of liquid aldehyde **11a**: IR (neat) C=O 1740 (m), 1720 (m) cm^{-1} (the presence of a broad, medium OH band at 3445 cm^{-1} and the weakness of the carbonyl bands suggesting part of the compound existing in the masked hydrate, i.e., 2,5-dihydroxytetrahydrofuran, form); ^1H NMR δ 0.94 (t, 3, J = 6 Hz, Me), 1.1–1.8 (m, 8, methylenes), 2.42 (t, 2 J = 7 Hz, $COCH_2$), 2.75 (d, 2, J = 5 Hz, 2 H-3), 3.43 (s, 3, OMe), 4.01 (t, 1, J = 5 Hz, H-2), 9.72 (s, 1, CHO); ^{13}C NMR δ 13.7 (C-10), 22.1 (C-9), 23.1 (C-6), 28.4 (C-7), 31.2 (C-8), 42.9 (C-5), 58.3 (OMe), 81.9 (C-2), 202.2 (C-1), 206.5 (C-4). Anal. ($C_{11}H_{20}O_3$) C, H.

1-Oxo-5-*n*-pentyl-2-cyclopenten-4-ol (12a). A solution of 750 mg of ketone **9b** or 700 mg of aldehyde **11a** and 240 mg of polyphosphoric acid in 21 mL of 2:1 acetone–water was refluxed until aldehyde **11a** had disappeared totally (monitored by TLC; ca. 70 h). The acetone was evaporated and the residue was neutralized with sodium bicarbonate and extracted with ether. The extract was dried and evaporated. Chromatography of the viscous, liquid residue on silica and elution with 2:1 ether–hexane gave 188 mg (32%) of colorless liquid ketone **12a**: IR OH 3440 (br w), C=O 1718 (s) cm^{-1}; ^1H NMR δ 0.88 (t, 3, J = 7 Hz, Me), 1.2–2.6 (m, 8, methylenes), 2.62 (dt, 1, J = 4, 2 Hz, H-5), 4.6–4.7 (m, 1, OCH), 6.14 (d, 1, J = 6 Hz, H-2), 7.47 (dd, 1, J = 6, 2 Hz, H-3); ^{13}C NMR δ 13.9 (Me), 22.4 (δ-CH_2), 26.9 (α-CH_2), 28.5 (β-CH_2), 31.8 (γ-CH_2), 55.3 (C-5), 76.5 (C-4), 133.9 (C-2), 161.9 (C-3), 208.3 (C-1); exact mass m/e 168.1152 (calcd for $C_{10}H_{16}O_2$ m/e 168.1150).

1-Oxo-2-*n*-pentyl-2-cyclopenten-4-ol (13a). A 4:1 benzene–ether solution of 50 mg of ketone **12a** was kept adsorbed on a column of 10 g of basic Woelm alumina (activity III) for 16 h and then eluted with the same solvent mixture. Evaporation of the eluate gave 49 mg (98%) of liquid ketone **13a**: IR OH 3626 (w), 3440 (br w), C=O 1718 (s), C=C 1635 (w) cm^{-1}; ^1H NMR δ 0.88 (t, 3, J = 7 Hz, Me), 1.2–1.7 (m, 6, methylenes), 2.0–2.3 (m, 2, allyl Hs), 2.24 (dd, 1, J = 18, 2 Hz, H-5), 2.74 (dd, 1, J = 18, 6 Hz, H-5), 4.8–5.0 (m, 1, H-4), 7.1–7.2 (m, 1, H-3); ^{13}C NMR δ 13.8 (Me), 22.3 (δ-CH_2), 24.3 (α-CH_2), 27.0 (β-CH_2), 31.3 (γ-CH_2), 44.7 (C-5), 68.2 (C-4), 147.8 (C-2), 155.9 (C-3), 206.5 (C-1); exact mass m/e 168.1148 (calcd for $C_{10}H_{16}O_2$ m/e 168.1150).

