

24. Two Unusual Trimers of Diketene

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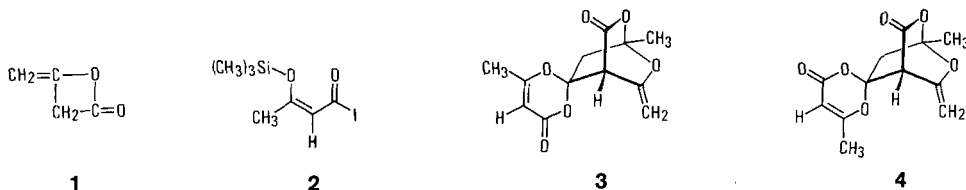
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Formation of two unknown, tricyclic trimers of diketene, **3** and **4**, was observed in diketene solutions containing $(\text{CH}_3)_3\text{SiCl}/\text{NaI}$ or TsOH .

Diketene (**1**), one of the smallest among the organic molecules, guards its secrets well. After its discovery in 1908 [1], forty years elapsed before its structure was definitely elucidated [2], and now, after five decades of existence as an important industrial product, it is still divulging, one by one, new facts about its amazing chemistry [3]. In this paper, we wish to report on two unknown trimers of diketene of quite unusual structures.

Recently, Yamamoto *et al.* [4] recommended, for *N*-acetoacetylation of primary amides, a new reagent prepared *in situ* from diketene and Me_3SiI (or Me_3SiCl and NaI) in MeCN . The active component of this reagent was tentatively formulated as trimethylsilyl enol ether **2** of acetoacetyl iodide.



We have now observed that, on standing at room temperature, the Yamamoto reagent developed two new crystalline compounds **3** and **4** which could be separated by silica-gel chromatography. These compounds were also formed when a solution of diketene in MeCN was heated at 50° in the presence of catalytic amounts of TsOH .

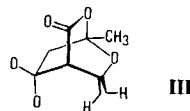
The MS of both **3** and **4** were practically identical and displayed each a molecular peak at m/z 252, suggesting two trimers of diketene, $\text{C}_{12}\text{H}_{12}\text{O}_6$; their (identical) elemental analyses were in agreement with the latter empirical formula.

The structural similarity of **3** and **4** manifests itself in their very similar IR and NMR spectra; this can be appreciated by comparing the IR and ^1H -NMR data (see *Exper. Part*) and the ^{13}C -NMR chemical shifts in Table 1. For structure elucidation, however, the one-bond connectivities of the C-atoms had to be determined from the ^{13}C , ^{13}C -coupling constants [5], in addition to the above-mentioned information.

Measurement of the ^{13}C , ^{13}C couplings from the ^{13}C -satellite signals in broad band decoupled ^{13}C -NMR spectra allowed to deduce the presence of two fragments **I** and **II**

Table 1. ^{13}C -NMR Chemical Shifts of **3** and **4**

	3	4
	C(1) 22.63	22.66
$\begin{array}{c} \text{(1)}\text{CH}_3 \\ \\ \text{(2)}\text{C}-\text{O} \\ \\ \text{(3)}\text{CH}_2 \\ \\ \text{(4)}\text{C}-\text{O} \\ \\ \text{(5)}\text{HC}-\text{C}(=\text{O})-\text{O} \\ \\ \text{(6)}\text{C}-\text{O} \\ \\ \text{(7)}\text{CH}_2 \end{array}$ I	C(2) 103.95	103.85
	C(3) 46.66	46.81
	C(4) 101.69	101.64
	C(5) 50.16	50.36
	C(6) 145.94	147.33
	C(7) 91.94	90.65
	C(8) 164.61	163.64
$\begin{array}{c} \text{(9)}\text{CH}_3 \\ \\ \text{(10)}\text{C}-\text{O} \\ \\ \text{(11)}\text{HC} \\ \\ \text{(12)}\text{C}-\text{O} \\ \\ \text{O} \end{array}$ II	C(9) 19.53	19.52
	C(10) 169.00	168.59
	C(11) 95.82	95.92
	C(12) 158.05	157.73



^{a)} δ values in ppm (± 0.02 ppm) at 100.6 MHz in CDCl_3 , concentrations ca. 60 mg/ml, $T = 25^\circ$, internal standard: TMS ($\delta = 0$ ppm).

with 8 and 4 contiguous C-atoms, respectively (Table 1). The values of the ^{13}C , ^{13}C -coupling constants and the ^{13}C -isotope effects on chemical shifts are shown in Table 2. The latter were determined by an *AB* analysis of the various two-spin systems.

