24. Two Unusual Trimers of Diketene

by **Ivan Ernest**[a])*, **Hans Fritz**[b]), and **Grety Rihs**[b])

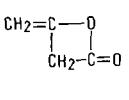
[a]) Pharmaceuticals Division and [b]) Central Function Research of *Ciba-Geigy Ltd.*, CH-4002 Basel

(3. XI. 86)

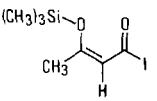
Formation of two unknown, tricyclic trimers of diketene, **3** and **4**, was observed in diketene solutions containing $(CH_3)_3SiCl/NaI$ or TsOH.

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.

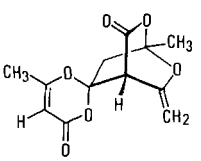
Recently, *Yamamoto et al.* [4] recommended, for *N*-acetoacetylation of primary amides, a new reagent prepared *in situ* from diketene and Me_3SiI (or Me_3SiCl and NaI) in MeCN. The active component of this reagent was tentatively formulated as trimethylsilyl enol ether **2** of acetoacetyl iodide.



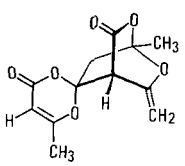
1



2



3



4

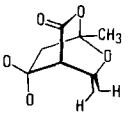
We have now observed that, on standing at room temperature, the *Yamamoto* reagent developed two new crystalline compounds **3** and **4** which could be separated by silica-gel chromatography. These compounds were also formed when a solution of diketene in MeCN was heated at 50° in the presence of catalytic 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, $C_{12}H_{12}O_6$; 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 ^{1}H-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		
		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		
	I	C(8) 164.61	163.64		**III**
		C(9) 19.53	19.52		
		C(10) 169.00	168.59		
		C(11) 95.82	95.92		
	II	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, $T = 25°$, 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, j	Isomer **3**			Isomer **4**		
	$J(C_i, C_j)$	$\Delta(C_i)$[b])	$\Delta(C_j)$[b])	$J(C_i, C_j)$	$\Delta(C_i)$[b])	$\Delta(C_j)$[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 $^{13}C_2$ isotopomer (C_i and $C_j = {}^{13}C$) and $^{13}C_1$ isotopomer (C_i or $C_j = {}^{13}C$) in Hz (±0.3 Hz); chemical shifts in the $^{13}C_2$ 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.* $^1J(^{13}C,^{13}C) = 29.5$ 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*.

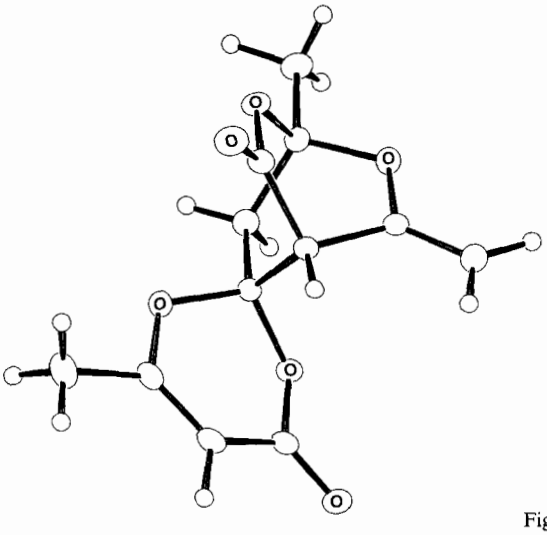
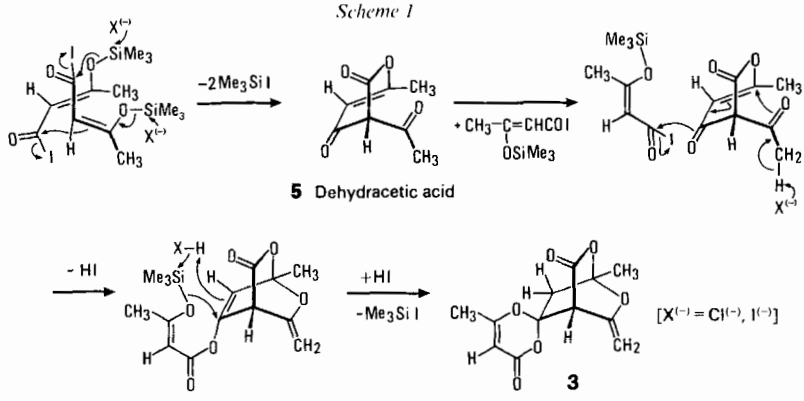
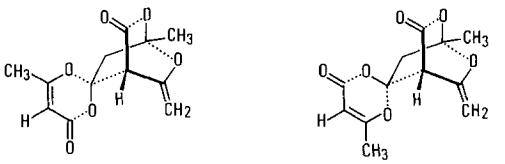


