

## Regioselective Ring-opening and Dimerisation of Methyl 3,3-Dimethylcyclopropenecarboxylate

Mark S. Baird\* and Helmi H. Hussain

Department of Organic Chemistry, University of Newcastle upon Tyne, NE1 7RU

William Clegg

Department of Inorganic Chemistry, University of Newcastle upon Tyne, NE1 7RU

Methyl 3,3-dimethylcyclopropenecarboxylate (**1**) undergoes dimerisation at 0 to  $-20^{\circ}\text{C}$  over a period of several days to give the bicyclobutane (**7**), which in turn rearranges to the triene (**2**). In the presence of an alkene no intermediates can be trapped. Dimerisation of (**1**) in the presence of copper(I) iodide leads to the tricyclohexane (**10**;  $\text{R} = \text{CO}_2\text{Me}$ ). X-Ray structure determinations are reported for compounds (**2**) and (**10**;  $\text{R} = \text{CO}_2\text{H}$ ).

Cyclopropenes with hydrogens at the 3-position are well known to undergo dimerisation through an ene-type process, leading to cyclopropylcyclopropenes.<sup>1</sup> When there is no hydrogen substituent at C-3, the cyclopropenes can be comparatively stable, although their ring-opening on thermolysis or photolysis has been widely reported.<sup>2</sup> The ester (**1**) has been found to undergo dimerisation and polymerisation at ambient temperature, although no structure has been reported for the dimer.<sup>3</sup> During the course of an examination of the chemistry of compound (**1**), we observed that while it could be stored for several weeks at  $-20^{\circ}\text{C}$  in ether solution, samples of the neat liquid deposited colourless crystals on being allowed to stand for several days at that temperature. These were shown to be of formula  $\text{C}_{14}\text{H}_{20}\text{O}_4$ , and on the basis of i.r. bands at 1724 and 1625  $\text{cm}^{-1}$ , singlets at  $\delta_{\text{H}}$  6.1 (2 H), 3.7 (6 H), and 1.8 (12 H) in the  $^1\text{H}$  n.m.r. spectrum and  $^{13}\text{C}$  n.m.r. signals at  $\delta$  169.4 (s), 137.6 (s), 124.8 (d), 51.0 (q), 23.1 (q), and 19.9 (q) were provisionally characterised as the ester (**2**). The data did not allow this structure to be completely distinguished from the corresponding *Z*-isomer, or indeed from the *E*- or *Z*-forms of the triene (**3**). However, the structure was established unequivocally by an X-ray study (Figure 1).

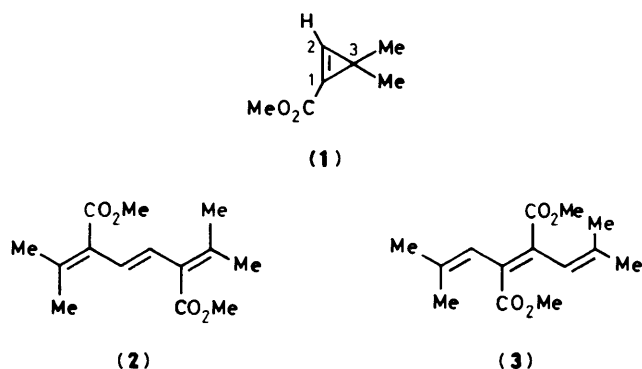


Figure 1. Molecular structure of compound (**2**)

By analogy with the known opening of cyclopropenes to vinylcarbenes,<sup>2</sup> it might be expected that the ester (**1**) could isomerise to (**4**) by cleavage of the 2,3-carbon-carbon bond. A formal dimerisation of this would then produce the triene (**2**). Indeed, hexatrienes have been obtained from other cyclopropenes by dimerisation, and the process has been explained in terms of a reaction between two carbenes; for example, the reaction of 3,3-dimethylcyclopropene with triethyl phosphite-copper(I) chloride, which leads to 2,7-dimethylocta-2,4,6-triene has been explained as a dimerisation of the carbene (**5**;  $\text{R} =$