To account for the molecular formulae, two connections of the C-atoms *via* common O-atoms have to be made in the C_8 fragment **I** and two sites for attachment for the C_4 fragment **II** have to be provided. Although several possibilities for connections exist, all but one lead to partial structures with four-membered rings which have to be excluded for

Table 2. One-Bond ^{13}C , ^{13}C -Coupling Constants^{a)} and ^{13}C -Isotope Effects on ^{13}C -NMR Chemical Shifts^{b)}

<i>i, j</i>	Isomer 3			Isomer 4		
	$J(\text{C}_i, \text{C}_j)$	$A(\text{C}_j)^{\text{b)}}$	$A(\text{C}_j)^{\text{b)}}$	$J(\text{C}_i, \text{C}_j)$	$A(\text{C}_j)^{\text{b)}}$	$A(\text{C}_j)^{\text{b)}}$
1,2	49.1	−0.8	−0.6	49.2	−0.9	^{c)}
2,3	40.6	−0.7	−0.8	40.7	^{c)}	−0.9
3,4	44.5	−0.7	−0.7	44.5	−0.9	^{c)}
4,5	37.7	−1.0	−0.8	38.1	^{c)}	−0.8
5,6	42.9	−0.7	−0.8	42.6	−0.8	^{c)}
5,8	50.6	−1.1	−0.3	50.8	−1.2	^{c)}
6,7	89.2	−2.5	−2.6	88.7	^{c)}	−2.6
9,10	49.6	−0.9	−0.6	49.7	−0.9	^{c)}
10,11	71.1	−2.5	−2.8	70.9	^{c)}	−2.8
11,12	72.6	−0.8	−0.3	72.7	−0.9	^{c)}

^{a)} 1J values in Hz (± 0.2 Hz) at 100.6 MHz, measured from ^{13}C -satellite signals in broad band decoupled ^{13}C -NMR spectra of saturated solutions in CDCl_3 (**3**: ca. 150 mg/ml; **4**: ca. 60 mg/ml); measuring temperature, 298 K.

^{b)} Difference of chemical shifts for C_i or C_j between $^{13}\text{C}_2$ isotopomer (C_i and $\text{C}_j = ^{13}\text{C}$) and $^{13}\text{C}_1$ isotopomer (C_i or $\text{C}_j = ^{13}\text{C}$) in Hz (± 0.3 Hz); chemical shifts in the $^{13}\text{C}_2$ two-spin system calculated by *AB* analysis.

^{c)} Because of limited solubility satellite signals could only be observed for the H-bearing C-atoms.

spectroscopic reasons: β -Lactones and diketenes are not compatible with the IR and NMR spectra; oxetanes can be excluded, because smaller ^{13}C , ^{13}C -coupling constants are expected for such structural elements (*e.g.* $J(^{13}\text{C}, ^{13}\text{C}) = 29.5 \text{ Hz}$ for oxetane; see [5]). The remaining possibility, *i.e.* connection of C(2) with C(6) and C(8), leads to the bicyclic fragment **III**, onto which fragment **II** can be attached in two ways. The resulting structures **3** and **4**, for which quite similar IR and NMR spectra are to be expected, are in very good agreement with all spectral parameters. However, a differentiation between **3** and **4** is not possible from the spectroscopic results. Therefore, an X-ray structure analysis of the lower-melting isomer was carried out. The result is given in the *Figure*.