Methyl 7-(3-Hydroxy-5-oxocyclopentenyl)heptanoate (13b). A solution of 500 mg of keto ester **9c** and 130 mg of polyphosphoric acid in 11 mL of 2:1 acetone–water was refluxed until the starting material and intermediate aldehyde had disappeared completely (monitored by TLC; ca. 84 h). The acetone was evaporated and the residue was diluted with water and ex-

tracted with ether. The extract was dried and evaporated. Chromatography of the viscous, liquid residue on silica gel and elution with 2:1 ether–hexane gave 150 mg of a mixture of ketones **12b** and **13b** (by TLC and ^{1}H NMR). A 4:1 benzene–ether solution of this mixture was kept adsorbed on a column of 15 g of basic Woelm alumina (activity III) for 16 h and then eluted with 4:1 to 2:1 benzene–ether. Evaporation of the eluates gave 120 mg (29% overall yield) of colorless, viscous, liquid keto ester **13b**, IR and ^{1}H NMR spectrally identical with recorded data.[14] Exact mass *m/e* 240.1363 (calcd for $C_{13}H_{20}O_4$ *m/e* 240.1361).

Alkylation of (*Z*)- and (*E*)-1,2-Dimethoxyethene (8a and 8d, Respectively). A 2.0 M pentane solution of *tert*-butyllithium, 1.1 equiv, was added to a stirring solution of dimethoxyethylene **8a** or **8d**, 16 mmol, in 10 mL of dry tetrahydrofuran at −78 °C under argon, and the mixture was stirred at this temperature for 2 h. The requisite alkyl halide, 1.1 equiv, was added, and the mixture was permitted to warm to room temperature slowly (ca. 3 h). Upon dilution with 50 mL of ether and separation of the organic phase the latter was extracted with brine, dried, and evaporated. The oily residue was purified by distillation under high vacuum (except for **8b**) (to avoid double bond isomerization).

Low-temperature distillation (at 46–50 °C (30 torr)) of the product of methylation of **8a** gave colorless, liquid (*Z*)-1,2-dimethoxy-1-propene (**8b**) (80%): IR (neat) C=C 1690 (m) cm^{-1}; ^{1}H NMR δ 1.65 (s, 3, Me), 3.52 (s, 3, OMe), 3.65 (s, 3, OMe), 5.29 (s, 1, olefinic H); ^{13}C NMR δ 14.0 (C-3), 56.2 (OMe), 59.2 (OMe), 128.7 (C-1), 135.6 (C-2); exact mass *m/e* 102.0678 (calcd for $C_5H_{10}O_2$ *m/e* 102.0680).

Distillation of the product of *n*-butylation of **8a** yielded colorless, liquid (*Z*)-1,2-dimethoxy-1-hexene (**8c**) (78%): IR (neat) C=C 1685 (m) cm^{-1}; ^{1}H NMR δ 0.90 (t, 3, J = 6 Hz, Me), 1.1–1.5 (m, 4, methylenes), 1.6–1.8 (m, 2, allyl Hs), 3.42 (s, 3, OMe), 3.68 (s, 3, OMe), 5.18 (s, 1, olefinic H); exact mass *m/e* 144.1148 (calcd for $C_8H_{16}O_2$ *m/e* 144.1150).

Distillation of the crude product of *n*-butylation of **8d**, i.e., (*E*)-1,2-dimethoxy-1-hexene (**8e**) [IR (neat) C=C 1675 (m) cm^{-1}; ^{1}H NMR δ 0.82 (t, 3, J = 6 Hz, Me), 1.1–1.4 (m, 4, methylenes), 2.10 (t, 2, J = 6 Hz, allyl Hs), 3.38 (s, 3, OMe), 3.42 (s, 3, OMe), 5.50 (s, 1, olefinic H)], yielded isomer **8c** (72%).