$\text{H}$ ),<sup>4</sup> or of an intramolecular 'dimerisation' in a copper complex (**6**).<sup>5</sup> However, the chance of two reactive intermediates is rather low under most circumstances,<sup>6</sup> and in general carbene 'dimers' have been explained in terms of the reaction of the carbene with a carbene precursor, e.g. of  $\text{R}_2\text{CX}^-$  with  $\text{R}_2\text{C}$ : followed by elimination of  $\text{X}^-$ .<sup>7</sup> Indeed, when the mother liquor from the formation of (**2**) from (**1**) was examined, a second dimer could be isolated. This showed a much more complex  $^{13}\text{C}$  n.m.r. spectrum than did compound (**2**), including two quaternary carbonyl carbons, two quaternary alkene carbons and six methyl groups; in addition there were two quaternary carbons at  $\delta$  46.0 and 21.8 and two tertiary carbons at 44.9 and 32.0. The  $^1\text{H}$  spectrum was also much more complex, showing two methoxy signals, two sharp methyl singlets at  $\delta$  1.31 and 1.02, a broad methyl singlet at 1.92 and a methyl doublet at 1.99 ( $J$  1.3

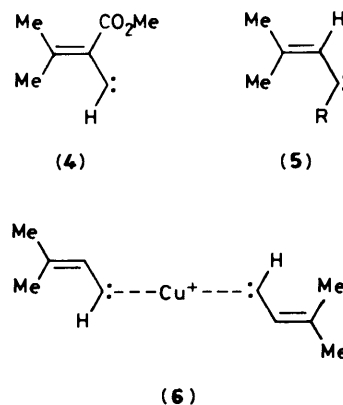
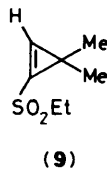
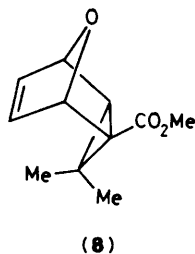
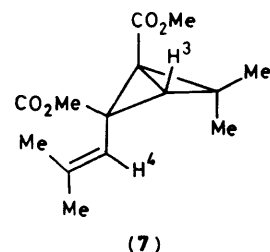


Figure 2. Molecular structure of compound (**10**;  $\text{R} = \text{CO}_2\text{H}$ )

Hz). In addition, a single hydrogen doublet appeared at  $\delta$  2.45 ( $J$  2.5 Hz), and a broad single hydrogen signal was seen at 2.74 (half-width 5 Hz); decoupling of the methyl group at  $\delta$  1.99 caused the signal at  $\delta$  2.74 to become a broad doublet ( $J$  2.5 Hz). On the basis of these data the structure could be assigned as the bicyclobutane (**7**), the signal at  $\delta$  2.74 being assigned to 4-H and that at 2.45 to 3-H; although the high chemical shift for the former is in agreement with the *endo*-stereochemistry,<sup>8a</sup> the coupling constant of 2.5 Hz between the ring hydrogens could correspond to either stereochemistry.

However, the value of  $^1J_{\text{CH}}$  for 4-H of 171 Hz, agreed well with that reported for coupling to an *endo*-hydrogen, and is rather larger than the corresponding value for coupling to an *exo*-hydrogen.<sup>9</sup> A related bicyclobutane formed by photochemical dimerisation of the 2-phenyl analogue of (**1**) has the alkenyl group *exo*.<sup>2e</sup>

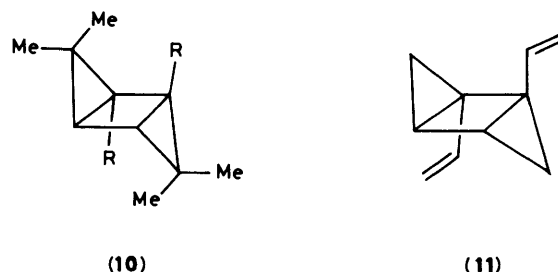
This bicyclobutane was itself unstable, and when allowed to stand for several days at ambient temperature was converted to the crystalline dimer (2);\* although it is not possible to say that (2), obtained from the dimerisation of (1), is all produced *via* (7), this does not seem unlikely. The origin of (7) itself would appear to be the addition of an intermediate carbene (4) to the cyclopropene (1); carbene additions to cyclopropenes have been described in a number of systems although usually only involving symmetrically substituted carbenes.<sup>10</sup> In most additions of carbenes bearing two different substituents to alkenes mixtures of *exo*- and *endo*- products are formed;<sup>7</sup> the observation of a single isomer in the present case may represent a real stereoselectivity in the reaction, but could also be explained by more rapid rearrangement of the *endo*-isomer of the bicyclobutane to the triene (2). In order to test for the formation of the carbene (4), compound (1) was allowed to stand in a large excess of 2,3-dimethylbut-2-ene; examination of the products by <sup>1</sup>H n.m.r. spectroscopy showed slow formation of the dimers (2) and (7), but no evidence for the trapping of a



