1.7 (d, J = 4 Hz, 6 H); MS m/e 166 (M^+), 97, 82, 69, 43. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.55; H, 8.54.

(1*E*,7*E*)-1,8-Diphenylocta-1,7-diene-3,6-dione (2j): ot 160–165 °C (1 mmHg); IR (Nujol) 1700, 1670, 1620, 1580, 1500, 970 cm^{-1}; ^1H NMR (CCl_4) δ 7.3 (d, J = 16 Hz, 2 H), 7.0 (m, 10 H), 6.5 (d, J = 16 Hz, 2 H), 2.7 (s, 4 H); MS m/e 290 (M^+), 144, 131, 103, 77, 55. Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.88; H, 6.21.

(1*E*)-1-Phenyl-1-heptene-3,6-dione (2k): ot 165–170 °C (0.5 mmHg) (lit.[33] bp 127–128 °C (0.3 mmHg); IR (Nujol) 1720, 1690, 1660, 1610, 1580, 1500, 1000, 760, 700 cm^{-1}; ^1H NMR (200 MHz) δ 7.6 (d, J = 16 Hz, 1 H), 7.4 (m, 5 H), 6.7 (d, J = 16 Hz, 1 H), 3.0–2.7 (m, 4 H), 2.2 (s, 3 H); MS m/e 202 (M^+), 144, 132, 103, 91, 77, 55, 43.

(1*E*,4*E*)-1-Phenyl-6-hydroxy-1,4-heptadien-3-one (15k): ot 150 °C (1.5 mmHg); IR (neat) 3400, 3010, 1660, 1640, 1580, 1500 cm^{-1}; ^1H NMR (CCl_4) δ 7.6 (d, J = 16 Hz, 1 H), 7.4 (m, 5 H), 7.1 (dd, J = 16, 3 Hz, 1 H), 6.9 (d, J = 16 Hz, 1 H), 6.5 (d, J = 16 Hz, 1 H), 4.5 (m, 1 H), 2.1 (s, 1 H), 1.3 (d, J = 5 Hz, 3 H); MS m/e 202 (M^+), 201, 186, 131, 103, 91, 77, 43. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.93. Found: 77.44; H, 6.63.

(2*E*)-2-Undecene-4,7-dione (21): ot 120–130 °C (1 mmHg); IR (neat) 3050, 1720, 1680, 1640, 970 cm^{-1}; ^1H NMR (CCl_4) δ 6.8 (dq, J = 16, 4 Hz, 1 H), 6.0 (d, J = 16 Hz, 1 H), 2.6–2.2 (m, 6 H), 1.8 (d, J = 4 Hz, 3 H), 1.4–1.1 (m, 4 H), 0.9 (t, J = 7 Hz, 3 H); MS m/e 182 (M^+), 167, 140, 125, 97, 85, 69, 57, 43. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.97; H, 9.67.

Transformation of 15h into 2h. A mixture of **15h** (50 mg, 0.25 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (7 mg, 0.0125 mmol), n-Bu_3P (5 mg, 0.025 mmol), and acetonitrile (2 mL) was refluxed for 16 h. Following a workup similar to that described above, **2h** was isolated, yield: 41 mg (82%). Similarly, **2k** was obtained from **15k** in 75% yield after refluxing for 20 h.

^1H NMR Studies of the Reaction. Under Ar, a mixture of **1a** (11 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (10 mg, 0.02 mmol), n-Bu_3P (8 mg, 0.04 mmol), and $CDCl_3$ (0.5 mL) was placed into a 5-mm NMR tube; then it was sealed and preserved at rt for 8 h. Three multiplet signals appeared at δ = −12.9, −16.2, and −18.7 when the sample was measured on the Varian XL-200 spectrometer.

Acknowledgment. We thank the National Natural Science Foundation of China and Academia Sinica for financial support.

Registry No. **1a**, 3031-66-1; **1b**, 24434-07-9; **1c**, 135468-08-5; **1d**, 105653-97-2; **1e**, 4482-17-1; **1f**, 135468-12-1; **1g**, 135468-06-3; **1h**, 135468-05-2; **1i**, 135468-07-4; **1j**, 135468-10-9; **1k**, 135468-09-6; **1l**, 135468-11-0; **2a**, 110-13-4; **2b**, 2955-65-9; **2c**, 110743-58-3; **2d**, 7018-92-0; **2e**, 495-71-6; **2f**, 583-05-1; **2g**, 2108-54-5; **2h**, 123183-95-9; **2i**, 135468-13-2; **2j**, 135468-14-3; **2k**, 120760-00-1; **2l**, 135468-15-4; $IrH_5(i\text{-}Pr_3P)_2$, 53470-70-5; $Pd_2(dba)_3{\cdot}CHCl_3$, 52522-40-4; Bu_3P, 998-40-3; Ph_3P, 603-35-0; $Pd(OAc)_2$, 3375-31-3.