(*Z*)-2,3-Dimethoxy-2-heptene (8f). A 2.1 M pentane solution (3.2 mL) of *tert*-butyllithium was added to a stirring solution of 321 mg of diether **8c** in 1.5 mL of TMEDA at −40 °C under argon, and the mixture was stirred at this temperature for 2 h. Methyl iodide (1 mL) was added and the mixture permitted to warm to room temperature. Ether (30 mL) was added and the mixture washed with brine, dried, and evaporated. Passage of a pentane solution of the residual oil through a short basic alumina (activity III) column yielded 211 mg (60%) of colorless, liquid diether **8f**: IR (neat) C=C 1685 (m) cm^{-1}; ^{1}H NMR δ 0.93 (t, 3, J = 6 Hz, Me), 1.1–1.6 (m, 4, methylenes), 1.77 (s, 3, olefinic Me), 2.08 (t, 2, J = 6 Hz, allyl Hs), 3.52 (s, 3, OMe), 3.56 (s, 3, OMe); exact mass (M − C_3H_6) *m/e* 116.0837 (calcd for $C_6H_{12}O_2$ *m/e* 116.0837).

3-Methoxy-2,5-undecanedione (11b). A solution of 1.16 g (7.0 mmol) of 1-diazo-2-octanone (**3**) in 10 mL of methylene chloride was added dropwise over a 4-h period to a solution of 732 mg (7.0 mmol) of ether **8b** and 20 mg of $Rh_2(OAc)_4$ in 10 mL of methylene chloride. The mixture was kept at room temperature for 0.5 h and then passed through a short Florisil column, which was washed subsequently with methylene chloride. Evaporation of the combined organic solutions yielded crude dimethoxycyclopropyl ketone **9d**: IR (neat) C=O 1732 (s) cm^{-1}; ^{1}H NMR δ 0.88 (t, 3, J = 6 Hz, Me), 1.1–1.7 (m, 8, methylenes), 1.50 (s, 3, c-Pr Me), 2.0–2.6 (m, 3, $COCH_2$, COCH), 3.40, 3.46 (s, 3 each, methoxyls), 4.1–4.2, 4.7–4.8 (m, 1, OCH for two isomers). A mixture of the ketone and 10 mL of 2 N hydrochloric acid in 40 mL of methylene chloride was stirred for 1 h and then neutralized with sodium bicarbonate solution. Upon separation the aqueous solution was extracted with methylene chloride. The combined extract and organic reaction solution were dried and evaporated, leaving 1.12 g (73% two-step yield) of liquid diketone **11b**: IR (neat) C=O 1705 (s) cm^{-1}; ^{1}H NMR δ 0.87 (t, 3, J = 6 Hz, Me), 1.1–1.8 (m, 8, methylenes), 2.22 (s, 3, COMe), 2.43 (t, 2, J = 7 Hz, C-6 Hs), 2.75 (d, 2, J = 6 Hz, C-4 Hs), 3.41 (s, 3, OMe), 4.08 (t, 1, J = 6 Hz, OCH). Anal. ($C_{12}H_{22}O_3$) C, H.

Tetrahydropyrethrolone Methyl Ether (13c). A mixture of 250 mg of diketone **11b** and 2.5 mL of 2% sodium hydroxide solution in 5 mL of methanol was stirred at room temperature under argon for 1 h. It then was acidified with saturated ammonium chloride solution and extracted with ether. The extract was dried and evaporated. Chromatography of the residue on silica gel and elution with 4:1 hexane–ethyl acetate afforded 189 mg (88%) of liquid keto ether **13c**: IR (neat) C=O 1711 (s) cm^{-1}; ^{1}H NMR δ 0.87 (t, 3, J = 7 Hz, Me), 1.1–1.5 (m, 6, methylenes), 2.02 (s, 3, olefinic Me), 2.17 (t, 2, J = 6 Hz, allyl Hs), 2.33 (d, 1, J = 2 Hz, $COCH_2$ H trans to OMe), 2.52 (d, 1, J = 6 Hz, $COCH_2$ H cis to OMe), 3.39 (s, 3, OMe), 4.28 (dd, 1, J = 6, 2 Hz, OCH); semicarbazone: mp 122–123 °C (EtOH) (lit.[21] mp 122–123 °C).

