The same procedure was used for diazotization in the presence of 4-methylanisole, replacing the THF with 2 mL of 4-methylanisole. From **1b** (eluant CH_2Cl_2–hexane 1:4): **2b**, 385 mg (55%), and **6b**, 81 mg (6%), mp 84–85 °C (Et_2O–hexane). From **1c** (eluant CH_2Cl_2–hexane 1:4): **2c**, 82 mg (16%), **6c**, 141 mg (12%), mp 105–106 °C (Et_2O–pentane), and **7c**, 20 mg (2%), mp 103–104 °C (Et_2O–pentane).

Irradiation of 4q. Compound **4q** (350 mg, 1.36 mmol) was dissolved in EtOH (80 mL), N_2 was bubbled through the solution for 5 min, and irradiation was carried out for 3 h. Evaporation of the solvent afforded a mixture of diethyl acetoxyfumarate and diethyl acetoxymaleate (285 mg 91%): bp 90–95 °C (0.4 mm); IR 1767, 1725, 1650, 1620 cm^{-1}; NMR δ 6.7 (s, 0.23), 6.17 (s, 0.77), 4.38 (m, 4), 2.38 (s, 0.69), 2.32 (s, 2.31), 1.36 (m, 6). The same mixture with a different E/Z ratio was synthesized following a literature procedure.[16]

Preparation of 4q from Diethyl Aminofumarate. Diethyl aminofumarate[17] (2 g, 10.7 mmol) was dissolved in AcOH (40 mL) and a solution of $NaNO_2$ (7.4 g) in H_2O (15 mL) was added with stirring at room temperature over a period of 1 h. After workup as described for the diazotizations, the products were isolated by silica gel column chromatography (eluant hexane–Et_2O, 8:1): **4q**, 161 mg (6%); **8**, 240 mg (9%), bp 98–100 °C (0.2 mm).

Registry No. **1a**, 15783-70-7; **1b**, 29278-09-9; **1c**, 14246-77-6; **1d**, 96129-31-6; **1e**, 49750-31-4; **1f**, 96129-32-7; **1g**, 96129-33-8; **1h**, 67960-26-3; **1i**, 67960-27-4; **1k**, 96129-34-9; **1l**, 96129-35-0; **1m**, 96129-36-1; **1n**, 53983-15-6; **1o**, 96129-37-2; **1p**, 96129-38-3; **1q**, 15911-21-4; **1r**, 96129-39-4; **1s**, 41230-51-7; **1t**, 19747-21-8; **1u**, 96129-40-7; **2a**, 7223-30-5; **2b**, 2216-94-6; **2c**, 935-02-4; **2d**, 1942-30-9; **2e**, 3450-67-7; **2f**, 5324-64-1; **2g**, 28995-88-2; **2h**, 32501-94-3; **2i**, 13894-21-8; **2k**, 13295-94-8; **2l**, 96129-41-8; **2m**, 35283-08-0; **3o**, 1969-74-0; **3p**, 28048-30-8; **4q**, 96129-42-9; **4r**, 96129-43-0; **5d**, 96129-44-1; **5m**, 96129-45-2; **5n**, 96129-46-3; **5o**, 91477-03-1; **5p**, 96129-47-4; **6b**, 96129-48-5; **6c**, 96129-49-6; **7c**, 96129-50-9; **8**, 5349-99-5; PhC(Cl)=NOH, 698-16-8; $R'CH_2CN$ (R^1 = CN), 109-77-3; $R'CH_2CN$ (R^1 = $C_6H_4NO_2$-*p*), 555-21-5; $R'CH_2CN$ (R^1 = SO_2Ph), 7605-28-9; $R'CH_2CN$ (R^1 = $SO_2C_6H_4Me$-*p*), 5697-44-9; $R'CH_2CN$ (R^1 = 4-pyridyl), 13121-99-8; $R'CH_2CN$ (R^1 = pyrazinyl), 5117-44-2; EtOCOC(Cl)=NOH, 14337-43-0; $R'CH_2CN$ (R^1 = $C_6H_4NO_2$-*o*), 610-66-2; diethyl acetoxyfumarate, 56715-92-5; diethyl acetoxymaleate, 56715-93-6; diethyl aminofumarate, 36016-13-4.

