Ozonolysis of Cyclic Enol Ethers: An Efficient Strategy to Aldol and Homoaldol Compounds

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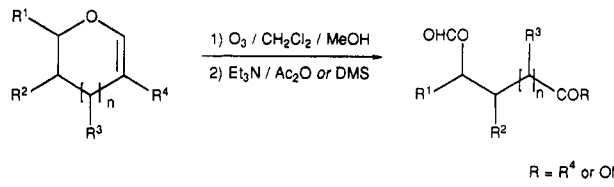
Received November 24, 1992

In our ongoing studies to develop asymmetric, catalytic methodology to functionalized acyclic compounds, we envisioned substituted cyclic enol ethers 1 as direct precursors to aldol and homoaldol products. Since a variety of catalytic,[1] as well as noncatalytic,[2] methods to enantiomerically enriched dihydrofurans and dihydropyrans are known, we investigated the possibility of their oxidative ring opening by ozonolysis to develop a new access to aldol[3] and homoaldol[4] products.

Although enol ethers play an important role in synthetic chemistry, their ozonolysis has not widely been studied.[5] In particular, there are only a few accounts on the ozonolysis of cyclic enol ethers.[6] Nevertheless, Danishefsky[7] et al. have noted that dihydro-γ-pyrones can be unmasked as *aldol* compounds by ozonolysis. In this paper we wish to report that dihydropyrans 1 ($n = 1$) are excellent equivalents for *homoaldol* as well as dihydrofurans 3 ($n = 0$) for *aldol* compounds.

Our results are summarized in Table I. Since ozonolysis of 3,4-dihydro-2*H*-pyran under reductive conditions leads to a mixture of products,[6d] it was desirable for the cleavage



of β-unsubstituted enol ethers to create a stable ester[8] rather than an aldehyde functionality. Therefore, the dihydropyrans **1d–f**, as well as the dihydrofurans **3** were ozonolyzed in a dichloromethane/methanol mixture under conditions developed by Schreiber[9] for carbocycles. According to this procedure the hydroperoxides, which are generated in situ, are dehydrated with triethylamine/acetic anhydride after azeotropic removal of methanol with benzene. These conditions could be successfully applied to cyclic enol ethers; however, it was discovered that the removal of methanol can be omitted with equally good results. *This variation is especially useful for large-scale preparations, since the hydroperoxides which result from the ozonolysis of e.g. **3a** are very explosive and should only be handled at low temperatures.* Thus, the 3-formyloxy ester **4a** was conveniently prepared by this protocol (entry 10) as the sole product. Also, 3,4-dihydro-6-phenyl-2*H*-pyran (**1e**) (entry 8) gave rise to the 4-formyloxy ester **2e** in 91% isolated yield accompanied by minor amounts (<3% as judged by ^{1}H NMR of the crude) of an unidentified byproduct. In an even better yield (94%) the 3-formyloxy ester **4b** was obtained through ozonolysis of 5-phenyl-2,3-dihydrofuran **3b** (entry 11). Cinnamylaldehyde was identified as the only byproduct (<3% by ^{1}H NMR).

Chiral dihydrofurans and dihydropyrans are opened under the applied conditions without loss of optical purity (entries 9 and 11). Multiple functionalized dihydropyran derivatives with usual protecting groups are also readily transformed into the corresponding acyclic compounds by ozonolysis (entries 4, 5, and 9).[10] Moreover, the resulting products are stable to epimerization, since e.g. in **4b** the formyl group prevents racemization via a retroaldol/aldol process.

To test the limits of this fragmentation, a series of vinyl-substituted dihydropyrans were subjected to ozonolysis (entries 1–3, 6, 7). In all cases a selective cleavage of the electron-rich enol ether double bond[11] was observed. Derivatives **1a**, **1b-CO$_2$Et**, and **1d-CO$_2$Et**, substituted by an electron-withdrawing group, readily gave rise to the allylformates **2a**, **2b-CO$_2$Et**, and **2d-CO$_2$Et** in high yields (81, 95, and 96%, respectively). Best results were obtained to use a slight excess (≈1.1 equiv) of ozone to reach complete conversion of the starting material. No side reactions, especially no cleavage of the remaining double bond, were observed under these conditions. For the ozonolysis of **1b-Ph** and **1d-Ph**, however, it was crucial to use just 1 equiv of ozone and to carry out the reaction in a rapidly stirred vessel in order to achieve a selective cleavage of the enol ether double bond.[12] This way **2b-Ph**

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(2) (a) Kinoshita, T.; Hirano, M.; Yoshida, N. *Synthesis* **1991**, 384–386. (b) Ireland, R. E.; Wilcox, C. S.; Thaisrivongs, S. *J. Org. Chem.* **1978**, *43*, 786–787. (c) Fraser-Reid, B. *Acc. Chem. Res.* **1985**, *18*, 347–354. (d) Holder, N. L. *Chem. Rev.* **1982**, *82*, 287–332.