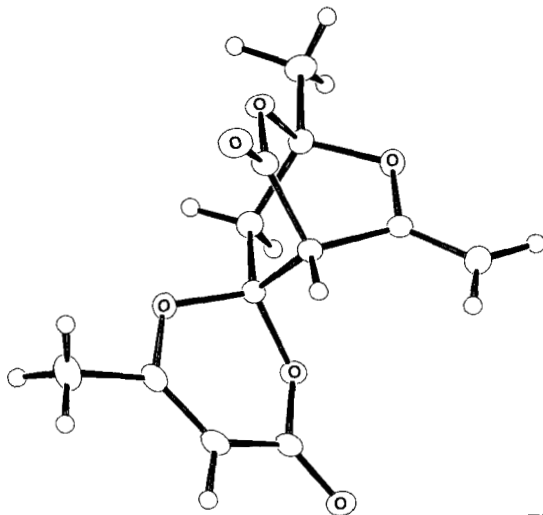
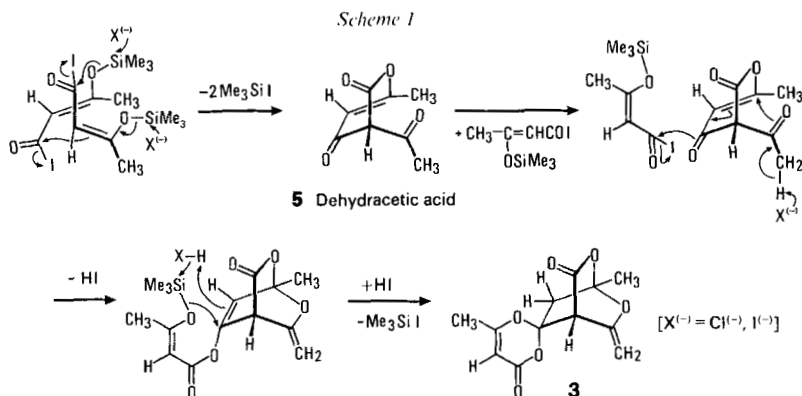
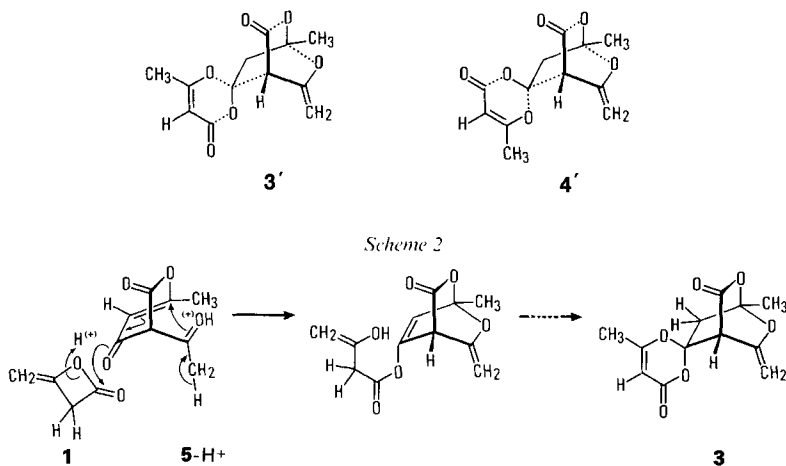


Figure. Molecular structure of **3**

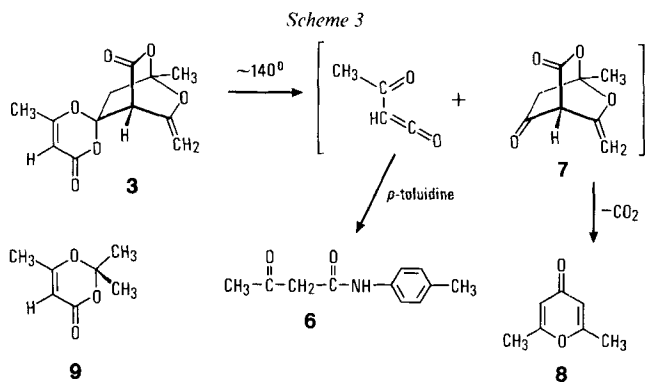
The formulae **3'** and **4'** schematically demonstrate how three molecules of diketene compose the framework of the trimers. On the other hand, we can only speculate about the detailed mechanism of the trimerization. *Scheme 1* presents such a speculation about the formation of the trimer **3** from the Yamamoto reagent; we anticipate a primary formation of the trimethylsilyl enoether **2** and dehydracetic acid (**5**) as a further inter-





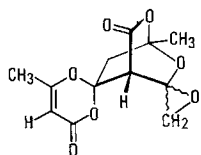
mediate (in fact, small amounts of **5** always accompanied the trimers in the crude reaction product). Similarly, *Scheme 2* illustrates our idea about the final stages of the *p*-toluenesulfonic-acid catalyzed trimerization.

