26.6, 21.1, 20.8, 15.1; IR (neat) ν_{max} 3428, 2958, 2868, 1620, 1500, 1456, 1402, 1360, 1126, 1064, 862, 786, 726 cm^{-1}; EIMS, *m/e* (rel intensity) 213 (M$^+$, 57), 198 (base), 184 (10), 169 (19), 154 (7), 90 (5), 77 (3); CIMS (2-methylpropane), *m/e* (rel intensity) 214 (M + H$^+$, base); EIHRMS, *m/e* 213.1514 ($C_{15}H_{19}N$ requires 213.1518).

***trans*-Trikentrin A (2).** A solution of **16** (75 mg, 0.29 mmol) and LiOH·H_2O (26 mg, 0.62 mmol, 2.1 equiv) in THF–H_2O–CH_3OH (3:1:1) (2 mL) was allowed to stir at 25 °C for 1 h. The reaction mixture was treated with 10 mL of saturated NH_4Cl and was extracted with methylene chloride (5 mL × 5). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Chromatography (SiO_2, 17 × 1.4 cm, 0–5% EtOAc–hexane) afforded 58 mg (63 mg theoretical, 92%) of **2** as a white crystalline solid: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.01 (1 H, brs), 7.16 (1 H, dd, *J* = 3.1, 2.4 Hz), 6.83 (1 H, s), 6.59 (1 H, dd, *J* = 3.3, 2.0 Hz),[18] 3.52 (1 H, ddq, *J* = 7.3, 3.7, 7.3 Hz), 3.41 (1 H, ddq, *J* = 7.1, 7.1, 7.1 Hz), 2.93 (2 H, q, *J* = 7.7 Hz), 2.04 (1 H, ddd, *J* = 12.3, 7.5, 3.9 Hz), 1.96 (1 H, ddd, *J* = 12.4, 7.3, 7.3 Hz), 1.36 (3 H, t, *J* = 7.5 Hz), 1.33 (3 H, d, *J* = 7.1 Hz), 1.30 (3 H, d, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 142.9, 135.5, 132.5, 127.6, 126.5, 123.2, 114.4, 101.8, 43.9, 38.0, 36.1, 26.6, 20.9, 20.1, 15.0; IR (KBr) ν_{max} 3394, 2952, 2920, 2864, 1624, 1498, 1448, 1404, 1374, 1318, 1126, 1104, 1058, 896, 866, 786, 732 cm^{-1}; EIMS, *m/e* (rel intensity) 213 (M$^+$, 49), 198 (base), 184 (11), 169 (23), 154 (10), 90 (5), 77 (4); CIMS (2-methylpropane), *m/e* (rel intensity) 214 (M + H$^+$, base); EIHRMS, *m/e* 213.1523 ($C_{15}H_{19}N$ requires 213.1518.

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Dipivaloylketene and Its Unusual Dimerization to a Permanently Stable α-Oxoketene

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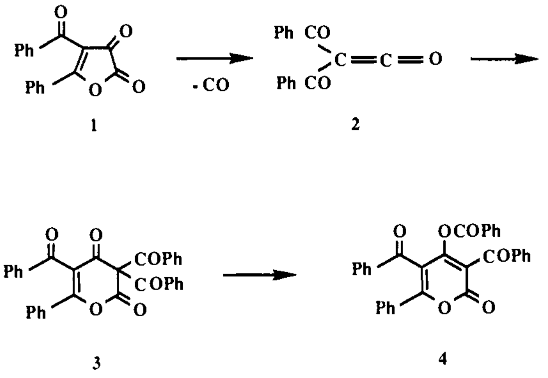
Abstract: Dipivaloylketene (**8**) is obtained by flash vacuum pyrolysis of 5-*tert*-butyl-4-pivaloyl-2,3-dihydrofuran-2,3-dione (**7**) at temperatures between 250 and 500 °C. It is stable in solution below 0 °C and dimerizes at room temperature to **10**, which involves an unusual [2+4] cycloaddition reaction between one α-oxoketene unit and the carbonyl double bond of a second molecule, thus preserving the ketene functionality. The structure of the highly hindered ketene **10** was proved by X-ray crystallography. This compound is stable for months in the open air at high humidity.