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(5) (a) Griesbaum, K.; Kim, W.-S. *J. Org. Chem.* **1992**, *57*, 5574–5577. (b) Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335–362. (c) Griesbaum, K.; Kim, W.-S.; Nakamura, N.; Mori, M.; Nojima, M.; Kusabayashi S. *J. Org. Chem.* **1990**, *55*, 6153–6161. (d) Keul, H.; Kuckowski, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 5370–5371. (e) Mori, M.; Tabuchi, T.; Nojima, M.; Kusabayashi, S. *J. Org. Chem.* **1992**, *57*, 1649–1652. (f) Wojciechowski, B. J.; Chiang, C.-Y.; Kuczkowski, R. L. *J. Org. Chem.* **1989**, *55*, 1120–1122. (g) Bailey, P. S. *Ozonisation in Organic Chemistry*; Academic Press, Inc.: New York, 1982; Vol. 39-II.

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(7) Danishefsky, S.; Kato, N.; Askin, D.; Kerwin, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 360–362.

(8) Cf. Marshall, J. A.; Garofalo, A. W.; Sedrani, R. C. *Synlett* **1992**, 643–645.

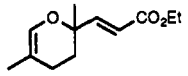
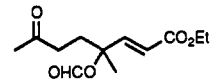
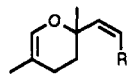
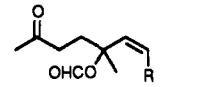
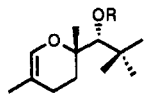
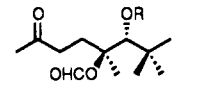
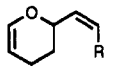
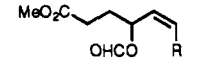
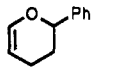
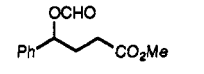
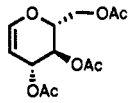
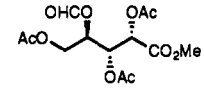
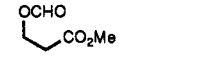
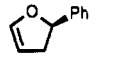
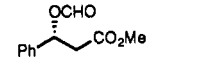
(9) Schreiber, S. L.; Claus, R. E.; Reagan, J. *Tetrahedron Lett.* **1982**, *23*, 3867–3870.

(10) The ozonolysis of the unprotected derivative **1c-H**, however, resulted only in mixtures of oxidized products.

(11) Cf. Corey, E. J.; Katzenellenbogen, J. A.; Gilman, W. W.; Roman, S. A.; Erickson, B. W. *J. Am. Chem. Soc.* **1968**, *90*, 5618–5620.

0022-3263/93/1958-3169$04.00/0

Table I. Ozonolysis of Cyclic Enol Ethers

entry	enol ether	method[a]	product	yield, %[b]
1	 **1a**	A	 **2a**	81
2	 **1b-CO_2Et**	A	 **2b-CO_2Et**	95
3	**1b-Ph**	A	**2b-Ph**	79
4	 **1c-Ac**[c]	A	 **2c-Ac**[c]	69
5	**1c-$SiMe_3$**[c]	A	**2c-$SiMe_3$**[c]	88
6	 **1d-CO_2Et**	B	 **2d-CO_2Et**	96
7	**1d-Ph**[d]	B	**2d-Ph**[d]	76
8	 **1e**	B	 **2e**	91
9	 **1f**	B	 **2f**	77
10	 **3a**	B	 **4a**	66
11	 **3b**[e]	B	 **4b**[e]	94

[a] The ozonolysis was carried out in mixtures of dichloromethane/methanol at −78 °C. Method A: workup with dimethyl sulfide. Method B: workup with triethylamine/acetic anhydride. [b] Isolated yield. [c] 1:1 mixture of enantiomers. [d] 6:1 mixture of (*Z*)/(*E*) isomers. [e] 71% ee according to GC analysis.