(33) Stetter, H.; Hilboll, G.; Heinrich, K. *Chem. Ber.* **1979**, *112*, 84.

Synthesis of α-Methylene β-Lactones, Novel Heterocycles

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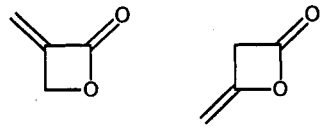
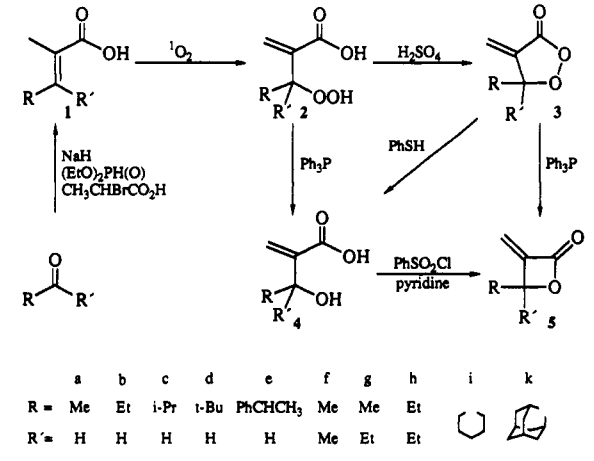
Triphenylphosphine deoxygenation of β-alkyl, β,β-dialkyl-, and β,β-spirocycloalkyl-substituted α-methylene-β-peroxy lactones **3a–k**, which are readily available by photooxygenation of the corresponding α,β-unsaturated carboxylic acids **1**, and cyclization of the resulting α-methylene-β-hydroperoxy acids **2** constitute a convenient method for the preparation of a variety of α-methylene β-lactones **5**. Alternatively, the α-methylene-β-hydroxy carboxylic acids **4** can be directly cyclized by benzenesulfonyl chloride in pyridine into these novel four-membered ring heterocycles **5**.

Ketene dimers (β-methylene β-lactones) have been known for a long time and play a prominent role in organic synthesis.[1] It is surprising that the regioisomeric α-methylene β-lactones are essentially unknown;[2] hitherto no general preparative method existed for this novel heterocycle.



In anticipation that this highly functionalized oxetane ring system could serve as a useful building block, we devised the reaction sequence in Scheme I as a general method of preparation, which makes these labile compounds readily available for the first time. Decisive in this synthetic methodology was convenient access[3] to the α-

Scheme I. Synthetic Pathways to α-Methylene β-Lactones 5



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[⊥] Doctoral Thesis, University of Würzburg, April 1990.
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Table I. Reaction Conditions, Isolation Methods, Yields, and Physical Constants of α-Methylene-β-peroxy Lactones 3[a]

α-methylene-β-peroxy lactone	time			column chromatography[e]			yields (%)	ot (°C) (Torr)[g,h]
	photoox[b]	cycl[c]	isolation method[d]	ratio[f]	temp (°C)	R_f value		
3b	48 h	48 h	A/B	50:1	0	0.65[i]	50	50 (0.1)
3c	48 h	6 h	A/B	50:1	0	0.62[i]	57	50 (0.1)
3d	4 d	24 h	A/B	20:1	20	0.68	12	55 (0.1)
3e[j]	6 d	24 h	A/B	10:1	20	0.68	17[k]	90 (0.1)
3g	48 h	24 h	A/B	10:1	20	0.68	47	50 (0.1)
3h	48 h	48 h	A/B	10:1	20	0.69	53	55 (0.1)
3i	14 h	24 h	A/B	15:1	20	0.64	53	95 (0.1)

[a] For **3a** and **3f**, cf. ref 3a,b and for **3k** ref 8. [b] 150-W sodium lamp, external irradiation at −5 to 0 °C, except **3i,k** for which a 400-W sodium lamp was used under internal irradiation at −5 to 0 °C. [c] 20 °C. [d] A: column chromatography. B: distillation. [e] CH_2Cl_2 as eluent, silica gel (32–63 μm). [f] Adsorbant to substrate ratio. [g] Kugelrohr distillation. [h] Microanalysis, cf. supplementary material. [i] Silica gel (63–230 μm). [j] dr 90:10, determined by NMR. [k] When the methyl ester was used instead of the carboxylic acid **1e**, the α-methylene-β-peroxy lactone **3e** was obtained in 93% overall yield.

methylene-β-peroxy lactones **3** through photooxygenation of the acrylic acid derivatives **1**, followed by acid-catalyzed cyclization, and our previously established[4] deoxygenation of cyclic peroxides by triphenylphosphine.

We now extend our preliminary results[3c] by showing that the reaction sequence in Scheme I constitutes a general preparation of these synthetically useful compounds to afford a variety of β-alkyl-, β,β-dialkyl-, and β-spirocycloalkyl-substituted derivatives. In the subsequent paper we describe transformations of the α-methylene β-lactones, which should be of preparative interest.