Introduction

There is considerable current interest in the chemistry of ketenes[2] because of their use as synthetic building blocks, because of mechanistic considerations,[3] and because of the discovery of a number of unusual rearrangements.[4]

α-Oxoketenes are particularly reactive and cannot normally be isolated under usual reaction conditions. Several examples have been detected by low-temperature IR spectroscopy at 77 K or in Ar matrix at ca. 12 K.[3a–b,4a–b,5] Steric hindrance makes the ketenes persistent; thus, isopropyl(isopropylcarbonyl)ketene is reported to be observable by IR spectroscopy in CCl_4 solution, at 20 °C for 2–3 days,[6] and *tert*-butyl(*tert*-butylcarbonyl)ketene to be stable under similar conditions for several months.[7] *tert*-Butyl(ethoxycarbonyl)ketene is similarly persistent.[8]

Dibenzoylketene (**2**), generated from furandione **1**, is stable at 77 K but under ordinary reaction conditions dimerizes to α-pyrone **4** in a process involving a [2+4] cycloaddition of one ketene molecule to the C=C bond of another (eq 1), followed by an acyl 1,3-shift.[4a]



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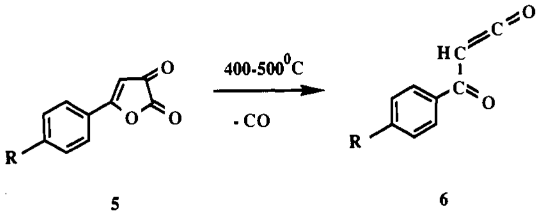
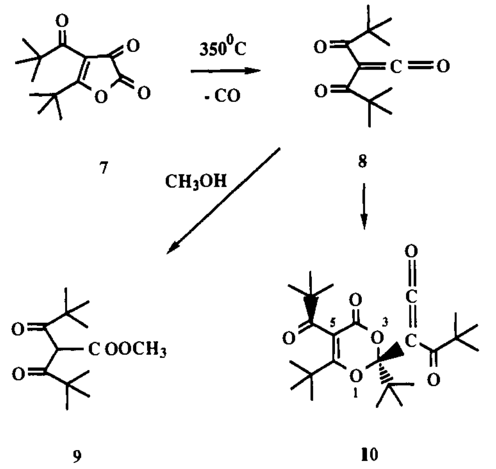
In other research, we have demonstrated[9a] that flash vacuum pyrolysis (FVP) of furandiones **5** at 400–500 °C (10^{-4} Torr) resulted in CO extrusion and formation of monoacylketenes **6** (R = H, CH_3, OC_2H_5, Cl), which give rise to very strong absorptions at 2135–2148 cm^{-1} when condensed on a KBr disk at 77 K (eq 2). Ketenes of the type **6** are trappable in [2+4] cycloaddition reactions in solution[9b] but like **2** are not detectable at room temperature.



(2)

We now report the generation of the first persistent diacylketene, viz., dipivaloylketene (**8**), as well as its unusual dimerization to give a dimer (**10**), which is still an acylketene and is permanently stable in the presence of oxygen and moisture (eq 3).



(3)

Table I. Selected Bond Lengths (Å) for **10**

atoms	distance	atoms	distance
O(1)–C(2)	1.41 (1)	C(2)–O(3)	1.43 (1)
O(3)–C(4)	1.38 (1)	C(4)–C(5)	1.47 (2)
C(5)–C(6)	1.33 (2)	C(6)–O(1)	1.36 (1)
C(4)–O(41)	1.19 (1)	C(2)–C(25)	1.54 (2)
C(25)–C(26)	1.35 (2)	C(26)–O(27)	1.13 (1)
C(25)–C(28)	1.44 (2)	C(28)–O(29)	1.27 (2)