and **2d-Ph** were obtained in 79 and 76% yield, respectively, along with about 10% of unchanged starting materials, which were easily separated by chromatography. γ-Oxygenated α,β-unsaturated carbonyl compounds and allyl alcohols like **2a,b,d** have been recognized as important intermediates for organic synthesis.[13] In addition, allyl formates are potential precursors for allyl vinyl ethers, which can be further transformed by Claisen rearrangements.[14]

In summary, the strategy described here to prepare formyl-protected aldol and homoaldol compounds should be useful because of the mild reaction conditions under which the products are obtained and the high regioselectivity of the fragmentation. The aldol and homoaldol products are obtained as formyloxy esters, which appears to be advantageous with regard to the stability of optically pure compounds. Nevertheless, the formyl group can selectively be removed even in the presence of acetate groups with secondary amines. In the case of the 4-formyloxy esters, an acid-catalyzed transesterification to the corresponding γ-lactones can be carried out. Both transformations proceed quantitatively in most cases.[15]

Experimental Section

The ozonolyses were performed on a Fischer ozone generator (Model 502). Calibration of the ozone apparatus was carried out by treating 20 mmol of 3,4-dihydro-2*H*-pyran with ozone according to the described proedure (see below) at a constant flow of oxygen (55L/h) at a constant current (50 V, 0.06 A) until the mixture aquired just slightly the characteristic blue color of ozone (41 min ≅ 0.5 mmol of ozone/min).

General Procedure for the Ozonolysis of Cyclic Enol Ethers 1 and 3. A solution of 20 mmol of the enol ether, 170 mg (2 mmol) of $NaHCO_3$, and 2 mL (50 mmol) of methanol in 25 mL of dichloromethane was treated with 1 equiv of ozone at −78 °C. Subsequently, 3 mL (40 mmol) of dimethyl sulfide (method A) or 3.5 mL (25 mmol) of triethylamine and 5 mL (53 mmol) of acetic anhydride (method B) were added and the mixture was allowed to warm up to room temperature and stirred for 12 h at this temperature. The mixture was extracted three times with 30 mL of water each, dried over magnesium sulfate, and concentrated; the residue was distilled or purified by filtration on silica gel.

4-(Formyloxy)-4-methyl-7-oxooct-2(*E*)-enoic acid ethyl ester (2a): a colorless oil; R_f 0.46 (50:50 hexane/ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.66 (s, 3 H, 4-methyl), 2.15 (s, 3 H, CH_3CO), 2.01–2.51 (m, 4 H, 5(6)-H), 4.22 (q, *J* = 7.2 Hz, 2 H, CO_2CH_2), 5.94 (d, *J* = 15.9 Hz, 1 H, olefin-H), 6.89 (d, *J* = 15.9 Hz, 1 H, olefin-H), 8.03 (s, 1 H, OCHO); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.07 (+, $CO_2CH_2CH_3$), 24.05 (+, 4-methyl), 29.85 (+, C-8), 33.18 (−, C-5*), 37.50 (−, C-6*), 60.62 (−, CO_2CH_2), 81.90 (C_{quat}, C-4), 120.51 (+, olefin-C), 148.68 (+, olefin-C), 165.74 (C_{quat}, C-1), 206.74 (C_{quat}, C-7); IR (neat) 1710 (CO) cm^{-1}; MS (EI (70 eV)) *m/e* 197 (24, $M^+ - C_2H_5O$), 151 (50, $M - H_2CO_2C_2H_5$), 43 (100). Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.87; H, 7.99.

4-(Formyloxy)-4-methyl-7-oxooct-2(*Z*)-enoic acid ethyl ester (2b-CO_2Et): a colorless oil; R_f 0.44 (50:50 hexane/ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.70 (s, 3 H, 4-methyl), 2.08 (s, 3 H, 8-H), 2.28 (m, 2 H), 2.49 (m, 2 H), 4.09 (q, *J* = 7.2 Hz, 2 H, $CO_2CH_2CH_3$), 5.73 (d, *J* = 13.1 Hz, 1 H, olefin-H), 6.06 (d, *J* = 13.1 Hz, 1 H, olefin-H), 7.92 (s, 1 H, OCHO); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.02 (+, $CO_2CH_2CH_3$), 23.82 (+, 4-methyl), 29.69 (+, C-8), 32.69 (−, C-5*), 37.93 (−, C-6*), 60.37 (−, CO_2CH_2), 83.44 (C_{quat}, C-4), 119.70 (+, C-2), 146.71 (+, C-3), 159.56 (+, OCHO), 165.25 (C_{quat}, C-1), 207.31 (C_{quat}, C-7); IR (neat) 1720 (CO) cm^{-1}; MS (EI (80 eV))

(12) A slight excess of ozone resulted in side products by additional cleavage of the remaining double bond which were difficult to separate from the products.