Results and Discussion

Acrylic acids **1b–k** were prepared by the Horner–Emmons–Wittig reaction and allowed to react with singlet oxygen (tetraphenylporphine (TPP) photosensitization) in $CHCl_3$ or CCl_4 to afford the β-hydroperoxy acids **2** (Scheme I). Cyclization of the latter by catalytic amounts of sulfuric acid gave the corresponding α-methylene-β-peroxy lactones **3** in 12–57% yields (see Table I).

The sequence **1** → **2** → **3** (Scheme I) constitutes an effective and general method for preparing the α-methylene-β-peroxy lactones **3** in good yields (up to 60% overall) and of analytical purity by microanalysis. The characterization of peroxides **3** rests mainly on IR and NMR spectral data. The carbonyl frequencies (1770–1795 cm^{-1}) are characteristic for such five-membered-ring cyclic peroxy lactones. Also, the proton chemical shifts at δ 5.7–5.8 and 6.2–6.4, except for derivatives **3e** (**3k**) at δ 4.99/5.42 (6.04) and δ 6.16/6.30 (6.35), the carbon resonances at δ 120–125 of the exomethylenic group, and the β-carbon of the β-peroxy lactone ring at δ 85–98 are in support of the proposed structure. In this way, these cyclic peroxides, which include β-alkyl-, β,β-dialkyl-, and β-spirocycloalkyl-substituted derivatives, have become available for the first time.

The high regioselectivity[3a,5] of the photooxygenation to afford exclusively the β-hydroperoxy acids **2** (Scheme I) by ene reaction at the α-methyl group of the acrylic acid derivatives **1** is of particular advantage in the preparation of these precursors for the α-methylene-β-peroxy lactones **3**. Bulky and branched β-alkyl substituents as in the cases **1d–e** required longer photooxygenation times, an established reactivity trend[6] for the ene reaction of singlet oxygen even for simple alkenes.

Table II. Reaction Conditions, Isolation Methods, Yields, and Physical Constants of α-Methylene β-Lactones 5[a]

α-methylene β-lactones	temp (°C)	time (min)	isolation[b] method	yield[c] (%)	ot (°C) (Torr)[d,e]
5a	−50	15	A[f]/B	34	30 (0.1)[g]
5b	−78	10	B	48	30 (0.1)
5c	−78	15	B	50 (13)	35 (0.1)
5d	−30	15	B	39	50 (0.1)
5e	−40	40	A	53 (41)	
5h	−45	15	B	9	55 (0.1)
5i	−45	15	B	40	95 (0.1)

[a] **5f** and **5g** were only spectroscopically detected and for **5k**, cf. ref 8. [b] A: column chromatography. B: distillation. [c] Yields in parentheses are for the $PhSO_2Cl$ in pyridine cyclization. [d] Kugelrohr distillation. [e] Microanalysis, cf. supplementary material. [f] Silica gel (32–63 μm), 50:1 adsorbant to substrate, 10:1:1 CH_2Cl_2/petroleum ether (30–50)/ether solvent mixture as elueant, at −30 °C, R_f 0.67. [g] Exact mass by mass spectrometry.

The deoxygenation of the α-methylene-β-peroxy lactones **3** with triphenylphosphine led to the desired α-methylene β-lactones **5** in yields of 34–53% in all but one case (see Table II). The α-methylene β-lactones **5** were characterized by their IR and NMR spectral data. The carbonyl frequencies at 1820–1845 cm^{-1} are characteristic for β-lactones; however, it should be noted that the additional ring strain caused by the exomethylenic substituent outweighs the α,β-conjugation effect. The proton chemical shifts (δ 5.4 and 5.9) and the carbon resonances of the exomethylenic group (δ 113–116) and the β-carbon of the β-lactone ring at δ 76–87 for the monosubstituted and δ 87–92 for the disubstituted cases confirm the structural assignment. For the spiroadamantyl system **5k**, the only crystalline derivative, an X-ray structure was determined (see ref 8). The planar β-lactone ring is clearly evident. Complete X-ray crystallographic data are provided in the supplementary material.

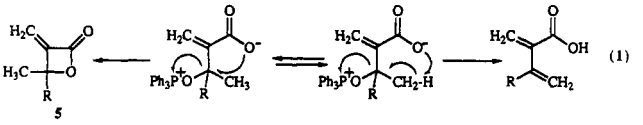
The triphenylphosphine deoxygenation of the β-peroxy lactones is effective for β-alkyl-monosubstituted derivatives **3a–e** to afford the corresponding α-methylene β-lactones **5a–e**. Attempts to improve the deoxygenation yields by using $(EtO)_3P$ or $(Me_2N)_3P$ failed in that even at low temperatures (−78 °C) only highly impure β-lactone **5** in low yields could be spectroscopically detected. The con-