On heating in boiling xylene, both trimers **3** and **4** partially depolymerized releasing the originally spiro-annellated diketene equivalent; the latter could be trapped by *p*-toluidine as *N*-(*p*-tolyl)acetoacetamide (**6**; *Scheme 3*). In this respect, the trimers remind of

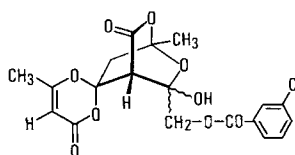


the more simple, but similarly built diketene-acetone addition product, *i. e.* of 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (**9**), which on pyrolysis also liberates a diketene equivalent and acetone [6] [7]. In the case of the trimers **3** and **4**, however, the ketone **7** – the other expected split of the trimer molecule – could never be detected; instead of it, 2,6-dimethyl-4-pyrone (**8**), a product of a (*retro*-Diels-Alder?) decarboxylation of **7**, was repeatedly isolated (*Scheme 3*). The 4-pyrone **8** was also formed on prolonged heating of **3** in MeOH at 50° with a catalytic amount of *p*-toluenesulfonic acid.

With 1 equiv. of *m*-chloroperbenzoic acid in CH_2Cl_2 , the trimer **3** was epoxidized on its exocyclic double bond giving a single epoxide **10** (of undetermined configuration) in a moderate yield of 40%. No further oxidation took place with excess of peracid; however,



10



11

on prolonged treatment in the presence of the *m*-chlorobenzoic acid formed, a partial opening of the epoxide to the *m*-chlorobenzoate **11** was observed.

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Experimental Part

General. M.p.: *Kofler*; uncorrected. IR spectra: absorptions in cm^{-1} . $^1\text{H-NMR}$ (400.1 MHz) and $^{13}\text{C-NMR}$ spectra (100.6 MHz): *Bruker WM 400* spectrometer; chemical shifts are given as δ values in ppm with respect to tetramethylsilane as internal reference ($= 0$ ppm), coupling constants *J* in Hz. *R_f* values: *Merck* silica gel 60 *F₂₅₄* TLC plates. MS: *Varian CH 7* spectrometer.

1,6'-Dimethyl-5-methylidenespiro[2,6-dioxabicyclo[2,2,2]octane-8,2'-4'-H-dioxine]-3,4'-dione (3 and 4). A. *With Me₃SiCl/NaI.* To a stirred soln. of 8.72 g (0.104 mol) of freshly distilled diketene and 15.5 g (0.104 mol) of NaI in 240 ml of MeCN in an ice/H₂O bath, a soln. of 13.1 ml (11.27 g, 0.1033 mol) of Me₃SiCl in 80 ml of MeCN was added within 30 min. After another 4 h of stirring at r.t., the resulting dark orange mixture was diluted with 1 l of CH₂Cl₂ and successively washed with H₂O (300 ml) and sat. aq. NaHCO₃ soln. (300 ml). The aq. washings were reextracted with CH₂Cl₂ (300 ml) and the combined org. phases dried over MgSO₄ and evaporated: 5.58 g of crude product which was chromatographed on a *Merck* silica-gel column (100 g) with toluene/AcOEt 9:1. After a forerun (0.48 g) mainly containing **5**, the trimer **3** (1.95 g, 22.4%) was eluted followed, after a small mixed fraction (0.34 g), by **4** (1.36 g, 15.6%). Both products were crystalline and were recrystallized from CH₂Cl₂/Et₂O/pentane. B. *With TsOH as Catalyst.* A soln. of 6.57 g (78.15 mmol) of freshly distilled diketene and of 640 mg (3.36 mmol, 4.2 mol-%) of TsOH · H₂O in 180 ml of MeCN was stirred under Ar at 50° for 20 h. Similar workup and chromatography as above afforded 0.32 g of a forerun (containing **5**), 1.91 g of a fairly pure **3**, 0.21 g of a mixed fraction, and 0.76 g of almost pure **4**. Crystallization of the individual parts from CH₂Cl₂/Et₂O/pentane, combined with prep. TLC (*Merck* silica gel plates) of the mother liquors, finally yielded 1.44 g (21.9%) of pure **3** and 0.69 g (10.5%) of pure **4**. **Trimer 3:** M.p. 148–150° (CH₂Cl₂/Et₂O/pentane). *R_f* (toluene/AcOEt 3:2) 0.46. IR (CH₂Cl₂): 1797, 1750, 1671, 1646, 1388, 1347, 1301, 1282, 1195, 1081, 1068, 998, 953, 926, 839, 820. $^1\text{H-NMR}$ (CDCl₃): 5.40 (*q*, *J* = 1, 1 H); 4.58 (*d*, *J* = 2.5, 1 H); 4.30 (*d*, *J* = 2.5, 1 H); 4.18 (*s*, 1 H); 2.64 (*s*, 2 H); 2.03 (*d*, *J* = 1, 3 H); 1.72 (*s*, 3 H). $^{13}\text{C-NMR}$: *Table 1*. MS (110°): 252 (*M*⁺), 224, 210, 182, 168, 153, 126, 124, 98, 96, 85, 84. Anal. calc. for C₁₂H₁₂O₆ (252.22): C 57.15, H 4.80, O 38.06; found: C 56.93, H 4.92, O 38.05.