(13) (a) Ibuka, T.; Yamamoto, Y. *Synlett* **1992**, 769–777. (b) Oppolzer, W.; Radinov, R. N. *Helv. Chim. Acta* **1992**, *75*, 170–173.

(14) Reissig, H.-U. In *Organic Synthesis Highlights*; Mulzer, J., Altenbach, H.-J., Braun, M., Krohn, K., Reissig, H.-U., Eds.; VCH: Weinheim, 1991; pp 199–204.

(15) Reiser, O.; Niklaus, A.; Hillers, S. Unpublished.

m/e calcd for $C_{11}H_{17}O_3$ (M^+ – OCHO) 197.1177, found 197.1177; 197 (24, M^+ – OCHO), 151 (50, $M^+ - H_2CO_2C_2H_5$), 43 (100, CH_3CO).

5-(Formyloxy)-5-methyl-7-phenylhept-6(*Z*)-en-2-one (2b-Ph): a colorless oil; R_f 0.59 (50:50 hexane/ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.49 (s, 3 H, 5-methyl), 2.13 (s, 3 H, CH_3CO), 2.14 (m, *J* = 7.7 Hz, 2 H, CH_2CH_2CO), 2.53 (t, *J* = 7.7 Hz, 2 H, CH_2CO), 5.75 (d, *J* = 12.8 Hz, 1 H, olefin-H), 6.60 (d, *J* = 12.8 Hz, 1 H, olefin-H), 7.22–7.35 (m, 5 H, phenyl-H), 7.81 (s, 1 H, OCHO); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 25.50 (+, 5-methyl), 29.88 (+, C-1), 34.73 (–, C-3*), 38.07 (–, C-4*), 82.87 (C_{quat}, C-5), 127.20 (+, olefin-C), 127.91 (+, phenyl-C), 128.66 (+, phenyl-C), 130.42 (+, phenyl-C), 133.50 (+, olefin-C), 136.65 (C_{quat}, phenyl-C), 159.71 (+, OCHO), 207.49 (C_{quat}, C-2); IR (neat) 1720 (CO) cm^{-1}; MS (EI (70 eV)) *m/e* 246 (3, M^+), 200 (29, M – HCO_2H), 157 (100), 142 (78), 129 (97). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.08; H, 7.42.

5-(Formyloxy)-5,7,7-trimethyl-6-acetoxyoctan-2-one (2c-Ac): a colorless oil; (R_f 0.26 (80:20 hexane/ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.05 (s, 9 H, $C(CH_3)_3$), 1.63 (s, 3 H, 5-methyl), 2.11 (s, 3 H, OAc*), 2.14 (s, 3 H, CH_3COCH_2*), 2.12–2.19 (m, 2 H, CH_2), 2.36–2.70 (m, 2 H, CH_2), 5.13 (s, 1 H, 6-H), 7.99 (s, 1 H, OCHO); ^{13}C NMR (250 MHz, $CDCl_3$) δ 20.81 (+), 22.72 (+), 28.39 (+, $C(CH_3)_3$), 29.96 (+, C-1), 30.58 (–), 36.20 (C_{quat}, $C(CH_3)_3$), 37.62 (–), 79.22 (+, C-6), 86.74 (C_{quat}, C-5), 159.57 (+, OCHO), 170.22 (C_{quat}, $OCOCH_3$), 207.32 (C_{quat}, C-2); IR (neat) 1725 (CO) cm^{-1}; MS (EI (70 eV)) *m/e* 215 ($M^+ - C_4H_9$, 16). Anal. Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.88; H, 8.92.

5-(Formyloxy)-5,7,7-trimethyl-6-(trimethylsiloxy)octan-2-one (2c-SiMe$_3$): a colorless oil; bp 150°/0.5 mmHg; R_f 0.3 (5:1 hexane/ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.13 (s, 9 H, $SiMe_3$), 0.97 (s, 9 H, $C(CH_3)_3$), 1.46 (s, 3 H, CH_3), 2.03 (m, 1 H), 2.12 (s, 3 H, CH_3), 2.32 (m, 1 H), 2.45 (m, 2 H), 3.87 (s, 1 H, 6-H), 8.00 (s, 1 H, OCHO); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 0.80 (+, $SiMe_3$), 21.86 (+, CH_3), 28.51 (+, $C(CH_3)_3$), 29.81 (+, CH_3), 31.12 (–), 36.58 (C_{quat}, $C(CH_3)_3$), 37.92 (–), 81.92 (+, C-6), 88.89 (C_{quat}, C-5), 160.29 (+, OCHO), 207.69 (C_{quat}, C-2); IR (neat) 1715 (CO) cm^{-1}; MS (EI (70 eV)) *m/e* 245 (17, $M^+ - C_4H_9$), 199 (39, $M - C_4H_9HCO_2H$), 159 (100, $C_4H_9CHOSiMe_3$). Anal. Calcd for $C_{15}H_{30}O_4Si$: C, 59.56; H, 10.01. Found: C, 59.54; H, 10.02.