Supplementary Material Available: Table IV containing principal infrared bands and NMR data for **1d,f,g,1e–o,p,r,u**, **2l**, **4q,r**, **5d,m–p**, **6b,c,7c**, and **8** (1 page). Ordering information is given on any current masthead page.

Notes

Facile Synthesis of Acyl-Substituted Lactone Derivatives from Acyclic Keto Esters

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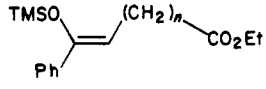
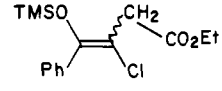
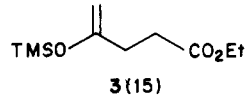
We have recently described the selective formation of trimethylsilyl enol ethers from the corresponding keto esters using trimethylsilyl iodide in the presence of hexamethyldisilazane.[1] In this fashion, the trimethylsilyl enol esters **1** and **2** were generated in high yield. In the case



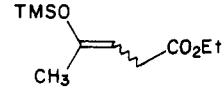
1a *n* = 1
1b *n* = 2



2



3 (15)



4 (85)

of ethyl levulinate, which yields a mixture of both **3** and **4**, the chemoselectivity is maintained, but the reaction is less regioselective. In spite of this, the internal olefin **4** is still the major component of the product mixture.[1]

Since trimethylsilyl enol ethers are extremely useful synthetic reagents,[2] we felt that derivatives such as **1–4** which contain multiple but differentiated chemical functionality offered considerable synthetic potential. In this regard, if the Lewis acid catalyzed condensation of carbonyl derivatives such as aldehydes and ketones[3] could be directed selectively to the silyl enol ether site, the resulting β-hydroxy ketones would be potential lactone precursors due to the presence of the proximate ester functionality.[4] We report here the realization of this goal and describe the production of synthetically useful acyl-substituted γ-butyro- and δ-valerolactone derivatives.[6]

The condensation of **1a** with trioxane in the presence of titanium tetrachloride leads to the formation of the corresponding aldol **6** (R_1 = R_2 = H) in excellent crude yield. The aldol is, however, extremely prone to cyclization and produces the lactone **5** (Table I) in the presence of traces of acid. This cyclization occurs even upon prolonged standing over $MgSO_4$ drying agent. Similarly, the condensation of **1a** with benzaldehyde proceeds as shown above. Although both diasterioisomers **6a** and **6b** are initially generated, most of **6a** undergoes spontaneous intramolecular cyclization under the workup conditions to yield **7a**. The stability of **6b** is much greater, and it is easily isolated from the reaction mixture. Attempts to cyclize **6b** using Lewis acids (BF_3·Et_2O, $TiCl_4$, $SnCl_4$, etc.) resulted primarily in a retroaldol reaction to regenerate methyl β-benzoylpropionate and benzaldehyde. However, the use of protic acid catalysts such as p-toluenesulfonic acid caused rapid cyclization to the lactone **7b**. The structure and configuration of **7b** were indicated by the spectral data and were confirmed by X-ray analysis.[7] The reaction

(1) Miller, R. D.; McKean, D. C. *Synthesis* **1979**, 730.
(2) Weber, W. P., "Silicon Reagents in Organic Synthesis"; Springer-Verlag: New York, 1983.
(3) Mukiayama, T.; Banno, K.; Narasaki, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503.
(4) The synthesis of β-benzoyl and β-acetyl butyrolactone in low yield by the base-catalyzed condensation of the respective β-keto acids with formaldehyde has been reported.[5]
(5) Rothe, J.; Zimmer, H. *J. Org. Chem.* **1959**, *24*, 586.
(6) (a) Mukiayama, T.; Hanna, T.; Inoue, T.; Sato, T. *Chem. Lett.* **1974**, 381. (b) Mukiayama, T.; Wada, M.; Hanna, T. *Chem. Lett.* **1974**, 1181. (c) Sato, T.; Junichi, H.; Nakamura, H.; Mukiayama, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1055.