Table II. Selected Bond Angles (deg) for **10**

atoms	angle	atoms	angle
C(6)–O(1)–C(2)	117.7 (8)	O(1)–C(2)–O(3)	109.0 (8)
C(2)–O(3)–C(4)	118.5 (8)	O(3)–C(4)–C(5)	114 (2)
C(4)–C(5)–C(6)	119 (1)	C(5)–C(6)–O(1)	120 (1)
O(1)–C(2)–C(25)	108.0 (9)	O(3)–C(2)–C(25)	110.2 (8)
C(2)–C(25)–C(26)	114 (1)	C(25)–C(26)–O(27)	177 (2)
C(2)–C(25)–C(28)	128 (1)	C(25)–C(28)–C(30)	127 (1)

Table III. Selected Torsion Angles (deg) for **10**

atoms	angle
O(1)–C(2)–O(3)–C(4)	-48 (1)
C(2)–O(3)–C(4)–C(5)	20 (1)
O(3)–C(4)–C(5)–C(6)	13 (1)
O(3)–C(2)–C(25)–C(26)	-148 (1)
C(2)–C(25)–C(28)–C(29)	-12 (2)
C(4)–C(5)–C(6)–O(1)	-14 (2)
C(5)–C(6)–O(1)–C(2)	-17 (1)
C(6)–O(1)–C(2)–O(3)	47 (1)
C(21)–C(2)–C(25)–C(26)	92 (1)
C(26)–C(25)–C(28)–C(29)	170 (1)

Results

The *tert*-butylpivaloylfurandione **7** was prepared from dipivaloylmethane and oxalyl chloride.[10] FVP of this material at 350 °C (10^{-4} Torr) with Ar matrix isolation of the product at 12 K gave a sharp band due to CO (2138 cm^{-1}) and a very strong ketene absorption at 2131 cm^{-1} (Figure 1a). (A small amount of CO_2 (2340 cm^{-1}) also appears). When the pyrolyzate was collected as a neat solid at 77 K, the ketene absorption appeared at 2119 cm^{-1}, CO and CO_2 did not appear, and the remainder of the spectrum was identical with but less well resolved than that shown in Figure 1. This compound remained stable on warmup, in vacuum to −30 °C. In an analogous experiment, the pyrolyzate was dissolved in CD_2Cl_2 below −50 °C and examined by ^1H and ^{13}C NMR spectroscopies. The ^1H NMR spectrum showed only one peak (δ 1.14). The ^{13}C NMR featured five signals in excellent agreement with expectations for dipivaloylketene (**8**). The compound remained stable on brief warming of the CD_2Cl_2 solution to room temperature, and a reexamination of the ^{13}C NMR spectrum after storing the solution at −20 °C for 2 weeks showed only minor changes. Addition of methanol caused rapid disappearance of the ketene as observed by ^{13}C NMR and IR spectroscopies, and slow evaporation of this solution gave the crystalline ester **9**, the structure of which was established by ^1H and ^{13}C NMR.

Evaporation of a CD_2Cl_2 solution of ketene **8** gave a material that still contained a ketene function (2115 (s) cm^{-1}). However, closer inspection of the IR spectrum and, in particular, the NMR spectra revealed that a very different compound had formed. The proton NMR spectrum showed four different *tert*-butyl groups (1:1:1:1). The carbon NMR spectrum also exhibited the four *tert*-butyl groups, as well as eight additional quaternary carbon atoms. The ensemble of data is best reconciled with dimer structure **10**. Infrared examinations demonstrated that **10** started forming immediately when a solution of **8** was evaporated, and this process was complete in 15 min. The IR spectrum of crystalline **10** is illustrated in Figure 1b. Ketene **10** is extremely stable: There was no change in the spectral properties after keeping it in the open air at temperatures up to 30 °C and humidity up to 80% for 2 months. The structure was confirmed by X-ray crystallography, which also clearly demonstrates the highly hindered ketene functionality.