4-(Formyloxy)-4-hept-2(*Z*)-enedioic acid 1-ethyl ester 7-methyl ester (2d-CO$_2$Et): a colorless oil R_f 0.13 (10:1 hexane/ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 2.02–2.11 (m, 2 H), 2.39–2.45 (m, 2 H), 3.66 (s, 3 H, CO_2CH_3), 4.18 (q, *J* = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 5.86 (d, *J* = 11.5 Hz, 1 H, olefin-H), 6.05 (dd, *J* = 11.5, 7.8 Hz, 1 H, olefin-H), 6.35 (m, 1 H, 4-H), 8.04 (s, 1 H, OCHO); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.10 (+, $CO_2CH_2CH_3$), 28.89 (–), 29.72 (–), 51.66 (+, CO_2CH_3), 60.57 (– $CO_2CH_2CH_3$), 70.53 (+, C-4), 121.61 (+, olefin-C), 145.41 (+, olefin-C), 160.14 (+, OCHO), 165.08 (C_{quat}), 173.01 (C_{quat}); IR (neat) 1720 (CO) cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 54.19; H, 6.15.

4-(Formyloxy)-6-phenylhex-5(*Z*)-enoic acid methyl ester (2d-Ph) (6:1 mixture of (*Z*)/(*E*) isomers): a colorless oil; R_f 0.15 (10:1 hexane/ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.93–2.16 (m, 2 H), 2.33–2.39 (m, 2 H), 3.62 (s, 3 H, CO_2CH_3 (cis)), 3.65 (s, 3 H, CO_2CH_3 (trans)), 5.59 (dd, *J* = 11.7, 9.3 Hz, 1 H, 5-H (cis)), 5.79–5.92 (m, 1 H, 4-H), 6.11 (dd, *J* = 15.9, 7.3 Hz, 1 H, 5-H (trans)), 6.63 (d, *J* = 11.7 Hz, 1 H, 6-H (cis)), 6.65 (d, *J* = 15.8 Hz, 1 H, 6-H (trans)), 7.23–7.40 (m, 5 H, phenyl-H), 8.02 (s, 1 H, OCHO(cis)), 8.09 (s, 1 H, OCHO(trans)); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 29.50 (–), 29.86 (–), 51.64 (+, CO_2CH_3), 70.09 (+, C-4), 127.57 (+), 128.45 (+), 128.48 (+), 128.64 (+), 132.95 (+), 135.81 (C_{quat}), 160.14 (+, OCHO), 172.97 (C_{quat}, CO_2CH_3); IR (neat) 1730 (CO) cm^{-1}; MS (EI (70 eV)) *m/e* 219 (35, M^+ – CHO), 188 (25, M – HCO_2Me), 128 (100). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.70; H, 6.57.

4(Formyloxy)-4-phenylbutanoic acid methyl ester (2e): bp 90 °C/0.1–0.2 mmHg; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.06–2.49 (m, 4 H, 2(3)-H), 3.63 (s, 3 H), CO_2CH_3), 5.89 (t, *J* = 6.4 Hz, 1 H, 4-H), 7.30 (m, 5 H, phenyl-H), 8.07 (s, 1 H, OCHO); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 29.79 (–, C-2*), 31.09 (–, C-3*), 51.51 (+, CO_2CH_3), 74.60 (+, C-4), 126.28 (+, phenyl-C), 128.19 (+, phenyl-C), 128.47 (+, phenyl-C), 138.99 (C_{quat}, phenyl-C), 160.03 (+, OCHO), 172.80 (+, C-1); IR (neat) 1730 (CO) cm^{-1}; MS (EI (70 eV)) *m/e* calcd for $C_{12}H_{13}O_4$: 222.0892, found 222.0892; 222 (9, M^+), 194 (19, M – CO), 163 (15, M – CO_2Me), 43 (100, CH_3CO). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.12; H, 6.24.