Trimer 4: M.p. 180–181° (CH₂Cl₂/Et₂O/pentane). *R_f* (toluene/AcOEt 3:2) 0.39. IR (CH₂Cl₂): 1798, 1757, 1670, 1646, 1388, 1347, 1301, 1285, 1203, 1141, 1065, 999, 956, 932, 908, 874, 843, 819. $^1\text{H-NMR}$ (CDCl₃): 5.41 (*q*, *J* = 1, 1 H); 4.52 (*d*, *J* = 2.5, 1 H); 4.22 (*d*, *J* = 2.5, 1 H); 4.18 (*s*, 1 H); 2.67 (*d*, *J* = 15, 1 H); 2.63 (*d*, *J* = 15, 1 H); 2.04 (*d*, *J* = 1, 3 H); 1.72 (*s*, 3 H). $^{13}\text{C-NMR}$: *Table 1*. MS (90°): 252 (*M*⁺), 224, 210, 182, 168, 153, 126, 124, 98, 96, 85, 84, 69. Anal. calc. for C₁₂H₁₂O₆ (252.22): C 57.15, H 4.80, O 38.06; found: C 57.18, H 4.92, O 37.96.

Pyrolysis of 3 and 4 in the Presence of *p*-Toluidine. A soln. of 126.1 mg (0.50 mmol) of **3** and 54.5 mg (0.51 mmol) of *p*-toluidine in 3 ml of xylene was heated under reflux and under Ar (bath temp. 150°). After 1.5 h, the mixture was diluted with CH₂Cl₂ and successively washed with cold 1N aq. H₂SO₄ and with 8% aq. NaHCO₃ soln. The crude product (147 mg) as obtained by evaporation of the org. part was chromatographed on several anal. TLC plates (*Merck*; toluene/AcOEt 1:1) yielding **6** and **8**. *N*-(*p*-Tolyl)acetacetamide (**6**): 84.3 mg, 88.2%. Less polar. M.p. 92–93° (CH₂Cl₂/Et₂O/pentane; [8]: 95°). IR and $^1\text{H-NMR}$: identical with those of an authentic sample. Anal. calc. for C₁₁H₁₃NO₂ (191.23): C 69.09, H 6.86, N 7.33, O 16.74; found: C 68.79, H 6.84, N 7.29, O 16.71.