Figure. *Molecular structure of* **3**

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 enolether **2** and dehydracetic acid (**5**) as a further inter-

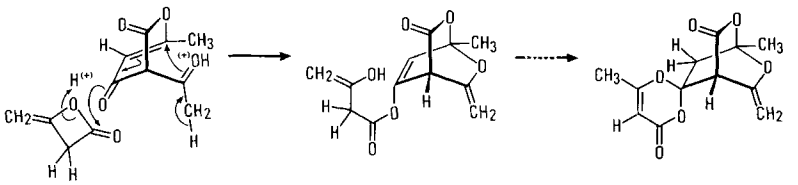
Scheme 1





3′ 4′

Scheme 2

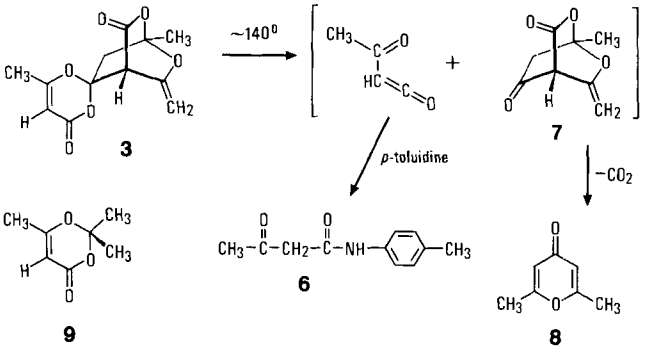


1 5-H+ 3

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

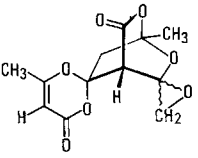
Scheme 3



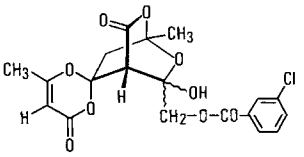
3 9 6 7 8

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.

The authors would like to express their thanks to Dr. *H. Bickel* for his interest and support of the above reported study. Warm thanks are further due to Mr. *S. Moss* (Spectroscopic Services, *Ciba-Geigy Ltd.*) for the IR spectra, to Mr. *O. Hosang* (Spectroscopic Services, *Ciba-Geigy Ltd.*) for the mass spectra, to Dr. *W. Padowetz* and his coworkers (Analytical Department, *Ciba-Geigy Ltd.*) for the elemental analyses, and to Messrs. *P. Felber* and *W. Reburn* for their excellent technical assistance.