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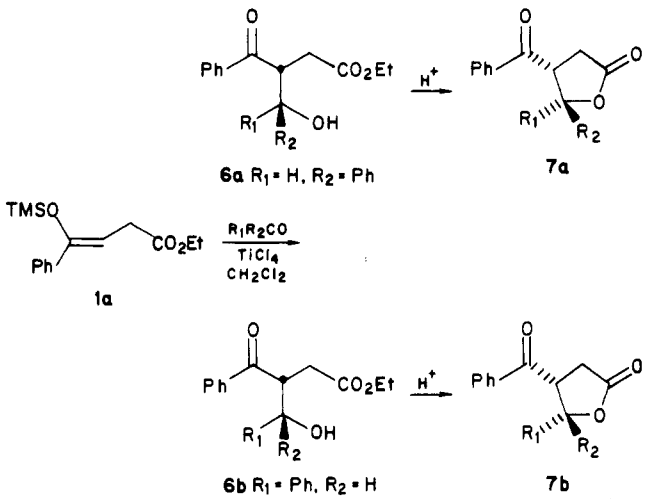


leading ultimately to γ-butyrolactones is quite general as shown by the results in Table I. For those condensation products involving aldehydes other than formaldehyde, diasteriosomeric aldols are produced initially but the trans-substituted γ-butyrolactone forms spontaneously upon workup. The aldols derived from ketones, in general, lactonize much more slowly and usually require subsequent treatment with acid. In practice the crude mixture of aldol(s) was converted by using p-toluenesulfonic acid directly to the lactones prior to purification.

The procedure is successful even for the preparation of sensitive lactones such as **11** which, although quite reactive, could be prepared from **2** in 48% yield. The lactone **11** is, as expected, very prone to eliminate the elements of HCl to produce the corresponding butenolide derivative. We also found that the thermodynamically equilibrated mixture of trimethylsilyl enol ethers **3** and **4**[1] can be successfully employed directly without separation. The presence of 15–20% of **3** in the starting material causes no difficulties, since the terminal aldol produced concurrently during the initial condensation does not lactonize upon subsequent acid treatment. The lactones are thus easily separated from any uncyclized aldol product.

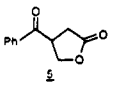
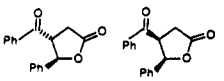
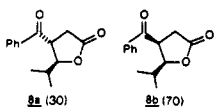
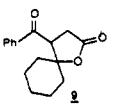
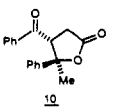
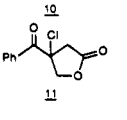
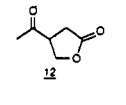
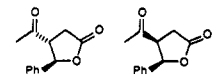
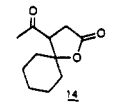
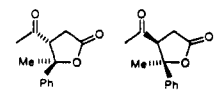
The procedure is not limited to the formation of γ-butyrolactones. The use of **1b** in the sequence leads to the formation of acyl-substituted δ-valerolactones (see Table II). Interestingly, in the case of benzaldehyde the trans lactone **17** is now the major product.[8] In contrast, in the formation of the butyrolactones the cis lactone constituted the major isomer. The formation of the six-membered lactones is not spontaneous and requires treatment with a protic acid catalyst. In these cases, the lactonization is often facilitated by the use of 4-Å molecular sieves.

Further studies on the synthetic utility of the acyl-substituted lactones are in progress.

Experimental Section

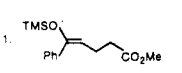
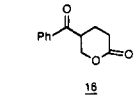
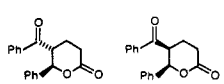
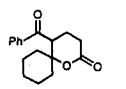
All solvents were routinely dried and distilled before use. The ^{1}H NMR spectra were recorded on a Varian Instruments EM-390 using tetramethyl silane as an internal standard. Infrared spectra were taken on a Perkin–Elmer 297 instrument. GLPC analyses were accomplished with a Hewlett-Packard 5750 instrument using a glass column (0.25 in. × 6 ft) packed with 10% SE-30 on Gas Chrom Q. Flash chromatographic purifications were performed as described by Still and co-workers.[10]