carbene by the added alkene. In agreement with an earlier report,<sup>11</sup> reaction of the cyclopropene (1) with furan leads to the [4 + 2]-cycloadduct (8) in good yield after 48 h at 20 °C, the only other product being a low yield of dimer (7). The failure to trap a carbene intermediate may suggest that the reaction in fact follows a different mechanism. However, the regioselective ring opening of (1) by cleavage of the 2,3-carbon-carbon bond to give (4) rather than by cleavage of the 1,3-bond to give (5; R = CO<sub>2</sub>Me) is similar to that reported for 1-chloro-3,3-dimethylcyclopropene; in that case also it was not possible to trap the carbene.<sup>12</sup> The regioselectivity is apparently the reverse of that observed for the sulphone (9) where cleavage of the 1,3-bond is reported.<sup>2c</sup>

The formation of carbenes from cyclopropenes has in some cases been promoted by the presence of a copper(I) halide catalyst.<sup>4,5</sup> Compound (1) was therefore allowed to stand at 0 °C with copper(I) iodide, in the presence of dihydropyran. However, instead of the product of carbene trapping by the alkene, a third dimer of (1) was obtained in good yield. This showed a very simple <sup>13</sup>C n.m.r. spectrum with only one carbonyl singlet, one methoxy carbon, and two methyl signals at δ 20.8 and 18.0 as well as two singlets (δ 45.0 and 37.4) and

a doublet (δ 37.4). The proton spectrum was also very simple, showing just four singlets at δ<sub>H</sub> 3.7 (6 H), 1.9 (2 H), 1.35 (6 H), and 1.25 (6 H). This compound was assigned the tricyclic skeleton (10; R = CO<sub>2</sub>Me). The *trans*-1,2-arrangement of the ester groups was proved by a crystal structure determination on the corresponding diacid (10; R = CO<sub>2</sub>H), prepared in the



same way from 3,3-dimethylcyclopropenecarboxylic acid and a catalytic quantity of copper(I) iodide (Figure 2); the acid was converted to the ester by reaction with diazomethane in ether. Similar [2 + 2]-cycloadducts have been obtained in metal-induced reactions of alkylcyclopropenes<sup>13</sup> (although the regioselectivity is not high), from photochemical dimerisations,<sup>14</sup> and from a zeolite-induced dimerisation.<sup>15</sup> Moreover, the formation of the tricyclic compound (11) in a dehydrohalogenation reaction has been rationalised in terms of a thermal dimerisation of 1-vinylcyclopropene.<sup>16</sup>

### Discussion of Crystallographic Results

The triene skeleton of compound (2) (all carbon atoms except the ester methyl groups) is essentially planar (r.m.s. deviation =

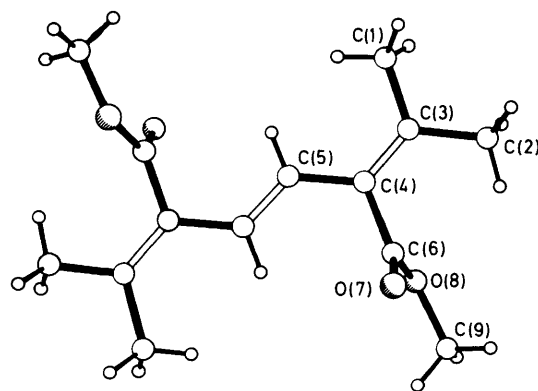


Figure 1. Molecular structure of compound (2)

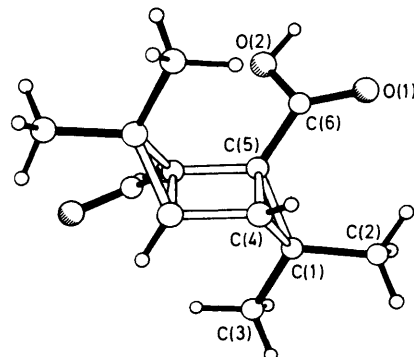


Figure 2. Molecular structure of compound (10; R = CO<sub>2</sub>H)

\* For related isomerisations of bicyclo[1.1.0]butanes to 1,3-dienes, see L. A. Paquette, ch. 4 in 'Alicyclic Compounds, MTP International Review of Science,' Organic Chemistry, Series 1, Volume 5, Butterworths, 1973; G. L. Closs and P. E. Pfeffer, *J. Am. Chem. Soc.*, 1968, **90**, 2452.