X-ray Crystallography

The six-membered 1,3-dioxine ring in **10** forms a skewed boat [deviations from the plane through all the atoms: O(1), 0.17; C(2), −0.28; O(3), 0.17; C(4), 0.04; C(5), −0.15; C(6), 0.05 Å]. The ketene group is nearly coplanar with the ketone at C(28) [torsional angle about the C(25)–C(28) bond: 170° (1); deviations from the plane: C(25), −0.04; C(26), −0.01, O(27), 0.04; C(28), −0.07, O(29), 0.07 Å]. There are no intermolecular interactions shorter than 3.6 Å.

An ORTEP drawing of the molecular structure is shown in Figure 2. The nearly planar s-trans α-oxoketene moiety in **10** is noteworthy (torsional angle C(26)–C(25)–C(28)–C(29) = 170° (1)). Also note that the oxoketene functionality at C(2) is cis to the *tert*-butyl group linked to C(5), thus providing severe sterical hindrance of any approach to the ketene.

Important bond lengths, bond angles, and torsion angles are listed in Tables I, II, and III. The data for the ketene functionality, in particular the very short C═O bond of 1.13 Å, is in agreement with the very limited known crystallographic data for other ketenes.[11]

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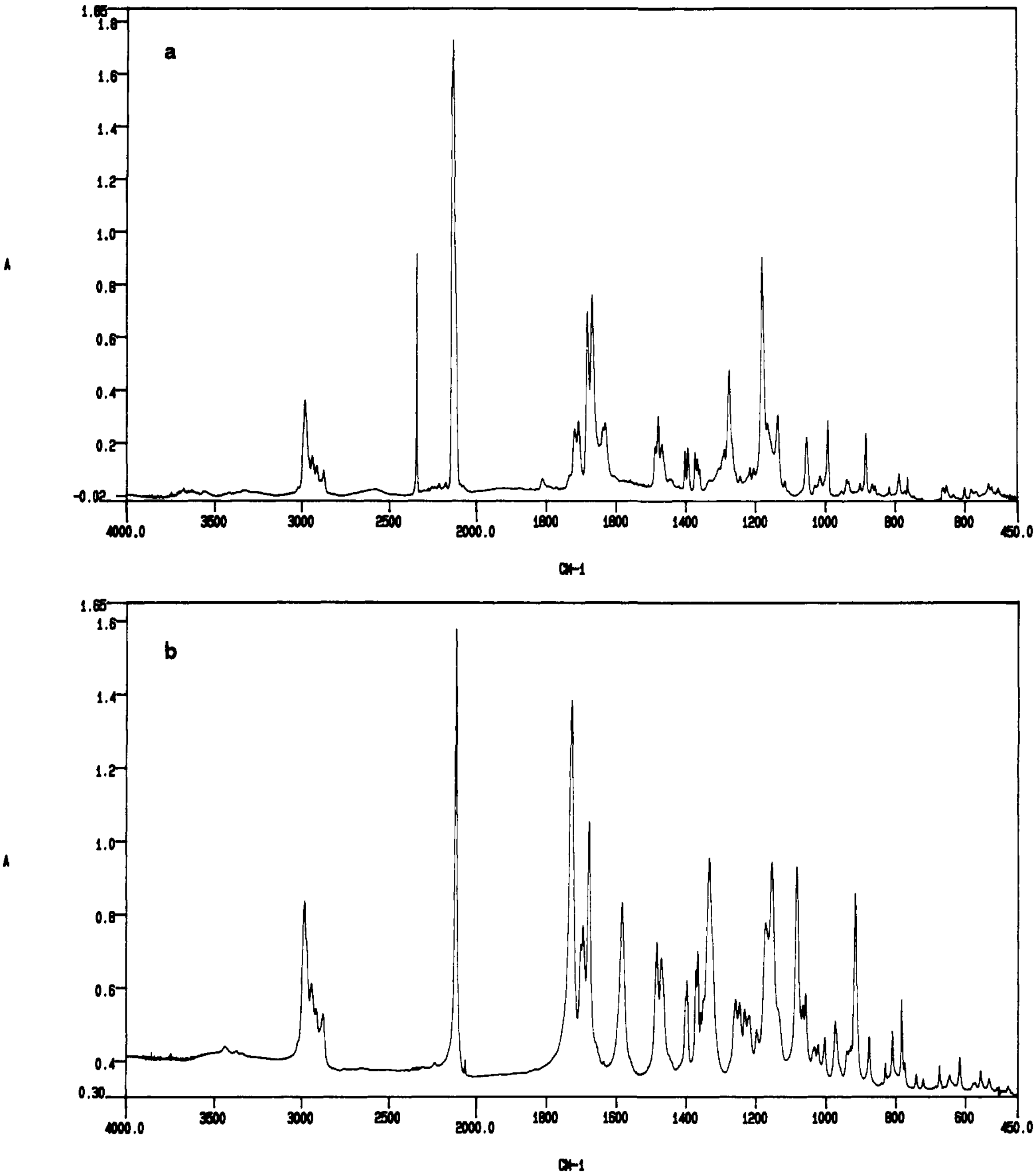