Table I. Synthesis of Acyl-Substituted γ-Butyrolactone Derivatives

	starting materials		relative reactn conditns	products	
1.	1a		(1) -78°, 4h (2) PTSA 25°, 15h	 5	[83] [a]
2.	1a	PhCHO	(1) -78°, 2h (2) PTSA 25°, 5h	 7a (20) [b] 7b (80) [b]	[80]
3.	1a		(1) -78°, 4h (2) PTSA 25°, 15h	 8a (30) 8b (70)	[75]
4.	1a		(1) -10°, 2h 25°, 2h (2) PTSA 25°, 16h	 9	[72]
5.	1a	$PhCOCH_3$	(1) -10°, 2h 25°, 2h (2) PTSA 25°, 16h	 10	[70]
6.	2		(1) -10°, 4h (2) PTSA 25°, 15h	 11	[48]
7.	3(15) 4(85)		(1) -78°, 2h -10°, 1h (2) PTSA 25°, 17h	 12	[60]
8.	3,4	PhCHO	(1) -78°, 2h -10°, 1h (2) PTSA 25°, 15h	 13a (40) 13b (60)	[58]
9.	3,4		(1) -10°, 2h 25°, 3h	 14	[60]
10.	3,4	$PhCOCH_3$	(1) -10°, 1h 0°, 2h (2) PTSA 25°, 4h	 15a (92) 15b (8)	[48]

[a] Isolated yield of purified product. [b] Relative yields.

Table II. Synthesis of Acyl-Substituted δ-Valerolactones

	starting materials		reactn conditns	products	
1.	 1b		(1) -78°, 2h -10°, 1h (2) PTSA 25°, 8h	 16	[57] [a]
2.	1b	PhCHO	(1) -78°, 2h -10°, 4h (2) PTSA 25°, 10h	 17a (85) [b] 17b (15) [b]	[50]
3.	1b		(1) -10°, 1h 25°, 3h (2) PTSA 25°, 7h	 18	[65]

[a] Isolated yield of purified product. [b] Relative yields.

(7) X-ray crystallographic data for **7b**: $C_{17}H_{14}O_3$: orthorhombic space group *Pbca*, a = 8.171 (1) Å, b = 16.826 (2) Å, c = 19.769 (3) Å, p = 1.30 g/cm^3.

(8) The configuration of the major isomer **17a** was tentatively assigned as trans based on consideration of its ^{1}H NMR spectrum. In this regard the appearance of the benzylic methine proton adjacent to the ring oxygen at δ 5.67, slightly upfield from the same proton in **17b** with a coupling constant of 9.3 Hz (vs. 3 Hz for **17b**) is consistent with the trans assignment.[9]

(9) Becker, E. D. "High Resolution NMR: Theory and Chemical Applications"; Academic Press: New York, 1980; Chapter 5.

Ethyl 3-chloro-3-benzoylpropionate used for the preparation of **2** was synthesized by the application of the procedure described by Warnhoff and Johnson.[11]

Ethyl 3-Chloro-4-(trimethylsiloxy)-4-phenyl-3-butenoate (2). Into a flask containing 35 mL of CH_2Cl_2, 2.14 mL (10.1 mmol) of hexamethyldisilazane, and 2.04 g (8.5 mmol) of ethyl 3-chloro-3-benzoylpropionate (prepared by the chlorination of ethyl 3-benzoylpropionate with sulfuryl chloride) was added 1.32 mL (93 mmol) of trimethylsilyl iodide. The reaction was stirred at 25 °C for 2 h and diluted with pentane. The organic phase was washed with cold 2 N H_2SO_4, saturated sodium bicarbonate, and water and dried over Na_2SO_4. The solvent was removed and the product distilled in a Kugelrohr apparatus (temperature 140 °C (0.05 mm) to yield 2.37 g (89%) of pure product. From the ^1H NMR spectrum, the distilled material appears to be a 1:1 *E*/*Z* mixture.

2: ^1H NMR ($CDCl_3$) δ −0.02 (s, 9 H), 1.0–1.32 (m, 3 H), 3.19 (s, 1 H), 3.42 (s, 1 H), 4.08 (q, J = 7.5 Hz, 2 H), and 7.12–8.52 (m, 5 H); IR (neat) 3070, 1743, 1605, 1248, 1185, 1155, 880, 850 cm^{-1}; mass spectroscopic molecular weight 312.