0.015 Å). The ester groups [C(4), C(6), O(7), O(8), C(9)] are planar (r.m.s.  $\Delta = 0.022$  Å) and inclined at  $75.9^\circ$  to the triene plane; both ester groups are required to be parallel by the molecular centre of inversion at the midpoint of the C(5)–C(5') bond (Tables 1 and 3).

The molecular structure of (10; R = CO<sub>2</sub>H) shows crystallographic C<sub>2</sub> symmetry. The tricyclic skeleton has a geometry similar to that observed previously for a centrosymmetric molecule with ester and phenyl substituents.<sup>17</sup> [The space group given in this reference as *P*2<sub>1</sub>/*c* should be *P*2<sub>1</sub>/*n*, an alternative setting]. As is common with crystalline carboxylic acids, the molecules associate *via* pairs of hydrogen bonds (O...O = 2.651 Å, O...H = 1.730 Å) around a centre of inversion: for a dicarboxylic acid, this results in hydrogen-bonded chains of molecules parallel to the *c* axis.

### Experimental

All new compounds were homogeneous by t.l.c. Column chromatography was carried out using Merck Kieselgel 60 7736 eluting with light petroleum. N.m.r. spectra were run in solution in deuteriochloroform and recorded at 200 or 300 MHz for <sup>1</sup>H and the corresponding frequencies for <sup>13</sup>C on Bruker Spectrospin instruments. Infra-red spectra were obtained on a Nicolet FT Spectrometer, while mass spectra were recorded on an AEI MS9 or a Kratos MS80 instrument using the e.i.-method. Melting points are uncorrected.

Light petroleum is taken to mean the fraction with b.p. 40–60 °C.

*Decomposition of Methyl 3,3-Dimethylcyclopropenecarboxylate (1).*—(a) A solution of the ester (1) (1.0 g) in ether (15 ml) was allowed to stand for 86 days at –20 °C. Removal of the solvent at 14 mmHg gave a residue which showed only the signals due to the starting ester by <sup>1</sup>H n.m.r. spectroscopy.

(b) The neat ester was allowed to stand at –10 °C. After 4 days colourless crystals had been deposited which were separated from the mother liquor by filtration and were characterised as *dimethyl 2,7-dimethylocta-2,4,6-triene-3,6-dicarboxylate*, m.p. 134–136 °C (Found: *M*<sup>+</sup> 252.1367. C<sub>14</sub>H<sub>20</sub>O<sub>4</sub> requires *M*, 252.1362),  $\delta_{\text{H}}$  6.10 (2 H, s), 3.68 (6 H, s), and 1.81 (12 H, s);  $\delta_{\text{C}}$  169.4 (s), 137.6 (s), 130.6 (s), 124.8 (d), 50.1 (q), 23.1 (q), and 19.9 (q);  $\nu_{\text{max}}$  1 724, 1 324, 1 215, and 1 081 cm<sup>-1</sup>.

The <sup>1</sup>H n.m.r. spectrum of the mother liquor showed major signals due to the starting material, together with additional signals comprising ca. 20% of the spectrum intensity. Column chromatography over silica, eluting with ether–light petroleum (4:6) gave the starting ester and a second fraction characterised as the isomeric *bicyclobutane (7)* (Found: *M*<sup>+</sup> 252.1381) which showed  $\delta_{\text{H}}$  3.71 (3 H, s), 3.62 (3 H, s), 2.74 (1 H, br s,  $w_{\frac{1}{2}}$  5 Hz), 2.45 (1 H, d, *J* 2.5 Hz), 1.99 (3 H, d, *J* 1.3 Hz), 1.92 (3 H, s), 1.31 (3 H, s), and 1.02 (3 H, s);  $\delta_{\text{C}}$  172.2 (s), 168.7 (s), 145.6 (s), 122.6 (s), 51.4 (q), 51.2 (q), 46.0 (s), 44.9 (d), 32.0 (d), 22.9 (q), 22.7 (q), and 21.8 (s);  $\nu_{\text{max}}$  1 723 cm<sup>-1</sup>. Irradiation of the signal at  $\delta_{\text{H}}$  1.99 caused that at 2.74 to be decoupled to a broad doublet (*J* 2.5 Hz). The coupling constants for the signals at  $\delta_{\text{C}}$  44.9 and 32.0 were 171 and 200 Hz respectively.