(2*S*,3*R*,4*R*)-4-(Formyloxy)-2,3,5-triacetoxypentanoic acid methyl ester (2f): white needles, mp 52 °C; bp 150°C/0.001 Torr mmHg; $[\alpha]^{20}_D$ +38.1° (*c* = 1.16, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.99 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 2.10 (s, 3 H, OAc), 3.66 (s, 3 H, CO_2Me), 4.12 (dd, *J* = 12.6, 4.8 Hz, 1 H, 5-H), 4.25 (dd, *J* = 12.6, 2.5 Hz, 1 H, 5′-H), 5.16 (d, *J* = 2.1 Hz, 1 H, 2-H), 5.34 (m, 1 H, 4-H), 5.58 (d, *J* = 9.0, 2.1 Hz, 1 H, 3-H), 7.97 (s, 1 H, OCHO); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 20.31 (+, CH_3CO), 20.37 (+, CH_3CO), 20.59 (+, CH_3CO), 52.78 (+, CH_2CH_3), 61.47 (–, C-5), 67.63 (+, C-2*), 68.34 (+, C-3*), 69.34 (+, C-4*), 159.17 (+, OCHO), 167.29 (C_{quat}, CO_2Me), 169.18 (C_{quat}, CH_3CO), 169.99 (C_{quat}, CH_3CO), 170.52 (C_{quat}, CH_3CO); IR (CCl_4) 1720–1740 (CO) cm^{-1}; MS (EI (70 eV)) *m/e* 275 (9, M^+ – CH_3CO), 261 (4, M – CH_3COCH_2), 203 (30, M – $CH_3COCHCO_2CH_3$), 43 (100, CH_3CO). Anal. Calcd for $C_{13}H_{18}O_{10}$: C, 46.71; H, 5.43. Found: C, 46.79; H, 5.31.

3-(Formyloxy)propionic acid methyl ester (4a): a colorless liquid; bp 171 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.53 (t, *J* = 6.2 Hz, 2 H, 2-H), 3.53 (s, 3 H, CO_2Me), 4.25 (t, *J* = 6.2 Hz, 2 H, 3-H), 7.86 (s, 1 H, OCHO); ^{13}C NMR (60 MHz, $CDCl_3$) δ 33.27 (–, C-2), 51.69 (+, CO_2CH_3), 59.07 (–, C-3), 169.45 (+, OCHO), 170.64 (C_{quat}, C-1); IR (neat) 1720 (CO) cm^{-1}; MS (EI (70 eV)) *m/e* 103 (19, M^+ – CHO), 101 (31, M – OCH_3), 87 (22, M – OCHO), 55 (100, CH_2CHCO). Anal. Calcd for $C_5H_8O_4$: C, 45.46; H, 6.10. Found: C, 45.60; H, 6.14.

3-(Formyloxy)-3-phenylpropionic acid methyl ester (4b): bp 75 °C/0.1–0.2 mmHg; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.79 (dd, *J* = 16.1, 4.9 Hz, 1 H, 2-H), 3.02 (dd, *J* = 16.1, 9.1 Hz, 1 H, 2-H), 3.67 (s, 3 H, CO_2CH_3), 6.28 (dd, *J* = 9.1, 4.9 Hz, 1 H, 3-H), 7.36 (m, 5 H, Phenyl-H), 8.04 (s, 1 H, OCHO); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 40.91 (–, C-2), 51.83 (+, CO_2CH_3), 71.86 (+, C-3), 126.41 (+, phenyl-C), 128.55 (+, phenyl-C), 128.62 (+, phenyl-C), 138.41 (C_{quat}, phenyl-C), 159.69 (+, OCHO), 169.97 (C_{quat}, C-1); IR (neat) 1720 (CO) cm^{-1}; MS (EI (70 eV)) *m/e* 208 (33, M^+), 180 (42, M – CO), 148 (57, M – HCO_2Me), 131 (100, M – Ph). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.80. Found: C, 63.60; H, 5.81.

Acknowledgment. Financial support of the Deutsche Forschungsgemeinschaft (RE 948/1-2) and of Fonds der Chemischem Industrie as well as generous chemical gifts of BASF, Degussa, and Fluka are gratefully acknowledged. O.R. thanks the Deutsche Forschungsgemeinschaft for a Habilitationsstipendium. For the GC analysis of **4b** we are indebted to Prof. W. König and B. Gehrcke, Universität Hamburg.