General Procedure for Preparation of the Lactones. Into a flask charged with 2 mmol of the trimethylsilyl enol ether, 5 mL of CH_2Cl_2, and 2.1 mmol of the carbonyl derivative cooled to −78 °C was added 231 μL (2:1 mmol) of distilled titanium tetrachloride in 5 mL of CH_2Cl_2 over 0.5 h with a syringe pump. After 2.5 h at −78 °C (the actual conditions varied with the reactivity of the carbonyl derivative, see Tables I and II), the mixture was diluted with 25 mL of CH_2Cl_2 and 5 mL of water. Upon warming to 25 °C, the layers were separated and the organic phase was washed with saturated brine, saturated sodium bicarbonate, and water and dried over Na_2SO_4. In a few cases the aldol(s) were actually separated by flash chromatography, but in general it was most convenient to dilute the reaction mixture containing the aldol(s) with benzene and to cyclize to the lactone(s) using PTSA (12–19 h, 25 °C). The benzene was washed with saturated $NaHCO_3$ and water and dried over Na_2SO_4. The lactones were purified by flash column chromatography[10] on silica gel.

5 (83%): mp 64–66 °C[5]; ^1H NMR ($CDCl_3$) δ 2.85 (m, 2 H), 4.18–4.63 (m, 3 H), 7.48 (m, 3 H), 7.87 (m, 2 H); IR (neat) 3070, 2990, 2940, 2880, 1780, 1600, 1585, 1235, 1180, 1160, 1030, 1010, 705, 690 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.47; H, 5.30. Found: C, 69.02; H, 5.29.

6a: oil (16%); ^1H NMR ($CDCl_3$) δ 1.05 (t, J = 6.5 Hz, 3 H), 2.67–3.23 (m, 3 H), 3.87 (q, J = 6.5 Hz, 2 H), 4.17 (m, 1 H), 5.0 (m, 1 H), 7.17–7.6 (m, 3 H), 7.84 (m, 2 H); IR (neat) 3500, 3050, 3020, 2990, 2940, 1730, 1680, 1210, 1130, 700 cm^{-1}.

6b (64%): mp 80–82 °C; ^1H NMR ($CDCl_3$) δ 1.0 (t, J = 6.5 Hz, 3 H), 2.4 (d, d, J = 17.5, 6 Hz 1 H) 2.63–3.0 (m, 2 H), 3.89 (q, J = 6.5 Hz, 2 H), 4.29 (m, 1 H), 4.88 (d, d, J = 7.2, 5.4 Hz, 1 H)7.4–7.55 (m, 3 H), 7.95 (m, 2 H); IR (neat) 3050, 3070, 3040, 2990, 1730, 1680, 1250, 1210, 1030, 705 cm^{-1}. Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.93; H, 6.43.

7a (10%): oil; ^1H NMR ($CDCl_3$) δ 2.8–3.1 (m, 2 H), 4.23 (m, 1 H), 5.75 (d, J = 7.2 Hz, 1 H), 7.12–7.55 (m, 8 H), 7.73 (m, 2 H); IR (neat) 3080, 3060, 2930, 1780, 1675, 1600, 1580, 1220, 1015, 1000, 760, 700 cm^{-1}.

7b (60%): mp 125–127 °C; ^1H NMR ($CDCl_3$) δ 2.83 (d, d, J = 17.5, 9 Hz, 1 H), 3.37 (d, d, J = 17.5, 7.5 Hz, 1 H), 4.73 (m, 1 H), 5.87 (m, 1 H), 6.8–7.7 (m, 10, H); IR ($CDCl_3$) 3080, 2960, 1780, 1685, 1600, 1585, 1250, 1185, 1020, 855 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.48; H, 5.34.

8a: oil (25%); ^1H NMR ($CDCl_3$) δ 0.96 (d, J = 7 Hz, 3 H), 1.07 (d, J = 7 Hz 3 H), 1.91 (m, 1 H), 2.53–3.10 (m, 2 H), 4.08 (m, 1 H), 4.68 (t, J = 6 Hz, 1 H) 7.37 (m, 3 H), 8.0 (m, 2 H); IR (neat) 3050, 1775, 1680, 1598, 1580, 1220, 1015, 1000, 715, 690 cm^{-1}.