(c) The neat ester was allowed to stand for 4 days at 20 °C. N.m.r. spectroscopy then showed an extremely complex spectrum between  $\delta$  4–3.5 and 2.4–1.0.

*Decomposition of Methyl 3,3-Dimethylcyclopropenecarboxylate in the Presence of 2,3-Dimethylbut-2-ene.*—Methyl 3,3-dimethylcyclopropenecarboxylate (1) (100 mg) was allowed to stand at 20 °C in 2,3-dimethylbut-2-ene (300 mg). After 15 days, crystals had formed and n.m.r. spectroscopy showed no signals due to starting material. Filtration gave the diester (2) (23 mg,

23%), m.p. 134–136 °C which was identical by n.m.r. spectroscopy to a sample obtained above. Removal of the alkene from the mother liquor gave an oil (37 mg, 37%) which by n.m.r. spectroscopy consisted largely of the bicyclobutane (7). The n.m.r. spectrum showed no evidence for the incorporation of any of the alkene.

*trans-Dimethyl 3,3,6,6-Tetramethyltricyclo[3.1.0.0<sup>2,4</sup>]hexane-1,2-dicarboxylate (10; R = CO<sub>2</sub>Me).*—Methyl 3,3-dimethylcyclopropenecarboxylate (1) (170 mg) was stirred for 18 h at 20 °C with cuprous iodide (257 mg) in tetrahydrofuran (5 ml). The products were extracted with ether (2 × 15 ml) and filtered, and the organic layer was washed with water (2 × 20 ml), dried, and concentrated at 14 mmHg. Column chromatography of the resulting oil over silica, eluting with ether–light petroleum (2:8) gave *trans-dimethyl-3,3,6,6-tetramethyltricyclo[3.1.0.0<sup>2,4</sup>]hexane-1,2-dicarboxylate (10; R = CO<sub>2</sub>Me)* (100 mg, 59%) (Found: *M*<sup>+</sup> 252.1372. C<sub>14</sub>H<sub>20</sub>O<sub>4</sub> requires *M*, 252.1362) which showed  $\delta_{\text{H}}$  3.63 (6 H, s), 1.9 (2 H, s), 1.35 (3 H, s), and 1.25 (3 H, s);  $\delta_{\text{C}}$  172.2 (s), 51.5 (q), 45.0 (s), 37.4 (s), 37.4 (d), 20.8 (q), and 18.0 (q);  $\nu_{\text{max}}$  2 953, 1 720, 1 437, 1 221, and 755 cm<sup>-1</sup>. A second fraction was identical with the triene (2) (8 mg, 5%).

*trans-3,3,6,6-Tetramethyltricyclo[3.1.0.0<sup>2,4</sup>]hexane-1,2-dicarboxylic Acid.*—3,3-Dimethylcyclopropenecarboxylic acid (100 mg) was allowed to stand for 18 h with a catalytic quantity of cuprous iodide (5 mg) in ether (5 ml). After washing the reaction mixture with water and removing the solvent at 14 mmHg, a solid was obtained which showed very broad signals at high field in the <sup>1</sup>H n.m.r. spectrum; however, recrystallisation from ether and methanol gave a low yield (ca. 10%) of 3,3,6,6-tetramethyltricyclo[3.1.0.0<sup>2,4</sup>]hexanecarboxylic acid, m.p. 198–199 °C, which was used for the X-ray study. Treatment with diazomethane in ether gave the diester (10; R = CO<sub>2</sub>Me).