Experimental Part

General. M.p.: *Kofler;* uncorrected. IR spectra: absorptions in cm^{-1}. ^{1}H-NMR (400.1 MHz) and ^{13}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* F_{254}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 Me_3SiCl/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/H_2O bath, a soln. of 13.1 ml (11.27 g, 0.1033 mol) of Me_3SiCl 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 CH_2Cl_2 and successively washed with H_2O (300 ml) and sat. aq. $NaHCO_3$ soln. (300 ml). The aq. washings were reextracted with CH_2Cl_2 (300 ml) and the combined org. phases dried over $MgSO_4$ 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 CH_2Cl_2/Et_2O/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 · H_2O 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 CH_2Cl_2/Et_2O/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° (CH_2Cl_2/Et_2O/pentane). R_f (toluene/AcOEt 3:2) 0.46. IR (CH_2Cl_2): 1797, 1750, 1671, 1646, 1388, 1347, 1301, 1282, 1195, 1081, 1068, 998, 953, 926, 839, 820. ^{1}H-NMR ($CDCl_3$): 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}C-NMR: *Table 1.* MS (110°): 252 ($M^{+\cdot}$), 224, 210, 182, 168, 153, 126, 124, 98, 96, 85, 84. Anal. calc. for $C_{12}H_{12}O_6$ (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° (CH_2Cl_2/Et_2O/pentane). R_f (toluene/AcOEt 3:2) 0.39. IR (CH_2Cl_2): 1798, 1757,1670, 1646, 1388, 1347, 1301, 1285, 1203, 1141, 1065, 999, 956, 932, 908, 874, 843, 819. ^{1}H-NMR ($CDCl_3$): 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}C-NMR: *Table 1.* MS (90°): 252 ($M^{+\cdot}$), 224, 210, 182, 168, 153, 126, 124, 98, 96, 85, 84, 69. Anal. calc. for $C_{12}H_{12}O_6$ (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 CH_2Cl_2 and successively washed with cold 1N aq. H_2SO_4 and with 8% aq. $NaHCO_3$ 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)acetoacetamide* (**6**): 84.3 mg, 88.2%. Less polar. M.p. 92–93° (CH_2Cl_2/Et_2O/pentane; [8]: 95°). IR and ^{1}H-NMR: identical with those of an authentic sample. Anal. calc. for $C_{11}H_{13}NO_2$ (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 ^{1}H-NMR: identical with those of an authentic sample. Anal. calc. for $C_7H_8O_2$ (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 CH_2Cl_2 (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 · H_2O was heated at 50° for 43 h. After evaporation the residue was dissolved in CH_2Cl_2 and washed with sat. aq. $NaHCO_3$ soln. Evaporation of CH_2Cl_2 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 CH_2Cl_2 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% $NaHSO_3$ 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[4*H*-dioxine-2,8'-(2',6'-dioxabicyclo[2.2.2]octane)-3',2''-oxirane]-4,5'-dione* (**10**) was isolated. It was recrystallized from CH_2Cl_2/Et_2O/pentane. M.p. 161–162°. R_f (toluene/AcOEt 1:1) 0.42. IR (CH_2Cl_2): 1792, 1745, 1641, 1487, 1385, 1343, 1290–1240, 1215, 1197, 1125, 1100, 1082, 1068, 980, 921. ^{1}H-NMR ($CDCl_3$): 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 $C_{12}H_{12}O_7$ (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 CH_2Cl_2 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 (CH_2Cl_2): 1796, 1750, 1641, 1575, 1384, 1360, 1341, 1225, 1214, 1198, 1130, 1080, 1040, 925. ^{1}H-NMR ($CDCl_3$): 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, $P2_1/c$; $a = 8.163$, $b = 20.933$, $c = 7.545$ Å; $\beta = 115.46°$; $Z = 4$. On a *Philips PW 1100* diffractometer, 3419 independent reflections were measured, of which 2782 were considered observed ($I > 2\sigma(I)$). 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	*X/A*	*Y/B*	*Z/C*
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

REFERENCES

[1] F. Chick, N. T. M. Wilsmore, *J. Chem. Soc.* **1908,** *93,* 946.

[2] C. D. Hurd, C. A. Blanchard, *J. Am. Chem. Soc.* **1950,** *72,* 1461.

[3] See, *e.g.*, the review by R. J. Clemens, *Chem. Rev.* **1986,** *86,* 241.

[4] Y. Yamamoto, S. Ohnishi, Y. Azuma, *Synthesis* **1981,** 122.

[5] V. Wray, in 'Progress in NMR Spectroscopy', Eds. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon Press, Oxford, 1980, Vol. 13, p. 192.

[6] J. A. Hyatt, P. L. Feldman, R. J. Clemens, *J. Org. Chem.* **1984,** *49,* 5105; R. J. Clemens, J. A. Hyatt, *ibid.* **1985,** *50,* 2431.

[7] G. Jäger, J. Wenzelburger, *Liebigs Ann. Chem.* **1976,** 1689.

[8] H. E. Fierz-David, E. Ziegler, *Helv. Chim. Acta* **1928,** *11,* 776.

[9] R. C. Gibbs, J. R. Johnson, E. C. Hughes, *J. Am. Chem. Soc.* **1930,** *52,* 4895, 4902.

[10] P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declerq, M. M. Woolfson (Dept. of Physics, University of York, 1978), A system of computer programmes for the automatic solution of crystal structures from X-ray diffraction data.