Tetrahydropyrethrolone (13e). A 1.0 M methylene chloride solution of boron tribromide (1.5 mL) was added to a solution of 200 mg of keto ether **13c** in 5 mL of dry methylene chloride at −78 °C under argon, and the mixture was then allowed to warm to room temperature. Sodium bicarbonate solution was added and the mixture extracted with ether. The extract was washed with brine solution, dried, and evaporated under vacuum, leading to oily bromo ketone **13d**:[21] IR (neat) C=O 1708 (s), C=C 1638 (m) cm^{-1}; ^{1}H NMR δ 0.86 (t, 3, J = 7 Hz, Me), 1.1–1.5 (m, 6, methylenes), 2.15 (s, 3, olefinic Me), 2.17 (t, 2, J = 6 Hz, allyl Hs), 2.86 (d, 1, J = 2 Hz, $COCH_2$ H trans to Br), 2.96 (d, 1, J = 6 Hz, $COCH_2$ H cis to Br), 4.92 (dd, 1, J = 6, 2 Hz, BrCH). A solution of the bromo ketone and 400 mg of dry silver acetate in 5 mL of glacial acetic acid was refluxed for 45 min and the silver salts were then filtered. The filtrate was neutralized with sodium bicarbonate solution and extracted with ether. The extract was dried and evaporated, leading to tetrahydropyrethrolone acetate (**4**, Y = OAc). A solution of the latter in 5 mL of ethanol was mixed with 5 mL of a 0.5 M potassium carbonate solution and the mixture was stirred under argon at room temperature for 3 h. Water was added and the mixture was extracted with ether. The extract was dried and evaporated. Silica gel chromatography of the residue and elution with 3:1 hexane–ethyl acetate afforded 136 mg (73% overall yield) of liquid tetrahydropyrethrolone (**13e**): IR (CCl_4) OH 3405 (br m), C=O 1705 (s), C=C 1650 (m) cm^{-1}; ^{1}H NMR δ (CCl_4) 0.89 (t, 3, J = 7 Hz, Me), 1.1–1.6 (m, 6, methylenes), 2.01 (s, 3, olefinic Me), 2.09 (t, 2, J = 6 Hz, allyl Hs), 2.17 (d, 1, J = 2 Hz, $COCH_2$ H trans to OH), 2.52 (d, 1, J = 6 Hz, $COCH_2$ H cis to OH), 4.58 (dd, 1, J = 6, 2 Hz, OCH); semicarbazone: mp 173–174 °C (EtOH) (lit.[21] mp 172–173 °C).

Acknowledgment. E. W. and M.S.R. acknowledge gratefully support of the work at Rice University by the Robert A. Welch Foundation.

Registry No. 1, 50394-84-8; **3**, 58237-58-4; **4** (Y = OAc), 90428-68-5; **5**, 543-75-9; **6a**, 60170-67-4; **6b**, 98735-97-8; *cis*-**7a**, 98735-98-9; *trans*-**7a**, 98735-99-0; *cis*-**7b**, 98736-00-6; *trans*-**7b**, 98736-01-7; *cis*-**7c**, 98736-02-8; *trans*-**7c**, 98736-03-9; *cis*-**7d**, 98736-04-0; *trans*-**7d**, 98736-05-1; **8a**, 7062-96-6; **8b**, 61860-76-2; **8c**, 98736-06-2; **8d**, 7062-97-7; **8e**, 98736-07-3; **8f**, 98736-08-4; **9a**, 98736-09-5; **9b**, 98736-10-8; **9c**, 98736-11-9; **9d**, 98736-12-0; **10b**, 98736-13-1; **11a**, 98736-14-2; **11b**, 98736-16-4; **12a**, 78986-03-5; **12b**, 98818-31-6; **13a**, 78986-05-7; **13b**, 36627-22-2; **13c**, 98736-17-5; **13d**, 98736-18-6; **13e**, 28797-01-5; i, 872-36-6; ii, 98736-19-7; iii, 98736-20-0; iv, 98736-21-1; N_2CHCO_2Et, 623-73-4; $N_2CHCOMe$, 2684-62-0; MeBr, 74-83-9; $H_3C(CH_2)_3Br$, 109-65-9; MeI, 74-88-4; $N_2CHCOCO_2Et$, 14214-10-9; $N_2C(CO_2Me)_2$, 6773-29-1; 3-methoxy-5-butyl-2,5-dihydroxytetrahydrofuran, 98736-15-3.