(1) (a) Etienne, Y.; Fischer, N. In *The Chemistry of Heterocyclic Compounds*; A. Weissberger, Ed.; Wiley and Sons: New York, 1964; Vol. 19, Part II, pp 729–884.
(2) Lenz, R. W. *Pure Appl. Chem.* **1981**, *53*, 1729.
(3) (a) Adam, W.; Griesbeck, A. *Angew. Chem.* **1985**, *97*, 1071. (b) Adam, W.; Griesbeck, A.; Kappes, D. *J. Org. Chem.* **1986**, *51*, 4479. (c) Adam, W.; Hasemann, L.; Prechtl, F. *Angew. Chem.* **1988**, *100*, 1594.
(4) (a) Adam, W.; Narita, N.; Nishizawa, Y. *J. Am. Chem. Soc.* **1984**, *106*, 1843. (b) Adam, W.; Diehl, J. W. *J. Chem. Soc., Chem. Commun.* **1972**, 797.
(5) (a) Ensley, H. E.; Carr, R. V. C.; Martin, R. S.; Pierce, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 2836. (b) Orfanopoulos, M.; Foote, C. S. *Tetrahedron Lett.* **1985**, *26*, 5991.
(6) (a) Schulte-Elte, K. H.; Muller, B. L.; Rautenstrauch, V. *Helv. Chim. Acta* **1978**, *61*, 2777. (b) Schulte-Elte, K. H.; Rautenstrauch, V. *J. Am. Chem. Soc.* **1980**, *102*, 1738. (c) Orfanopoulos, M.; Grdina, M. B.; Stephenson, L. M. *Ibid.* **1979**, *101*, 275. Grdina, M. B.; Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 3111.
(7) Adam, W.; Baeza, J.; Liu, J.-C. *Ibid.* **1972**, *94*, 2000.
(8) Adam, W.; Hasemann, L. *Chem. Ber.* **1990**, *123*, 1449.

venience of the Ph_3P as deoxygenating agent derives from the ease of Ph_3PO removal by repetitive precipitation with petroleum ether.

Difficulties were encountered in the deoxygenation of the β,β-dialkyl-substituted derivatives **3f,g**, and only small amounts of highly impure β-lactones **5f,g** were obtained, which could not be purified for rigorous characterization. For this reason, the existence of these cases was only confirmed by spectral detection and comparison with the other isolated, pure α-methylene β-lactones. Fortunately, these difficulties were not experienced in the deoxygenation of the spirocycloalkyl-substituted derivatives **3i** and **3k** for which the pure β-lactones **5i** and **5k** (cf. ref 8) were obtained in reasonable yields.

Presumably, for the β,β-dialkyl-substituted cases **5f,g** with at least one methyl group, cyclization to the β-lactones is not able to compete with γ-hydrogen abstraction to afford the dienic acids (eq 1) as evidenced by the char-



acteristic carboxylic acid bands in the IR spectra. This competing elimination is suppressed for conformational reasons in the case of the β,β-diethyl and the β-spirocyclohexyl derivatives **3h** and **3i**. For the β-spiroadamantyl system **3k** γ-hydrogen abstraction is not possible because they are bridgehead hydrogens.

An established excellent method for the preparation of β-lactones is the cyclization of β-hydroxy acids with $PhSO_2Cl$ in pyridine.[7] This alternative route was employed for the synthesis of the α-methylene β-lactones **5c,e,k** (Table II) from their respective β-hydroxy carboxylic acids **4c,e,k** through the sequence **2** or **3** → **4** → **5** (Scheme I). The required hydroxy acids **4** were prepared by reduction of either the β-hydroperoxy acids **2** (cf. Experimental Section) or of the β-peroxy lactones **3**[8] or by coupling of the acrylate and aldehyde under DABCO catalysis[9] with subsequent saponification. While in the case of β-lactone **5k** superior yields were achieved for the direct cyclization method **4** → **5** ($PhSO_2Cl$/pyridine) compared to the deoxygenation method **3** → **5** (Ph_3P),[8] the inferior results are clearly evident for the β-lactones **5c,e**. As expected, the geminal effect of spiroadamantyl substitution promotes ring closure in the direct cyclization route **4** → **5**. The latter method should also be advantageous for α-methylene β-lactones without β-alkyl groups and for substituents at the exomethylene unit;[10,11] however, for the preparation of β-alkyl monosubstituted derivatives the deoxygenation of α-methylene-β-peroxy lactones is preferred.

Experimental Section

All melting points and boiling points are uncorrected. Solvents were purified according to standard procedures. All precautions must be taken when working with peroxides in view of their explosive nature.