Figure 1. (a) FTIR spectrum of dipivaloylketene (**8**) in Ar matrix at 12 K. The sharp band at 2340 cm^{-1} is due to CO_2. At higher resolution, CO is seen at 2138 cm^{-1}, close to the ketene peak at 2131 cm^{-1}. (b) FTIR spectrum (KBr) of **10**.

Conclusion

Dipivaloylketene (**8**) is a persistent diacylketene that can be handled in solution below room temperature (and for brief periods at higher temperatures). Unlike dibenzoylketene (**2**), which dimerizes with consumption of both ketene functions (eq 1), the hindered nature of **8** makes this approach sterically unfavorable, and the [2+4] cyclodimerization instead involves one molecule of ketene as a four-electron component adding to one of the C=O groups of the other molecule. This generates two neighboring tertiary carbon atoms in dimer **10**. The X-ray structure demonstrates the highly hindered nature of **10**: It is an s-trans α-oxoketene, and the ketene group is flanked by four *tert*-butyl groups. The pivaloyl group at C(5) is rotated out of conjugation with the C=C double bond, and the *tert*-butyl group is cis to the ketene function.

As a crystalline solid, ketene **10** is perfectly stable at room temperature in the presence of oxygen and moisture.

Experimental Section

The FVP apparatus for matrix isolation, for 77 K IR spectroscopy, and for preparative purposes was as previously reported.[4f] IR spectra were recorded on a Perkin-Elmer 1700X FTIR and NMR spectra on a Jeol GX 400 spectrometer.

The X-ray crystal structure was determined on an Enraf-Nonius CAD4 four-circle diffractometer[12a] with molybdenum X-radiation (gra-

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(11) For X-ray structures of ketenes (R(C=O) = 1.16 and 1.15 Å), see: Schubert, U.; Kron, J.; Hörnig, H. *J. Organomet. Chem.* **1988**, *355*, 243–256. Weiss, K.; Schubert, U.; Schrock, R. R. *Organometallics* **1986**, *5*, 397–398. For microwave and electron diffraction (R(C=O) = 1.16–1.17 Å), see: Runge, W. In *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S. Ed.; Wiley-Interscience: Chichester, England, 1980; Part 1, p 59–60. For theoretical calculations on CH_2=C=O, see: Dykstra, C. E.; Schaefer, H. F. In *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S. Ed.; Wiley-Interscience: Chichester, England, 1980; Part 1, p 20.