2,6-Dimethyl-4-pyrone (8): 42.1 mg, 67.8%. More polar. M.p. 133–134° ([9]: 132.1°). IR and ¹H-NMR: identical with those of an authentic sample. Anal. calc. for C₇H₈O₂ (124.14): C 67.73, H 6.50, O 25.78; found: C 67.39, H 6.40, O 25.61. Similar results (81.1% of **6** and 66.9% of **8**) were obtained in an analogical pyrolysis of **4**. No reaction occurred when **3** and *p*-toluidine were heated in boiling CH₂Cl₂ (40°) for 5 h.

Methanolysis of 3. A soln. of 126.1 mg (0.50 mmol) of **3** in 5 ml of MeOH containing 10.5 mg of TsOH · H₂O was heated at 50° for 43 h. After evaporation the residue was dissolved in CH₂Cl₂ and washed with sat. aq. NaHCO₃ soln. Evaporation of CH₂Cl₂ afforded 48 mg (77%) of crystalline **8** identical with an authentic sample.

Reaction of 3 with *m*-Chloroperbenzoic Acid. Trimer **3** (126.1 mg, 0.50 mmol) and 100 mg (ca. 0.5 mmol) of 85% *m*-chloroperbenzoic acid in 3 ml of CH₂Cl₂ was stirred at r.t. for 23.5 h. The crystalline precipitate of *m*-chlorobenzoic acid was filtered off, the filtrate washed with an ice-cold, 5% NaHSO₃ soln. and evaporated, and the residue chromatographed on 3 Merck silica gel plates (20 × 20 × 0.05 cm) using hexane/AcOEt 2:1. Along with 27 mg of unchanged **3**, 52 mg (39%) of 1',6'-dimethyldispiro[4H-dioxine-2,8'-(2',6'-dioxabicyclo[2.2.2]octane)-3',2''-oxirane]-4,5'-dione (**10**) was isolated. It was recrystallized from CH₂Cl₂/Et₂O/pentane. M.p. 161–162°. *R*_f (toluene/AcOEt 1:1) 0.42. IR (CH₂Cl₂): 1792, 1745, 1641, 1487, 1385, 1343, 1290–1240, 1215, 1197, 1125, 1100, 1082, 1068, 980, 921. ¹H-NMR (CDCl₃): 5.39 (*d*, *J* = 1, 1 H); 3.49 (*s*, 1 H); 3.23 (*d*, *J* = 3, 1 H); 2.89 (*d*, *J* = 3, 1 H); 2.71 (*d*, *J* = 15, 1 H); 2.65 (*d*, *J* = 15, 1 H); 2.07 (*d*, *J* = 1, 3 H); 1.74 (*s*, 3 H). Anal. calc. for C₁₂H₁₂O₇ (268.22): C 53.74, H 4.51, O 41.76; found: C 53.40, H 4.53, O 41.71.

In another experiment, 252 mg (1 mmol) of **3** in 3 ml of CH₂Cl₂ were stirred at r.t. with 2.2 mmol of 85% *m*-chloroperbenzoic acid, added in 3 portions within 33 h. After a total of 48 h, similar workup and chromatography as above afforded, along with 37.2 mg (14%) of **10**, 47.2 mg (11%) of the amorphous {3-hydroxy-1,6'-dimethyl-4',5'-dioxospiro[2.6-dioxabicyclo[2.2.2]octane-8,2'-4'H-dioxine]-3-yl}methyl *m*-chlorobenzoate (**11**): *R*_f (toluene/AcOEt 1:1) 0.34. IR (CH₂Cl₂): 1796, 1750, 1641, 1575, 1384, 1360, 1341, 1225, 1214, 1198, 1130, 1080, 1040, 925. ¹H-NMR (CDCl₃): 7.89 (*t*, *J* = 2, 1 H); 7.80 (*dt*, *J* = 7.5, 2, 1 H); 7.54 (*dm*, *J* = 7.5, 1 H); 7.30 (*t*, *J* = 7.5, 1 H); 5.60 (*d*, *J* = 12.5, 1 H); 5.43 (*br. s*, 1 H); 4.59 (*s*, 1 H); 4.51 (*d*, *J* = 12.5, 1 H); 2.72 (*d*, *J* = 15, 1 H); 2.62 (*d*, *J* = 15, 1 H); 2.10 (*br. s*, 3 H); 1.76 (*s*, 3 H).