α,β-Unsaturated Carboxylic Acids 1 (General Procedure). A mixture of 9.00 g (0.300 mmol) of NaH (80% suspension in paraffin oil) and 13.8 g (0.100 mmol) of diethyl phosphite in 250 mL of dry THF under N_2 was treated with a solution of 15.3 g (0.100 mmol) of α-bromopropionic acid in 100 mL of dry THF. After H_2 evolution had ceased, 0.100 mol of the desired aldehyde or ketone in 30 mL of dry THF was added and stirred for 2 d. After the addition of 10 mL of ethanol, the mixture was poured into 800 mL of water. The strongly basic solution was washed with methyl *tert*-butyl ether (MTB) to remove the paraffin oil (MTB extract was discarded), acidified to pH 2–3 with ca. 10% aqueous HCl, and extracted with MTB (3 × 150 mL). The latter MTB solution was washed with saturated NaCl solution (1 × 150 mL) and dried ($MgSO_4$) and the solvent evaporated (ca. 25 °C (15 Torr)). The crude product was purified by distillation or recrystallization. Below are given the spectral data and microanalyses of the hitherto unknown derivative **1e**, the others are reported in the literature.[12]

(*E*)-2,4-Dimethyl-4-phenyl-2-butenoic acid (1e): yield 9.50 g (50%); oven temp. 150 °C (0.1 Torr) (Kugelrohr); *E*:*Z* ratio = 98:2. ***E* Isomer:** ^1H NMR ($CDCl_3$, 200 MHz) δ 1.35 (d, *J* = 6.9 Hz, 3 H), 1.90 (d, *J* = 1.3 Hz, 3 H), 3.76 (dq, *J* = 9.9, 6.9 Hz, 1 H), 7.04 (dd, *J* = 9.9, 1.5 Hz, 1 H), 7.13–7.28 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 12.1 (q), 21.2 (q), 38.9 (d), 125.9 (s), 126.5 (d), 127.0 (d), 128.7 (d), 144.1 (s), 148.7 (d), 173.8 (s). ***Z* Isomer:** ^1H NMR ($CDCl_3$, 200 MHz) δ 1.35 (d, *J* = 6.9 Hz, 3 H), 1.90 (d, *J* = 1.3 Hz, 3 H), 4.18 (m, 1 H), 6.12 (dd, *J* = 10.0, 1.5 Hz, 1 H), 7.13–7.28 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.7 (q), 21.2 (q), 38.7 (d), 124.6 (s), 126.4 (d), 127.2 (d), 128.6 (d), 145.1 (s), 150.0 (s), 173.7 (s); IR (CCl_4) ν 3400–2500, 3015, 2970, 1690, 1640, 1295 cm^{-1}; MS (70 eV) *m*/*z* 190 (19) (M^+), 175 (2) ($M^+ - CH_3$), 145 (100) ($M^+ - COOH$), 130 (11) ($M^+ - CH_3 - COOH$), 77 (20) (C_6H_5). Anal. Calcd for $C_{12}H_{14}O_2$ (190.2): C, 75.76; H, 7.42. Found: C, 75.49; H, 7.43.

α-Methylene-β-peroxy Lactones 3 (General Procedure). A sample (8.00–32.5 mmol) of the particular α,β-unsaturated carboxylic acid **1** in 30–100 mL of $CHCl_3$ and a small amount of TPP (ca. 5 mg) were irradiated at 0 °C for 1 h to 6 d with a 150-W Philips G/98/2-SON (external irradiation) or a 400-W VIALOX NAV-TS 400-W sodium lamp (internal irradiation)[13] under continuous purging with dry oxygen gas. After addition of catalytic amounts (0.5 mL) of concd H_2SO_4 the solution was stirred at ca. 20 °C for 24–48 h, washed with water (1 × 30 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by Kugelrohr distillation or column chromatography. The reaction conditions, isolation methods, yields and physical constants for the individual cases are given in Table I, except **3a** and **3f** (ref 3a,b) and **3k** (ref 8).

5-Ethyl-4-methylene-1,2-dioxolan-3-one (3b): ^1H NMR (200 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.4 Hz, 3 H), 1.90 (m, 2 H), 5.28 (m, 1 H), 5.75 (dd, *J* = 2.4, 0.6 Hz, 1 H), 6.35 (dd, *J* = 2.6, 0.6 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 8.3 (q), 26.8 (t), 85.8 (d), 122.7 (t), 137.3 (s), 168.9 (s); IR (CCl_4) ν 3100, 2980, 1775, 1710 cm^{-1}.

4-Methylene-5-(1-methylethyl)-1,2-dioxolan-3-one (3c): ^1H NMR (200 MHz, $CDCl_3$) δ 1.03 (d, *J* = 6.8 Hz, 3 H), 1.04 (d, *J* = 6.8 Hz, 3 H), 2.08 (d septet, *J* = 6.8, 5.3 Hz, 1 H), 5.09 (dt, *J* = 5.2, 2.3 Hz, 1 H), 5.79 (d, *J* = 2.2 Hz, 1 H), 6.39 (d, *J* = 2.5 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.1 (q), 17.3 (q), 32.6 (d), 89.3 (d), 123.6 (t), 136.1 (s), 168.7 (s); IR (CCl_4) ν 3000, 2960, 1795, 1700 cm^{-1}.