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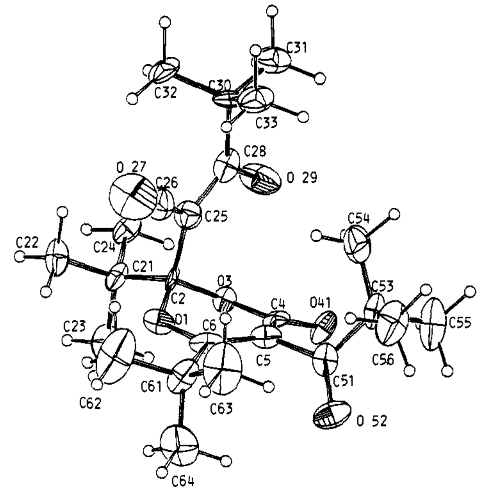

Figure 2. ORTEP drawing of the X-ray structure of **10** (30% probability thermal ellipsoids for non-hydrogen atoms).

phite monochromater). The crystal selected was a clear, colorless plate but a poor diffractor yielding only 953 observed reflections out of 4907 collected. The structure was solved with use of direct methods (TREF 200) in SHELXS 86.[12b] Full-matrix least-squares refinement[12c] was on F's; C, H, O scattering factors[12d] were used; hydrogen positions were calculated.

Dipivaloylketene (8). (i) 5-*tert*-Butyl-4-pivaloyl-2,3-dihydrofuran-2,3-dione[10] (**7**) (15 mg) was sublimed at 50 °C into the pyrolysis apparatus for low-temperature IR spectroscopy[4f] (10-cm quartz pyrolysis tube at 350 °C) at a pressure of $(2-4) \times 10^{-4}$ mbar. The product collected on a KBr disk at 77 K had the following IR: 2973, 2119 (vs), 1704, 1661, 1478, 1368, 1267, 1137, 1054, 999 cm^{-1}.

(ii) The same experiment carried out with Ar matrix isolation of the product at 12 K (pyrolysis temperature 350–500 °C; pressure 2×10^{-4} mbar) gave the IR spectrum shown in Figure 1a: 2979, 2939, 2131 (vs) 1682, 1666, 1477, 1274, 1180, 1135, 1053, 994, 885 cm^{-1}.

(iii) **7** (350 mg) was subjected to FVP (500 °C; 10^{-3} mbar) in the preparative apparatus[4f] by gentle sublimation in the course of 1 h. The product was collected on a cold finger (77 K) that had been previously coated with CD_2Cl_2. After the pyrolysis was completed, a further layer of CD_2Cl_2 was deposited on top of the sample; the cold finger was allowed to warm until CD_2Cl_2 started to melt, and at this point the apparatus was pressurized to 1 atm with dry N_2. The melting CD_2Cl_2 solution was collected in a flask at 77 K, from where a part was subsequently transferred to an NMR tube at −76 °C: ^{1}H NMR (CD_2Cl_2, −50 °C) δ 1.14 (s, t-C_4H_9); ^{13}C NMR (CD_2Cl_2, −50 °C) δ 26.3 (q, CH_3), 47.2 ($C(CH_3)_3$), 52.1 (*C*CO), 194.0 (C*C*O), 198.9 (*C*O). The compound was >90% pure according to the NMR spectra.

Brief warming of the CD_2Cl_2 solution to room temperature caused no change. Storing the solution at −20 °C for 2 weeks and rerecording the NMR spectra at room temperature showed that only minor decomposition had occurred. Additional peaks were ascribed to the formation of small amounts of dipivaloylacetic acid due to hydrolysis of the ketene, but this compound decarboxylated readily to dipivaloylmethane and was not examined further.

A recording of the IR spectrum of the CD_2Cl_2 solution as thin film at room temperature demonstrated that ketene **8** was still intact, but as soon as the solvent evaporated dimerization to **10** commenced. This process was complete in 15 min in the thin film on KBr, but a 100-mg sample took 24 h to completely dimerize to **10**.