*Reaction of Methyl 3,3-Dimethylcyclopropenecarboxylate with Furan.*—A mixture of methyl 3,3-dimethylcyclopropenecarboxylate (1) (400 mg) and furan (400 mg) was allowed to stand for 48 h at 20 °C, when n.m.r. spectroscopy showed no signals corresponding to starting material. The excess of furan was removed at 14 mmHg and 20 °C to give a pale yellow oil which was purified by column chromatography and characterised as the ester (8)<sup>11</sup> (411 mg, 67%) (Found: *M*<sup>+</sup> 194.0946. C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> requires *M*, 194.0943) which showed  $\delta_{\text{H}}$  6.64 (2 H, s), 5.12 (1 H, s), 4.84 (1 H, s), 3.64 (3 H, s), 1.56 (1 H, s), 1.50 (3 H, s), and 1.26 (3 H, s);  $\delta_{\text{C}}$  172.1 (s), 140.0 (d), 139.5 (d), 78.5 (d), 78.3 (d), 51.5 (q), 46.1 (s), 45.1 (s), 42.5 (d), 24.8 (q), and 18.8 (q);  $\nu_{\text{max}}$  1 731 and 1 284 cm<sup>-1</sup>. A minor fraction (50 mg, 8%) was identical with the bicyclobutane (7) by n.m.r. spectroscopy.

*Crystal Data for (2).*—C<sub>14</sub>H<sub>20</sub>O<sub>4</sub>, *M* = 252.3, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 8.763 0(6), *b* = 8.849 0(7), *c* = 9.294 0(7) Å,  $\beta = 100.291(5)^\circ$ , *V* = 709.10 Å<sup>3</sup> (from 2 $\theta$  values for 32 reflections, 20 < 2 $\theta$  < 40°), *Z* = 2, *D*<sub>x</sub> = 1.182 g cm<sup>-3</sup>, *F*(000) = 272,  $\mu = 0.67$  mm<sup>-1</sup> for Cu-K<sub>α</sub> radiation,  $\lambda = 1.541 84$  Å.

*Data Collection and Processing.*—Crystal size 0.7 × 0.6 × 0.6 mm, Siemens AED2 diffractometer,  $\omega/\theta$  scan, scan width = 1.02° +  $\alpha$ -doublet splitting, scan time = 14–56 s, 2 $\theta_{\text{max}}$  = 135°, index ranges: *h* –10→10, *k* –10→0, *l* –11→11. 2 488 Reflections measured, 1 249 unique (*R*<sub>int</sub> = 0.044), *I* > 2 $\sigma$ (*I*) for structure determination.

*Structure Solution and Refinement.*<sup>18</sup>—Direct methods, blocked cascade least-squares refinement to minimise  $\Sigma w\Delta^2$ ,  $\Delta = |F_{\text{o}}| - |F_{\text{c}}|$ ,  $w^{-1} = \sigma^2(F) + 0.000 53F^2$ . Anisotropic thermal parameters for all C and O atoms, H atoms in

**Table 1.** Atomic co-ordinates ( $\times 10^4$ ) for compound (2)

	x	y	z
C(1)	6 128(3)	3 238(2)	2 438(2)
C(2)	7 172(2)	4 515(2)	397(2)
C(3)	6 382(2)	3 154(2)	884(2)
C(4)	5 946(2)	1 966(1)	-5(2)
C(5)	5 188(2)	612(2)	418(1)
C(6)	6 303(2)	1 969(2)	-1 524(2)
O(7)	7 330(2)	1 270(2)	-1 899(2)
O(8)	5 308(2)	2 815(1)	-2 425(1)
C(9)	5 612(3)	2 961(2)	-3 902(2)

**Table 2.** Atomic co-ordinates ( $\times 10^4$ ) for compound (10; R = CO<sub>2</sub>H)

	x	y	z
C(1)	1 452(2)	4 034(2)	7 579(1)
C(2)	2 291(2)	4 094(3)	6 895(2)
H(2a)	2 778(27)	5 082(37)	7 092(23)
H(2b)	1 907(27)	4 148(34)	6 088(28)
H(2c)	2 770(31)	3 005(42)	7 003(25)
C(3)	2 019(2)	3 998(3)	8 795(2)
H(3a)	2 470(24)	4 997(34)	8 946(24)
H(3b)	2 472(27)	2 940(38)	8 952(25)
H(3c)	1 458(32)	4 021(34)	9 262(27)
C(4)	381(2)	5 020(2)	7 125(1)
H(4)	257(23)	5 778(32)	6 547(23)
C(5)	369(1)	2 935(2)	7 113(1)
C(6)	193(1)	1 726(2)	6 159(1)
O(1)	494(1)	2 073(1)	5 332(1)
O(2)	-307(1)	247(2)	6 286(1)
H	-337(34)	-469(44)	5 680(26)