5-(1,1-Dimethylethyl)-4-methylene-1,2-dioxolan-3-one (3d): ^1H NMR (200 MHz, $CDCl_3$) δ 1.01 (s, 9 H), 4.90 (t, *J* = 2.2 Hz, 1 H), 5.82 (d, *J* = 2.1 Hz, 1 H), 6.43 (d, *J* = 2.4 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.4 (3 × q), 36.0 (s), 91.6 (d), 124.8 (t), 135.2 (s), 168.8 (s); IR (CCl_4) ν 2960, 2905, 1780, 1665 cm^{-1}.

4-Methylene-5-(1-phenylethyl)-1,2-dioxolan-3-one (3e). Major diastereomer: ^1H NMR (250 MHz, $CDCl_3$) δ 1.45 (d, *J* = 7.0 Hz, 3 H), 3.06 (m, 1 H), 4.99 (d, *J* = 2.2 Hz, 1 H), 5.29 (dt, *J* = 7.9, 2.3 Hz, 1 H), 6.16 (d, *J* = 2.4 Hz, 1 H), 7.16–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$, 250 MHz) δ 16.9 (q), 44.6 (d), 88.4 (d), 124.6 (t), 127.6 (d), 128.1 (d), 128.8 (d), 135.6 (s), 140.1 (s), 168.5 (s). **Minor diastereomer:** ^1H NMR (250 MHz, $CDCl_3$) δ 1.40 (d, *J* = 7.4 Hz, 3 H), 3.29 (dt, *J* = 7.2, 5.8 Hz, 1 H), 5.39–5.45 (m, 2 H), 6.30 (d, *J* = 2.4 Hz, 1 H), 7.16–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.6 (q), 43.2 (d), 88.4 (d), 124.7 (t), 127.4 (d), 128.2 (d), 128.6 (d), 135.0 (s), 138.9 (s), 168.4 (s); IR (for the diastereomeric mixture) (CCl_4) ν 3090, 3075, 2975, 1784, 1670 cm^{-1}.

(9) Hoffmann, H. M. R.; Rabe, J. *Angew. Chem.* **1983**, *95*, 795.
(10) Campi, E. M.; Dyall, K.; Fallon, G.; Jackson, W. R.; Perlmutter, P.; Smallridge, A. J. *Synthesis* **1990**, 855.
(11) Adam, W.; Albert, R.; Hasemann, L.; Nava Salgado, V. O.; Nestler, B.; Peters, E.-M.; Peters, K.; Prechtl, F.; von Schnering, H. G. *J. Org. Chem.*, following paper in this issue.
(12) (a) Brittelli, D. R. *J. Org. Chem.* **1981**, *46*, 2514. (b) Coutrot, P.; Ghribi, A. *Synthesis* **1986**, 790.
(13) Adam, W.; Klug, G.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Tetrahedron* **1985**, *41*, 2045.

5-Ethyl-5-methyl-4-methylene-1,2-dioxolan-3-one (3g): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, J = 7.4 Hz, 3 H), 1.51 (s, 3 H), 1.82 (m, 2 H), 5.66 (d, J = 0.7 Hz, 1 H), 6.31 (d, J = 0.7 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 7.5 (q), 23.2 (q), 31.9 (t), 90.0 (s), 122.0 (t), 141.3 (s), 169.1 (s); IR (CCl_4) ν 3055, 2980, 2940, 1780, 1665 cm^{-1}.

5,5-Diethyl-4-methylene-1,2-dioxolan-3-one (3h): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, J = 7.3 Hz, 6 H), 1.83 (dq, J = 7.2, 0.7 Hz, 4 H), 5.61 (s, 1 H), 6.39 (d, J = 0.6 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 7.3 (2 × q), 30.4 (2 × t), 92.8 (s), 122.8 (t), 139.5 (s), 169.2 (s); IR (CCl_4) ν 2980, 2945, 2888, 1785, 1667 cm^{-1}.

4-Methylene-1,2-dioxaspiro[4.5]decan-3-one (3i): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25–2.11 (m, 10 H), 5.66 (d, J = 0.5 Hz, 1 H), 6.24 (d, J = 0.5, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.5 (2 × t), 24.5 (t), 34.8 (2 × t), 88.4 (s), 121.8 (t), 142.3 (s), 169.5 (s); IR (CCl_4) ν 2940, 2860, 1785, 1710 cm^{-1}.

α-Methylene β-Lactones 5 (General Procedure). To a solution of the particular α-methylene-β-peroxy lactone **3** (0.240–9.00 mmol) in $CHCl_3$ (1.5–35 mL) was added at low temperature (−78 to −30 °C) a corresponding equimolar amount of triphenylphosphine in $CHCl_3$ (1.5–35 mL). The reaction mixture was allowed to warm to ca. 20 °C and stirred until the peroxide test (KI, HOAc) was negative. Most of the solvent (ca. two-thirds) was evaporated, the Ph_3PO was precipitated by adding 10–100 mL of petroleum ether (bp 30–50 °C) and removed by filtration, and the remaining solvent was evaporated. If necessary, the precipitation–filtration operation was repeated to remove remaining Ph_3PO. The residue was purified by Kugelrohr distillation and/or column chromatography. The reaction conditions, isolation methods, yields, and physical constants are given in Table II, except **5f** and **5g**, which were only spectroscopically detected, and **5k** (ref 8).