Methyl Dipivaloylacetate (9). Addition of a few drops of CH_3OH to the CD_2Cl_2 solution of ketene **8** at room temperature caused rapid disappearance of the original NMR signals. Slow evaporation of the solution gave long needles of **9**: mp 49–50 °C; ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 18 H, $C(CH_3)_3$), 3.73 (s, 3 H, OCH_3), 5.36 (s, 1 H, HC(2)); ^{13}C NMR ($CDCl_3$) δ 26.6 (q of septets, ^1J = 127.1 Hz, ^3J = 4.7 Hz, $C(CH_3)_3$), 45.5 (m, ^2J = 4.0 Hz, $C(CH_3)_3$), 53.0 (q, ^1J = 147.9 Hz, OCH_3), 61.7 (d, ^1J = 131.1 Hz, H*C*(2)), 165.8 (6 peaks, probably d of q, ^2J = 8 Hz, ^3J = 4 Hz, *C*OOCH$_3$), 204.9 (m, $^3J \approx 5.7$ Hz; *C*O(tBu)); IR (film) 1750, 1716 cm^{-1}, no ketene absorption remained; HRMS calcd for $C_{13}H_{22}O_4$ m/z 242.15181, found 242.1522.

2-[3,3-Dimethyl-2-oxo-1-(oxomethylene)butyl]-2,6-di-*tert*-butyl-5-pivaloyl-1,3-dioxin-4(2*H*)-one (10). Evaporation of a CD_2Cl_2 solution of **8** at room temperature afforded white crystals of **10** in the course of 24 h. The ^{13}C NMR spectrum recorded during the dimerization process revealed no evidence for any other dimer than **10** being formed. Recrystallization from hexane gave **10**: mp 105–108 °C (colorless plates); ^{1}H NMR ($CDCl_3$) δ 1.07 (s), 1.19 (s), 1.22 (s), 1.23 (s), in a ratio 1:1:1:1; ^{13}C NMR ($CDCl_3$) δ 24.6, 27.3, 28.3, 29.0 (all q, $C(CH_3)_3$), 38.6, 43.8, 45.8, 46.5 (all $C(CH_3)_3$), 48.8 (*C*CO), 107.9 and 109.2 (C(5) and C(2)), 159.9, 174.1, 191.1, 197.6, 209.5 (4 C═O plus C(6)); IR (KBr) (see Figure 1b) 2978, 2940, 2875, 2115 (vs), 2061 (w), 1728 (s), 1694, 1677, 1582, 1482, 1469, 1395, 1371, 1365, 1332, 1257, 1246, 1231, 1197, 1153, 1082, 1066, 1057, 1023, 1004, 973, 916, 877, 830, 801, 783, 741, 721, 674 cm^{-1}. Anal. Calcd for $C_{24}H_{36}O_6$: C, 68.53; H, 8.64. Found: C, 68.57; H, 8.70.

X-ray crystal data: $C_{24}H_{36}O_6$, mol wt 420.55 Da, orthorhomic, space group *Pccn* (No. 56), a = 30.65 (1), b = 12.924 (3), c = 12.436 (3) Å, U = 4927 (2) Å^3, Z = 8, ρ_c = 1.13 g cm^{-3}, $F(000)$ = 1824 electrons; temp 293 K; crystal size 0.36 × 0.28 × 0.12 mm, $\mu_{\text{Mo}\,K\alpha}$ = 6.58 cm^{-1}; data were not corrected for absorption; 25 reflections used for cell dimensions ($12° < 2\theta < 22°$); λ = 0.71069 Å, graphite monochromator; 4907 reflections collected between $2° < 2\theta < 50°$; ω scan angle 0.38°; ω scan; 45-s max scan time; h, $0 \rightarrow 14$; k, $0 \rightarrow 15$; l, $0 \rightarrow 36$; standards (0, −2, 8), 329 (4); (4, 0, −8), 323 (3); (3, −5, −4), 408 (3); data collected on a CAD4 in 25.7 h; 2.5% decomposition with time; data were not corrected; 953 reflections were observed with $I_{\text{obs}} > 2\sigma I_{\text{min}}$; poor diffractor; R = 0.087, ωR = 0.076, $\omega = 4.2/(\sigma^2 F_o + ((7 \times 10^{-4})F_o^2))$; S = 4.0; final atomic shifts/av σ = 0.087; unaccounted for difference electron density 0.27 electrons Å^{-3}.

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Supplementary Material Available: Tables of X-ray crystallographic data for compound **10** (4 pages); table of observed and calculated structure factors for compound **10** (4 pages). Ordering information is given on any current masthead page.