**Table 3.** Bond lengths (Å) for compound (2)\*

C(1)-C(3)	1.501(3)	C(2)-C(3)	1.499(3)
C(3)-C(4)	1.349(2)	C(4)-C(5)	1.457(2)
C(4)-C(6)	1.500(2)	C(5)-C(5')	1.340(3)
C(6)-O(7)	1.195(2)	C(6)-O(8)	1.326(2)
O(8)-C(9)	1.450(2)		

\* Symmetry operator for primed atoms:  $1 - x, -y, -z$ **Table 4.** Bond lengths (Å) for compound (10; R = CO<sub>2</sub>H)†

C(1)-C(2)	1.518(3)	C(1)-C(3)	1.514(3)
C(1)-C(4)	1.491(3)	C(1)-C(5)	1.548(2)
C(2)-H(2a)	0.944(29)	C(2)-H(2b)	1.009(32)
C(2)-H(2c)	0.995(33)	C(3)-H(3a)	0.922(26)
C(3)-H(3b)	0.960(29)	C(3)-H(3c)	1.023(42)
C(4)-H(4)	0.907(27)	C(4)-C(5)	1.561(2)
C(4)-C(4')	1.505(4)	C(5)-C(6)	1.479(2)
C(5)-C(5')	1.505(4)	C(6)-O(1)	1.230(2)
C(6)-O(2)	1.299(2)	O(2)-H	0.930(34)

† Symmetry operator for primed atoms:  $-x, y, 3/2 - z$ 

calculated positions [C-H = 0.96 Å, H-C-H = 109.5°,  $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ], isotropic extinction parameter  $x = 5(2) \times 10^{-5}$  [ $F_c' = F_c/(1 + xF_c^2/\sin^2 2\theta)^{1/2}$ ]. 92 Parameters,  $R = 0.057$ ,  $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2} = 0.108$ , max. shift/e.s.d. = 0.006, mean = 0.001, slope of normal probability plot = 2.34, largest peak in final difference map = 0.33 eÅ<sup>-3</sup>, largest hole = -0.24 eÅ<sup>-3</sup>.

**Crystal Data for (10; R = CO<sub>2</sub>H).**—C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>,  $M = 224.3$ , monoclinic,  $C2/c$ ,  $a = 12.352(1)$ ,  $b = 7.486(1)$ ,  $c = 12.675(1)$  Å,  $\beta = 105.36(1)^\circ$ ,  $V = 1130.16$  Å<sup>3</sup> (from 30 reflections,  $30 < 2\theta < 40^\circ$ ),  $Z = 4$ ,  $D_x = 1.318$  g cm<sup>-3</sup>,  $F(000) = 480$ ,  $\mu = 0.78$  mm<sup>-1</sup> for Cu-K $\alpha$  radiation.

**Data Collection and Structure Determination.**—As for compound (2) except as follows. Crystal size 0.7 × 0.35 × 0.35 mm,  $2\theta_{\text{max.}} = 130^\circ$ , index ranges:  $h - 14 \rightarrow 9$ ,  $k - 8 \rightarrow 0$ ,  $l - 14 \rightarrow 14$ . 1 616 Reflections measured, 948 unique ( $R_{\text{int}} = 0.064$ ), 914 with  $F > 4\sigma(F)$ . Refinement with  $w^{-1} = \sigma^2(F)$ , H atoms freely refined with isotropic thermal parameters, extinction  $x = 8(3) \times 10^{-6}$ . 106 Parameters,  $R = 0.045$ ,  $R_w = 0.063$ , max. shift/e.s.d. = 0.007, mean = 0.002, slope = 2.68, largest peak = 0.15 eÅ<sup>-3</sup>, largest hole = -0.33 eÅ<sup>-3</sup>.

Atomic co-ordinates are given in Tables 1 and 2, bond lengths in Tables 3 and 4. Bond and torsion angles, and thermal and H-atom parameters, and packing plot for (8) have been deposited with the Cambridge Crystallographic Data Centre.\*

### Acknowledgements

We wish to thank the Arabian Gulf University for the award of a grant to H. H. H. and the S.E.R.C. for a research grant (W. C.).