4-Methyl-3-methylene-1-oxetan-2-one (5a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.60 (d, J = 6.3 Hz, 3 H), 5.12 (ddq, J = 6.3, 1.8, 1.7 Hz, 1 H), 5.47 (t, J = 1.8, Hz, 1 H), 5.91 (t, J = 2.0 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.0 (q), 76.2 (d), 114.8 (t), 147.1 (s), 163.3 (s); IR (CCl_4) ν 2990, 2935, 1823, 1712 cm^{-1}.

4-Ethyl-3-methylene-1-oxetan-2-one (5b): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.06 (t, J = 7.4 Hz, 3 H), 1.91 (m, 2 H), 4.94 (m, 1 H), 5.45 (s, 1 H), 5.93 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 8.5 (q), 26.3 (t), 80.4 (d), 114.9 (t), 149.5 (s), 163.4 (s); IR (CCl_4) ν 2970, 2890, 2860, 1823, 1710 cm^{-1}.

3-Methylene-4-(1-methylethyl)-1-oxetan-2-one (5c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.03 (d, J = 6.8 Hz, 3 H), 1.06 (d, J = 6.8 Hz, 3 H), 2.07 (septet, J = 6.8 Hz, 1 H), 4.72 (dt, J = 7.0, 1.8 Hz, 1 H), 5.46 (t, J = 1.8 Hz, 1 H), 5.94 (t, J = 1.8, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.9 (q), 17.5 (q), 31.4 (d), 83.9 (d), 115.2 (t), 145.1 (s), 163.5 (s); IR (CCl_4) ν 2980, 2945, 2880, 1845, 1715 cm^{-1}.

4-(1,1-Dimethylethyl)-3-methylene-1-oxetan-2-one (5d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.02 (s, 9 H), 4.67 (t, J = 1.8 Hz, 1 H), 5.43 (t, J = 1.7 Hz, 1 H), 5.96 (t, J = 1.9 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.5 (3 × q), 33.7 (s), 86.6 (d), 115.8 (t), 144.3 (s), 169.5 (s); IR (CCl_4) ν 2980, 2940, 2880, 1842, 1697 cm^{-1}.

3-Methylene-4-(1-phenylethyl)-1-oxetan-2-one (5e). Major diastereomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.34 (d, J = 7.1 Hz, 3 H), 3.19 (quin, J = 7.0 Hz, 1 H), 4.98 (dt, J = 6.8, 1.7 Hz, 1 H), 5.26 (t, J = 1.7 Hz, 1 H), 5.85 (t, J = 1.9 Hz, 1 H), 7.10–7.32 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0 (q), 41.1 (d), 81.3 (d), 115.3 (t), 127.3 (d), 127.7 (d), 128.6 (d), 139.6 (s), 144.3 (s), 162.2 (s). **Minor diastereomer**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (d, J = 6.9 Hz, 3 H), 3.72 (quin, J = 7.0 Hz, 1 H), 4.69 (t, J = 1.7 Hz, 1 H), 4.89 (dt, J = 8.8, 1.7 Hz, 1 H), 5.69 (t, J = 1.9 Hz, 1 H), 7.10–7.32 (m, 5 H); IR (CCl_4) ν 3075, 3040, 2980, 1845, 1714 cm^{-1}.

4,4-Dimethyl-3-methylene-1-oxetan-2-one (5f): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.63 (s, 6 H), 5.26 (s, 1 H), 5.80 (s, 1 H); IR (CCl_4) ν 1845 cm^{-1}.

4-Ethyl-4-methyl-3-methylene-1-oxetan-2-one (5g): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.03 (t, J = 7.5 Hz, 3 H), 1.61 (s, 3 H), 2.32 (q, J = 7.4 Hz, 2 H), 5.33 (d, J = 1.9 Hz), 5.85 (d, J = 1.9 Hz, 1 H); IR (CCl_4) ν 1845 cm^{-1}.

4,4-Diethyl-3-methylene-1-oxetan-2-one (5h): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.01 (t, J = 7.5 Hz, 6 H), 1.90 (q, J = 7.5 Hz, 4 H), 5.34 (d, J = 1.7 Hz, 1 H), 5.90 (d, J = 1.7 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 7.8 (2 × q), 28.8 (2 × t), 90.5 (s), 113.6 (t), 148.0 (s), 163.6 (s); IR (CCl_4) ν 2990, 2950, 1830, 1695 cm^{-1}.