8b (58%): mp 85–87 °C; ^1H NMR ($CDCl_3$) δ 0.78 (d, J = 6.9 Hz, 3 H), 0.9 (d, J = 6.9 Hz, 3 H), 1.45–1.95 (m, 1 H), 2.62 (d, d, J = 18, 7.5 Hz, 1 H), 3.12 (d, d, J = 18, 6.9 Hz, 1 H), 4.2–4.72 (m, 2 H), 7.29–7.65 (m, 3 H), 7.94 (m, 2 H); IR (neat) 3050, 2980, 2880, 1770, 1665, 1598, 1582, 1230, 1183, 1170, 1050, 735, 693 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.52; H, 6.95.

9 (72%): oil; ^1H NMR ($CDCl_3$) δ 0.77–2.12 (m, 10 H), 2.63 (d, d, J = 18.3, 4.2 Hz, 1 H), 3.23 (d, d, J = 18.3, 3.9 Hz, 1 H), 4.15 (t, J = 4.15 (t, J = 4.2 Hz, 1 H), 7.3–7.7 (m, 3 H), 7.9 (m, 2 H), IR (neat) 3070, 2840, 2870, 1770, 1673, 1600, 1580, 1230, 960, 790, 720 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.13; H, 6.99.

10 (70%): mp 91–92 °C; ^1H NMR ($CDCl_3$) δ 1.5 (s, 3 H), 2.62 (d, d, J = 18, 8.3 Hz, 1 H), 3.12 (d, d, J = 18, 6.8 Hz, 1 H), 4.5 (d, d, J = 8.3, 6.8 Hz, 1 H), 7.17–7.84 (m, 5 H); IR ($CHCl_3$) 3070, 2950, 2940, 1780, 1675, 1600, 1580, 1240, 955, 790, 770, 698 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.02; H, 5.81.

11 (48%): mp 51–53 °C; ^1H NMR ($CDCl_3$) δ 3.22 (ABq, J = 18.7 Hz, 2 H), 4.67 (ABq, J = 10.3 Hz, 2 H), 7.1–7.5 (m, 3 H), 7.8 (m, 2 H); IR (neat) 3080, 3020, 2940, 1795, 1680, 1180, 1040, 690 cm^{-1}.

12 (60%): oil; ^1H NMR ($CDCl_3$) δ 2.23 (s, 3 H), 2.48–2.83 (m, 2 H), 3.53 (m, 1 H), 4.19–4.60 (m, 2 H); IR (neat) 2930, 1780, 1720, 1175, 1035 cm^{-1}; mass spectroscopic molecular weight 128.

13a[12] (23%): oil; ^1H NMR ($CDCl_3$) δ 2.15 (s, 3 H), 2.7–2.97 (m, 2 H), 3.43 (m, 1 H), 5.52 (d, J = 7.5 Hz, 1 H), 7.37 (s, 5 H); IR ($CHCl_3$) 3040, 1780, 1720, 1365, 1170, 1145, 1020 cm^{-1}.

13b (35%): mp 77–79 °C; ^1H NMR ($CDCl_3$) δ 1.65 (s, 3 H), 2.48–3.22 (m, 2 H), 3.8 (m, 1 H), 5.73 (d, J = 7.5 Hz, 1 H), 7.08–7.5 (m, 5 H); IR ($CHCl_3$) 3040, 1785, 1715, 1260, 1020, 990 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.46; H, 5.91.

14 (60%): mp 62–63 °C; ^1H NMR ($CDCl_3$) δ 0.97–2.02 (m, 10 H), 2.25 (s, 3 H), 2.29–3.42 (m, 3 H); IR ($CHCl_3$) 2950, 1770, 1715, 1365, 1275, 1140, 970 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.51; H, 8.19.

15a (44%): mp 69.5–71.5 °C; ^1H NMR ($CDCl_3$) δ 1.62 (s, 3 H), 2.12 (s, 3 H), 2.27–3.15 (m, 2 H), 3.57 (t, J = 7 Hz, 1 H), 7.38 (s, 5 H); IR (CCl_4) 3070, 3040, 1790, 1720, 1220, 700 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.59; H, 6.46. Found: C, 71.73, H, 6.47.