\* See section 5.1.3, Instructions for Authors (1987), *J. Chem. Soc., Perkin Trans. 1*, 1987, January issue.

### References

- See e.g., P. Dowd and A. Gold, *Tetrahedron Lett.*, 1969, 85; F. J. Weigert, R. L. Baird, and J. R. Shapley, *J. Am. Chem. Soc.*, 1970, **92**, 6630; K. Komatsu, T. Niwa, H. Akari, and K. Okamoto, *J. Chem. Res.*, 1985, (M) 2846; A. Padwa and W. F. Reiker, *J. Am. Chem. Soc.*, 1981, **103**, 1859.
- See e.g., (a) M. S. Baird, S. R. Buxton, and J. Whitley, *Tetrahedron Lett.*, 1984, 1509; (b) A. Padwa, U. Chiacchio, A. Compagnini, A. Corsaro, and G. Purrello, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2671; (c) M. Franck-Neumann and J. J. Lohmann, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 323; (d) M. G. Steinmetz, Y.-P. Yen, and G. P. Poch, *J. Chem. Soc., Chem. Commun.*, 1983, 1504; (e) A. Padwa, G. D. Kennedy, G. R. Newcome, and F.R. Fronczek, *J. Am. Chem. Soc.*, 1983, **105**, 137.
- C. Dietrich-Buchecker and M. Franck-Neumann, *Tetrahedron*, 1977, **33**, 751.
- Y. V. Tomilov, V. G. Bordakov, N. M. Tsvetkov, I. E. Dolgii, and O. M. Nefedov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1982, 2413; Y. V. Tomilov, V. G. Bordakov, N. M. Tsvetkova, A. Y. Shteinschneider, and O. M. Nefedov, *ibid.*, 1983, 336.
- H. M. Stechl, *Chem. Ber.*, 1964, **97**, 2681.
- M. S. Baird, I. R. Dunkin, N. Hacker, M. Poliakoff, and J. J. Turner, *J. Am. Chem. Soc.*, 1981, **103**, 5190.
- See several references in W. Kirmse, 'Carbene Chemistry,' 2nd edn, New York, and e.g., H. D. Hartzler, *J. Am. Chem. Soc.*, 1959, **81**, 2024; *ibid.*, 1961, **83**, 4990.
- (a) W. Kirmse and H. Lechte, *Justus Liebigs Ann. Chem.*, 1970, **739**, 231; (b) Y. Gaoni, *Tetrahedron Lett.*, 1976, 503.
- M. Pomerantz and D. F. Hillenbrand, *J. Am. Chem. Soc.*, 1973, **95**, 5809.
- B. M. Trost and R. C. Atkins, *J. Chem. Soc., Chem. Commun.*, 1971, 1254; A. Monahan and D. Lewis, *J. Chem. Soc., Perkin Trans. 1*, 1977, 60; I. A. Dyakonov and M. I. Komendantov, *Zh. Org. Khim.*, 1961, **331**, 3881; W. Mahler, *J. Am. Chem. Soc.*, 1962, **84**, 4600.
- N. Galloway, B. R. Dent, and B. Halton, *Aust. J. Chem.*, 1983, **36**, 593.
- M. S. Baird and W. Nethercott, *Tetrahedron Lett.*, 1983, 509; M. S. Baird, S. R. Buxton, and H. H. Hussain, *J. Chem. Res.*, 1986, (S), 310.
- M. J. Doyle, J. McMeeking, and P. Binger, *J. Chem. Soc., Chem. Commun.*, 1976, 376.
- H. Tanida and S. Teratake, *Tetrahedron Lett.*, 1970, 4991; C. Deboer and R. Breslow, *ibid.*, 1967, 1033; H. Durr, *ibid.*, p. 1649.
- A. J. Schipperijn and J. Lukas, *Recl. Trav. Chim. Pays-Bas*, 1973, **93**, 572.
- W. E. Billups and L.-J. Lin, *Tetrahedron*, 1986, **42**, 1575.
- M. J. Bennett and J. T. Purdham, *Can. J. Chem.*, 1978, **56**, 1364.
- G. M. Sheldrick, 'SHELXTL: an integrated system for solving, refining, and displaying crystal structures from diffraction data,' revision 5, 1985, University of Göttingen.