3-Methylene-1,2-oxaspiro[3.5]nonan-3-one (5i): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.41–2.00 (m, 10 H), 5.43 (d, J = 1.8 Hz, 1 H), 5.81 (d, J = 1.7 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.0 (2 × t), 24.6 (t), 34.5 (2 × t), 87.3 (s), 113.1 (t), 150.1 (s), 163.9 (s); IR (CCl_4) ν 2950, 2860, 1825 cm^{-1}.

α-Methylene β-Lactones 5 via Benzenesulfonyl Chloride/Pyridine Cyclization. A solution of β-hydroxy acid **4** (0.1–0.48 mmol) in anhydrous pyridine (1.0–15 mL) was cooled to 0–5 °C, and 2 equivalents of benzenesulfonyl chloride were added. The reaction mixture was vigorously shaken and stored in the freezer at 0–5 °C for ca. 15 h. After being poured onto 5–50 g of crushed ice, the mixture was extracted with ether (5 × 5 mL). The combined ether layers were washed with saturated aqueous $NaHCO_3$ (5 mL) and water (5 mL), dried ($MgSO_4$), and evaporated (ca. 20 °C (20 Torr)). The crude product was purified by column chromatography (silica gel, ratio 50:1, CH_2Cl_2, 20 °C) for the α-methylene β-lactone **5c,e** or sublimation (130–150 °C (0.01 Torr)) for **5k**. The physical and spectral data are in good agreement with those obtained in the deoxygenation procedure with triphenylphosphine.

3-Hydroxy-4-methyl-2-methylenepentanoic Acid (4c). A mixture of 1.72 g (10.0 mmol) of methyl 3-hydroxy-4-methyl-2-methylenepentanoate, prepared according to the literature,[14] and 480 mg (12.0 mmol) of NaOH in 5 mL of water was stirred for 24 h at 20 °C. The mixture was washed with MTB (2 × 2 mL), acidified with 2 N HCl (pH 4), and extracted with MTB (5 × 5 mL). The combined organic layers were dried (Na_2SO_4) and evaporated to yield 1.37 g (95%) of colorless oil: IR (CCl_4) ν 3680–3100, 3000, 2980, 1710, 1640 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.85 (d, J = 6.8 Hz, 3 H), 0.92 (d, J = 6.7 Hz, 3 H), 1.90 (m, 1 H), 4.08 (d, J = 6.8 Hz, 1 H), 5.82 (d, J = 0.9 Hz, 1 H), 6.37 (d, J = 0.9 Hz, 1 H), 6.47 (br s, OH); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.5 (q), 19.5 (q), 32.6 (d), 77.5 (d), 128.2 (t), 140.7 (s), 170.8 (s). Anal. Calcd for $C_7H_{12}O_3$ (144.2): C, 58.31; H, 8.41. Found: C, 58.57; H, 8.43.

3-Hydroxy-2-methylene-4-phenylbutanoic Acid (4e). A solution of 3.80 g (20.0 mmol) of α,β-unsaturated carboxylic acid **1e** in 150 mL of CCl_4 was photooxygenated at 0 °C (250-W sodium lamp, by using an immersion well)[13] and treated successively with 6.50 g (24.8 mmol) of triphenylphosphine until the peroxide test was negative (8 h). The solvent was evaporated, the residue was dissolved in 50 mL of ether, 500 mL of water was added, and the mixture was basified to pH ca. 10 by KOH, washed with ether (3 × 30 mL), and then acidified with concd HCl (pH ~1). The water phase was separated, the aqueous layer was extracted with ether (8 × 50 mL), the combined organic layers were dried (Na_2SO_4), and the solvent was evaporated (ca. 20 °C (15 Torr)). Washing the residue four times with a 65:35 petroleum ether/ethyl acetate solvent mixture yielded 661 mg (21%) of colorless prisms: mp 108–109 °C; IR (CCl_4) ν 3580, 3520, 3040, 2960, 1680, 1615 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.33 (d, J = 7.0 Hz, 3 H), 3.21 (dd, J = 7.0, 6.2 Hz, 1 H), 4.55 (d, J = 6.1 Hz, 1 H), 5.77 (dd, J = 1.0, 0.8 Hz, 1 H), 6.35 (d, J = 0.8 Hz, 1 H), 7.18–7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 14.7 (q), 43.4 (d), 76.4 (d), 126.7 (d), 127.8 (d), 128.5 (d), 129.1 (t), 139.8 (s), 143.7 (s), 171.2 (s); MS (70 eV) m/z 206 (0.34) (M^+), 188 (2) ($M^+ - H_2O$), 143 (3), 105 (100) (C_8H_9).

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Supplementary Material Available: X-ray crystallographic data for α-methylene β-lactone **5k** comprised of the structural parameters, six tables that include atomic parameters and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, and H atom coordinates, and isotropic displacement parameters and table of microanalyses for compounds **3b–k** and **5a–k** except **3e** and **5d**, for which ^{1}H NMR spectra are supplied (10 pages). Ordering information is given on any current masthead page.

(14) Yamamoto, K.; Deguchi, R.; Tsuji, J. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3397.