Crystal-Structure Analysis of 3. Crystals were monoclinic, *P*2₁/*c*; *a* = 8.163, *b* = 20.933, *c* = 7.545 Å; β = 115.46°; *Z* = 4. On a Philips PW 1100 diffractometer, 3419 independent reflections were measured, of which 2782 were considered observed (*I* > 2σ(*I*)). The structure was solved by direct methods using the MULTAN 78 program system [10]. All the H-atoms could be located in difference maps and included in the refinement with isotropic temp. factors. For all the other atoms, anisotropic temp. factors were introduced. The refinement converged to a final value of *R* = 0.054. Atomic coordinates and bond distances are given in Table 3 and 4, respectively.

Table 3. Atomic Coordinates of **3**

Atom	<i>X/A</i>	<i>Y/B</i>	<i>Z/C</i>
C(1)	0.1426(2)	0.6148(8)	0.4025(3)
C(2)	−0.0280(3)	0.5766(9)	0.2968(3)
C(3)	−0.1955(3)	0.5966(9)	0.2442(3)
O(4)	0.0091(2)	0.5147(6)	0.2566(2)
C(5)	0.1965(3)	0.5047(6)	0.3099(3)
C(6)	0.2225(3)	0.4362(9)	0.2743(3)
O(7)	0.2955(2)	0.5161(6)	0.5205(2)
C(8)	0.2679(3)	0.5751(9)	0.5752(3)
O(9)	0.3385(2)	0.5908(7)	0.7443(2)
C(10)	0.2647(3)	0.5525(9)	0.2042(3)
C(11)	0.2358(2)	0.6199(8)	0.2627(3)
O(12)	0.1237(2)	0.6543(6)	0.0917(2)
C(13)	0.1083(3)	0.7191(9)	0.1142(3)
O(14)	−0.0198(2)	0.7461(6)	−0.0106(2)
C(15)	0.2580(3)	0.7478(9)	0.2769(3)
C(16)	0.4041(3)	0.7136(9)	0.3858(3)
C(17)	0.5803(3)	0.7377(9)	0.5401(3)
O(18)	0.4095(2)	0.6491(6)	0.3611(2)
H(19)	0.114(3)	0.659(9)	0.451(3)
H(20)	−0.305(3)	0.570(9)	0.171(3)

Table 3 (cont.)

Atom	X/A	Y/B	Z/C
H(21)	-0.199(3)	0.643(9)	0.290(3)
H(22)	0.361(3)	0.423(9)	0.312(3)
H(23)	0.191(3)	0.409(9)	0.349(3)
H(24)	0.165(3)	0.425(9)	0.146(3)
H(25)	0.388(3)	0.543(9)	0.235(3)
H(26)	0.205(3)	0.546(9)	0.067(3)
H(27)	0.252(3)	0.798(9)	0.289(3)
H(28)	0.605(3)	0.724(9)	0.670(3)
H(29)	0.566(3)	0.781(9)	0.543(3)
H(30)	0.676(3)	0.732(9)	0.499(3)

Table 4. Bond Distances in 3

C(1)–C(2)	1.503	C(8)–O(9)	1.198
C(1)–C(8)	1.513	C(10)–C(11)	1.525
C(1)–C(11)	1.547	C(10)–H(25)	0.95
C(1)–H(19)	1.06	C(10)–H(26)	0.95
C(2)–C(3)	1.318	C(11)–O(12)	1.416
C(2)–O(4)	1.393	C(11)–O(18)	1.425
C(3)–H(20)	1.00	O(12)–C(13)	1.379
C(3)–H(21)	1.04	C(13)–O(14)	1.205
O(4)–C(5)	1.420	C(13)–C(15)	1.440
C(5)–C(6)	1.491	C(15)–C(16)	1.330
C(5)–O(7)	1.460	C(15)–H(27)	1.06
C(5)–C(10)	1.526	C(16)–C(17)	1.497
C(6)–H(22)	1.08	C(16)–O(18)	1.366
C(6)–H(23)	0.91	C(17)–H(28)	0.96
C(6)–H(24)	0.91	C(17)–H(29)	0.92
O(7)–C(8)	1.353	C(17)–H(30)	0.97

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