15b (4%): mp 79.5–81.5 °C; ^1H NMR ($CDCl_3$) δ 1.79 (s, 3 H), 1.94 (s, 3 H), 2.57–3.12 (m, 2 H), 3.5 (d, d, J = 7.6 Hz, 1 H), 7.32 (s, 5 H); IR (CCl_4) 3070, 3020, 1785, 1715, 1240, 1205, 950 cm^{-1}.

16 (57%): mp 60–61 °C; ^1H NMR ($CDCl_3$) δ 2.04–2.4 (m, 2 H), 2.54–2.87 (m, 2 H), 3.64–4.1 (m, 1 H), 4.52 (d, J = 6.5 Hz, 2 H), 7.32–7.7 (m, 3 H), 7.91 (m, 2 H); IR ($CHCl_3$) 3030, 2970, 1740, 1680, 1350, 1180, 1065, 695 cm^{-1}; mass spectroscopic molecular weight, calcd for $C_{12}H_{12}O_3$ 204.0786, found 204.0790. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 69.67; H, 5.99.

17a (43%): mp 157–58 °C; ^1H NMR ($CDCl_3$) δ 2.0–2.34 (m, 2 H), 2.45–3.1 (m, 2 H), 3.77–4.14 (m, 1 H), 5.67 (d, J = 9.3 Hz, 1 He, 7.09–7.5 (m, 8 H), 7.69 (m, 2 H); IR ($CHCl_3$) 3030, 2960, 1740, 1675, 1345, 1040, 700 cm^{-1}; mass spectroscopic molecular weight, calcd for $C_{17}H_{16}O_3$ 280.1099, found 280.1097. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.89; H, 5.83.

17b (8%): mp 163–164.5 °C; ^1H NMR ($CDCl_3$) δ 2.08–2.35 (m, 2 H), 2.48–3.1 (m, 2 H), 3.95–4.3 (m, 1 H), 5.73 (d, J = 3 Hz, 1 Hz), 7.08–7.45 (m, 8 H), 7.63 (m, 2 H); IR ($CHCl_3$) 3030, 2950, 1735, 1680, 1220, 1160, 695 cm^{-1}.

18 (65%): mp 100–101 °C; ^1H NMR ($CDCl_3$) δ 1.0–2.49 (m, 12 H), 2.55–3.0 (m, 2 H), 3.82 (d, d, J = 7.5, 5.5 Hz, 1 H), 7.18–7.67 (m, 3 H), 7.97 (m, 2 H); IR ($CHCl_3$) 3020, 2950, 1720, 1675, 1275, 1220, 1130 cm^{-1}; mass spectroscopic molecular weight, calcd for $C_{17}H_{20}O_3$ 272.1412, found 272.1383. Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.18; H, 7.45.

Registry No. **1a**, 95891-66-0; **1b**, 95891-67-1; (*E*)-**2**, 95891-64-8; (*Z*)-**2**, 95911-43-6; **3**, 95547-14-1; **4**, 95891-65-9; **5**, 21034-22-0; **6a**, 95891-84-2; **6b**, 95891-85-3; **7a**, 95891-68-2; **7b**, 95891-69-3; **8a**, 95891-70-6; **8b**, 95891-71-7; **9**, 95891-72-8; **10**, 95891-73-9; **11**, 95891-74-0; **12**, 7400-67-1; **13a**, 95891-75-1; **13b**, 95891-76-2; **14**, 95891-77-3; **15a**, 95891-78-4; **15b**, 95891-79-5; **16**, 95891-80-8; **17a**, 95891-81-9; **17b**, 95891-82-0; **18**, 95891-83-1; $CH_2OCH_2OCH_2O$, 110-88-3; PhCHO, 100-52-7; $CH_3CH(CH_3)CHO$, 78-84-2; $CH_2(CH_2)_4CO$, 108-94-1; $PhCOCH_3$, 98-86-2; ethyl 3-chloro-3-benzoyl propionate, 95891-63-7.

(10) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(11) Warnhoff, E. W.; Johnson, W. S. *J. Am. Chem. Soc.* **1953**, *74*, 494.

(12) It appears from comparison of the spectral data that the trans isomer **13a** is the same material that was previously isolated by Mukiayama and co-workers.[6b] These workers made no mention of the cis isomer **13b**.